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(54) Dye fixing material.

(57) A dye fixing material having a dye fixing layer capable of receiving a diffusible dye formed in a heat developable light-sensitive material by heat development, the dye fixing material containing an oil-soluble fluorescent brightening agent on the side of the dye fixing layer, with a total amount of an anionic surface active agent or agents present on the side of the dye fixing layer falling within the range of from 20 to 200 mg/m^2.

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DYE FIXING MATERIAL

FIELD OF THE INVENTION

This invention relates to a dye fixing element for use in a process of forming an image by heat development.

BACKGROUND OF THE INVENTION

Photography using silver halide photographic materials has been most widely employed as it is superior in photographic characteristics such as sensitivity and gradation controllability as compared with other photographic techniques such as electrophotography and the diazo process.

Many methods have also been proposed for forming a color image by heat development. For example, methods for forming a color image by coupling between an oxidation product of a developing agent and a coupler are disclosed, e.g., in U.S. Patents 3,531,286, 3,761,270, and 4,021,240, Belgian Patent 802,519, and Research Disclosure , issue of Sep., 1975, pp. 31-32.

In these conventional heat development systems, a reduced silver image and a color image are simultaneously formed on the exposed area after heat development, which results in the formation of an impure color image.

To eliminate the above-described disadvantage, various improved methods have been proposed; for example, a method in which a light-sensitive material is heated to imagewise form or release a mobile (diffusible) dye, which is transferred to a mordanted image-receiving element with the aid of a solvent, such as water; a method in which the mobile dye is transferred to a dye fixing element with the aid of a high-boiling organic solvent; a method in which the mobile dye is transferred to a dye fixing element with the aid of a hydrophilic thermal solvent incorporated into the dye fixing element; and a method in which the mobile dye is a heat-diffusible or sublimating dye and it is transferred to a dye receiving element, e.g., a support. These methods are disclosed in U.S. Patents 4,463,079, 4,474,867, 4,478,927, 4,507,380, 4,500,626, and 4,483,914, JP-A-58-149046, JP-A-58-149047, JP-A-59-152440, JP-A-59-154445, JP-A-59-165054, JP-A-59-180548, JP-A-59-168439, JP-A-59-174832, JP-A-59-174833, JP-A-59-174834, and JP-59-174835 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

The color image obtained by the above-described image formation methods generally has a high fog density and is apt to suffer from stains on the white background or undergo unevenness on development. Further, the image, when preserved for a long time, undergoes changes in density or an increase of stain on the white background.

In order to solve the above-mentioned problem, it has been proposed to incorporate a fluorescent brightening agent into a dye fixing element as disclosed in JP-A-61-143752. Although this method brings about an improvement with respect to background stain immediately after image formation, the effects produced are not stable so that the image suffers from considerable unevenness and the like. For example, when the image is preserved for a long time under light, the density of the white background remarkably increases, while the density of the image seriously decreases.

JP-A-61-159644 discloses a method of incorporating a hydroquinone derivative, etc. into a dye fixing material for the purpose of improving dye image stability to light. While the image obtained by this method exhibits improved stability to light, it shows a serious increase in background density when preserved in the dark for a long time.

On the other hand, JP-A-1-159655 discloses an image formation method using a fluorescent brightening agent without causing unevenness on development, which provides an image free from changes in image density or unevenness even when preserved for a long time. In the disclosure, it is stated that a water-soluble fluorescent brightening agent is preferred from the standpoint of production. However, study by the present inventors revealed that an oil-soluble fluorescent brightening agent is preferred from the standpoint of light stability of the image. It has also turned out, however, that use of an oil-soluble fluorescent brightening agent in a dye fixing material causes deterioration of surface gloss with time.

It has thus been demanded to develop a dye fixing material which forms an image having satisfactory light and dark stability while retaining its properties (surface gloss) during preservation.

SUMMARY OF THE INVENTION

An object of this invention is to provide a dye fixing material which forms an image having satisfactory light and dark stability while retaining its properties (surface gloss) during preservation.

The above object of the present invention is accomplished by a dye fixing material having a dye fixing layer capable of receiving a diffusible dye formed in a heat developable light-sensitive material by heat development, said dye fixing material containing an oil-soluble fluorescent brightening agent on the side of the dye fixing layer, with the total amount of an anionic surface active agent or agents present on the side of the dye fixing layer falling within the range of from 20 to 200 mg/m^2.

DETAILED DESCRIPTION OF THE INVENTION

An anionic surface active agent is essentially used for stabilization of an emulsion, improvement of coating properties, and improvement of carrying properties or release properties of materials. The inventors have found by study that an anionic surface active agent is highly diffusible in a hydrophilic binder and, when preserved, diffuses and migrates to the surface to cause reduction in surface gloss.

It has also been found that an anionic surface active agent has an effect of accelerating diffusion of an oil-soluble substance in a hydrophilic binder, and reduction in surface gloss is also caused by the migration of such an oil-soluble substance to the surface.

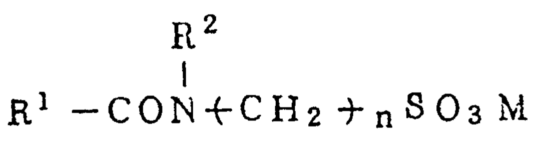
Therefore, in using an oil-soluble substance such as an oil-soluble fluorescent brightening agent as used in the present invention, it was ascertained that the amount of the anionic surface active agents should not exceed 200 mg/m^2 from the viewpoint of surface gloss. However, as mentioned in JP-A-62-173463, the anionic surface active agent should be present in an amount of at least 20 mg/m^2 for assuring releasability between a dye fixing material and a light-sensitive material. The total amount of an anionic surface active agent or agents present on the side of the dye fixing layer is generally from 20 to 200 mg/m^2, preferably from 25 to 150 mg/m^2 in the present invention.

Anionic surface active agents which can be used in the present invention are surface active agents having an anionic group exclusive of betaine type surface active agents. The anionic group herein referred to includes those capable of forming an anion, e.g., a carboxyl group, a sulfo group, a sulfinic acid group, a phospho group, a boric acid group, and a hydroxyl group, and salts thereof.

The anionic surface active agent may be used in any layer of a dye fixing material. It may be added directly in the form of an aqueous solution or in the form of a dispersion in a high-boiling organic solvent, an oil-soluble compound or a polymer. Preferred methods for relatively oil-soulble surface active agents include methods wherein these oil-soulble surface active agents are dissolved and added into a high boiling or a low boiling solvent, or wherein these oil-soulble surface active aggents are dissolved in a mixed solvent comprising a water-soulble organic solvent (e.g., methanol) and water. Preferred methods for relatively water-soulble surface active agents include methods wherein these water-soulble surface active agents are added in the form of itself or an aqueous solution.

The anionic surface active agent may be used either individually or, usually, in combinations of two or more thereof as disired.

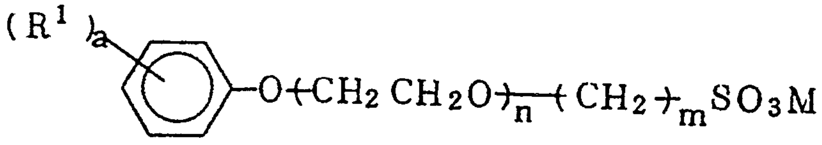
Anionic surface active agents which can be preferably used in the present invention are those represented by formulae (I) to (IX) shown below:



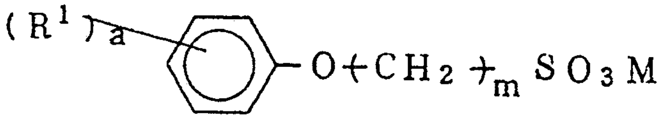
$$R^1-CON(R^2)\leftarrow CH_2 \rightarrow_n SO_3M \qquad (I)$$

wherein R^1 represents a fluorine-substituted or unsubstituted saturated or unsaturated hydrocarbon group having from 3 to 20 carbon atoms; R^2 represents a hydrogen atom or a hydrocarbon group having from 1 to 3 carbon atoms; n represents an integer of from 1 to 20; and M represents a monovalent alkali metal.

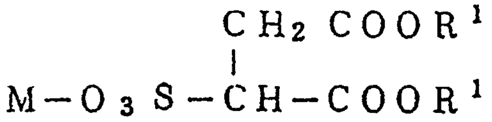
In formula (I), examples of R^1 include propyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, octadecyl, pentadecafluoroheptyl, heptadecafluorooctyl, heptacosafluorotridecyl, and tritriacontafluoroheptadecyl groups. Examples of the hydrocarbon groups represented by R^2 include methyl, ethyl, n-propyl and iso-propyl groups. n preferably represents an integer of from 1 to 8. M preferably represents Na or K.


(II)

wherein R^1, M, and n are as defined above; a represents 0, 1 or 2; and m represents an integer of from 1 to 6, and preferably from 2 to 4.


(III)

wherein R^1, M, m, and a are as defined above.



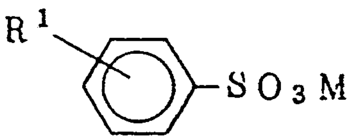
$$M-O_3S-\underset{}{\overset{CH_2COOR^1}{\overset{|}{C}H}}-COOR^1$$

(IV)

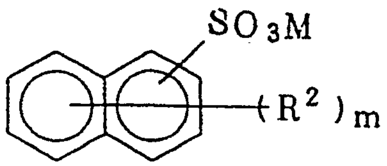
wherein R^1 and M are as defined above and the two R^1 groups may be the same or different.

R^1-O-SO_3M (V)

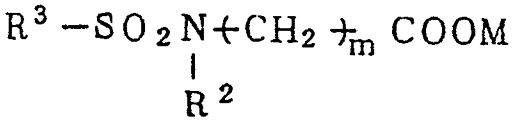
wherein R^1 and M are as defined above.


(VI)

wherein R^1 and M are as defined above.

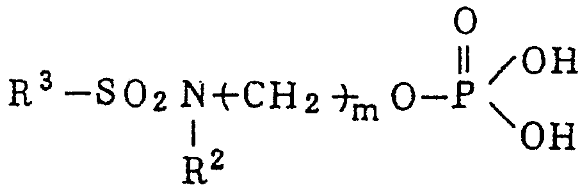

(VII)

wherein R^2, M, and m are as defined above.



$$R^3-SO_2\underset{\displaystyle R^2}{\underset{|}{N}}\!\left(CH_2\right)_m COOM \qquad \text{(VIII)}$$

wherein R^2, M, and m are as defined above; and R^3 represents a saturated or unsaturated hydrocarbon group having from 3 to 22 carbon atoms which may be partially or completely fluorinated.



$$R^3-SO_2\underset{\displaystyle R^2}{\underset{|}{N}}\!\left(CH_2\right)_m O-\overset{\displaystyle O}{\overset{\|}{P}}\!\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \qquad \text{(IX)}$$

wherein R^2, R^3, and m are as defined above.

In formulae (VIII) and (IX), R^3 preferably contains from 7 to 18 carbon atoms and includes, for example, pentadecanefluoroheptyl, heptadecafluorooctyl, heptacosafluorotridecyl, and tritriacontafluoroheptadecyl groups.

Specific but non-limiting examples of the anionic surface active agents which are preferably used in the present invention are shown below.

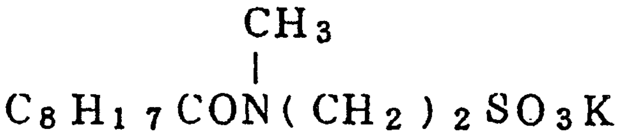
I − 1

$C_{11}H_{23}CONH\ \ CH_2SO_3Na$

I − 2

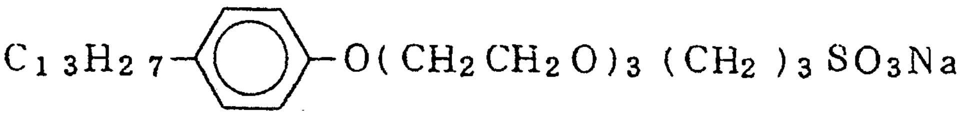
$C_7F_{15}CONH(CH_2)_2SO_3Na$

I − 3

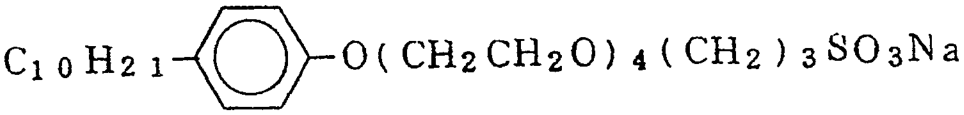


$$C_8H_{17}CO\overset{\displaystyle CH_3}{\overset{|}{N}}(CH_2)_2SO_3K$$

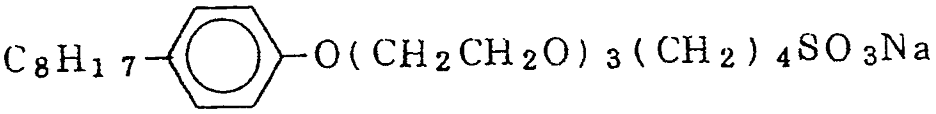
II − 1



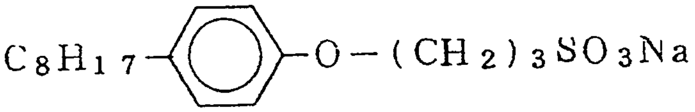
II − 2



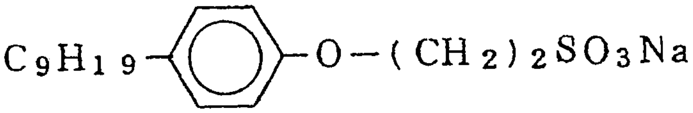
II − 3



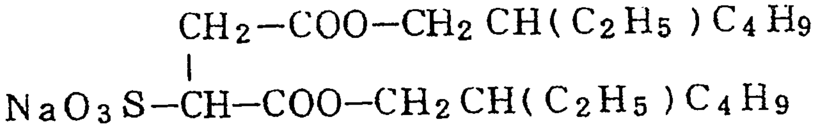
III − 1



III − 2



IV − 1



$$\begin{array}{l} \qquad\qquad CH_2-COO-CH_2CH(C_2H_5)C_4H_9 \\ \qquad\qquad | \\ NaO_3S-CH-COO-CH_2CH(C_2H_5)C_4H_9 \end{array}$$

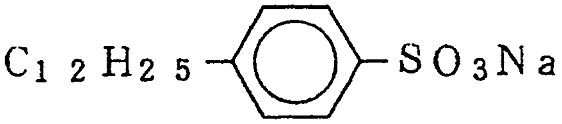
V − 1

$C_7H_{15}-O-SO_3K$

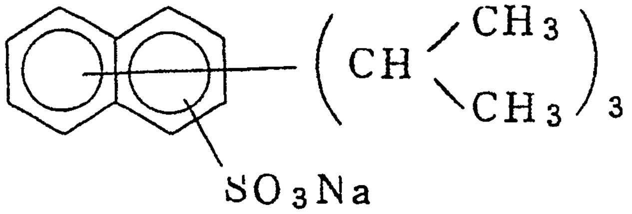
V - 2

$C_{12}H_{25}O-SO_3Na$

VI - 1



VII - 1



VIII - 1

$C_8F_{17}-SO_2NH(CH_2)_3COONa$

VIII - 2

$C_{17}F_{35}SO_2NH(CH_2)_4COONa$

IX - 1

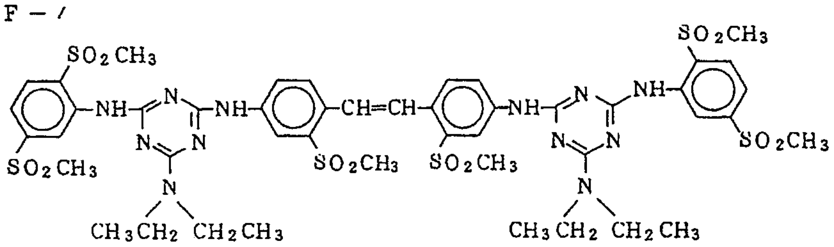
$C_{13}F_{27}SO_2NH(CH_2)_3OPO(OH)_2$

Fluorescent brightening agents which can be used in the present invention include those described in K. Veenkataraman (ed.), The Chemistry of Synthetic Dyes , Vol. V, Ch. 8. Examples of the fluorescent brightening agents include stilbene compounds, coumarin compounds, biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazoline compounds and carbostyril compounds.

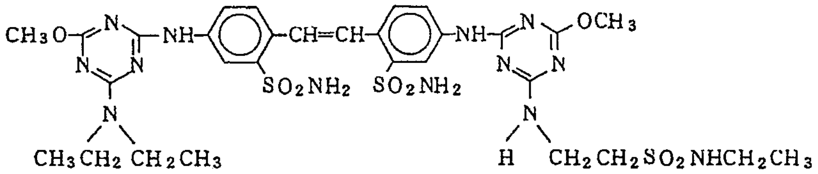
The fluorescent brightening agents to be used in the present invention are oil-soluble. The terminology "oil-soluble" as used herein means that they are substantially water-insoluble. More specifically, they exhibit water-solubility of not more than 100 mg in 100 g water at 20° C.

Specific but non-limiting examples of suitable fluorescent brightening agents are shown below.

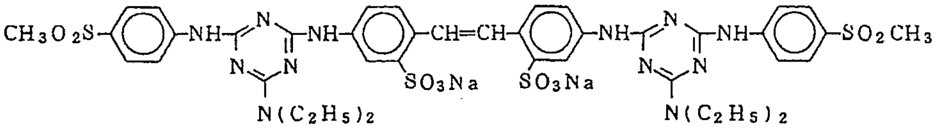
F – 1



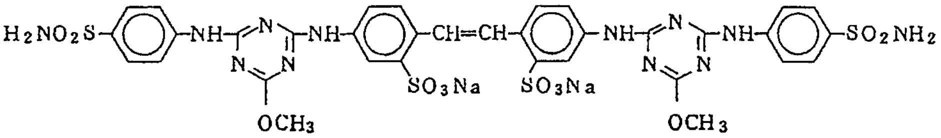
F – 2



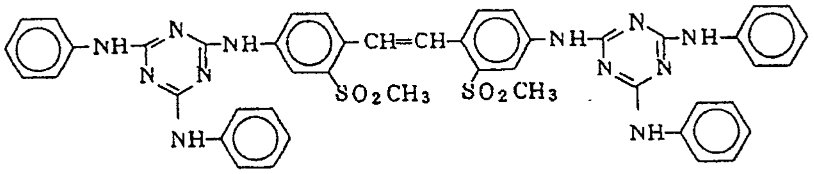
F – 3



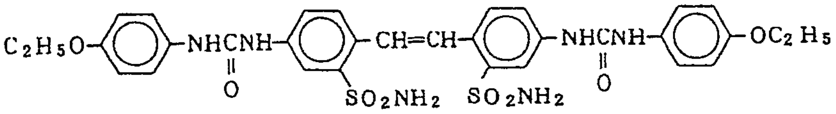
F – 4



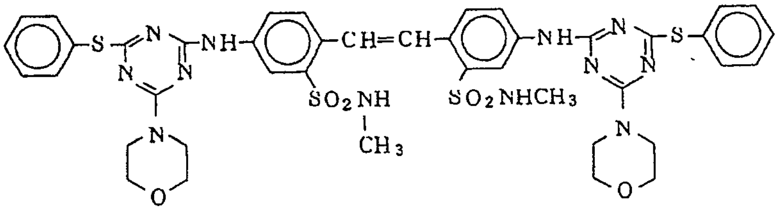
F − 5



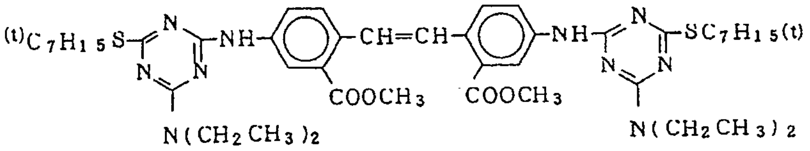
F − 6



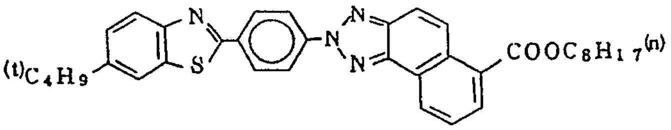
F − 7



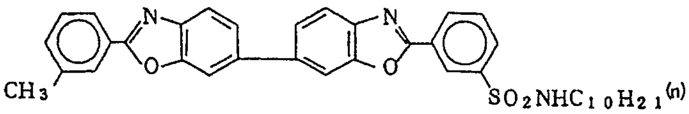
F − 8



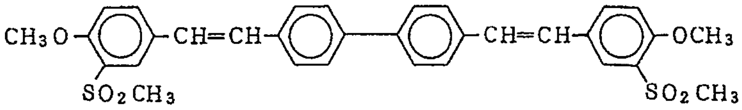
F − 9



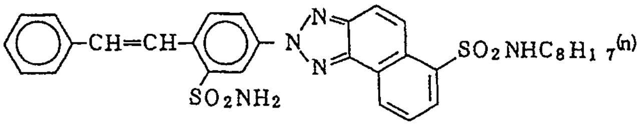
F－10



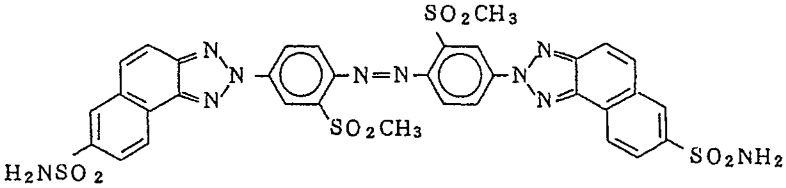
F－11



F－12



F－13



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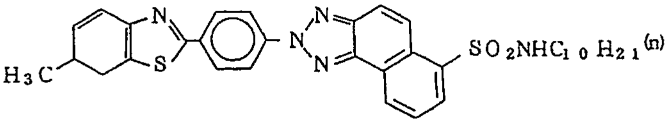

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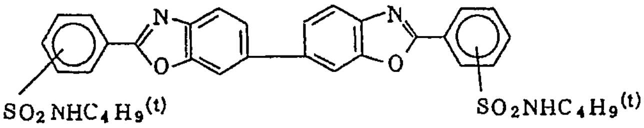

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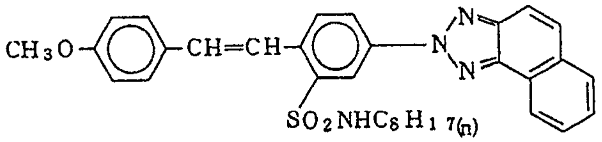

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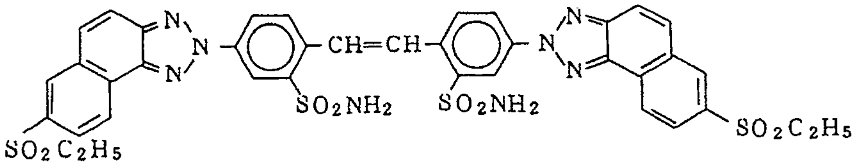

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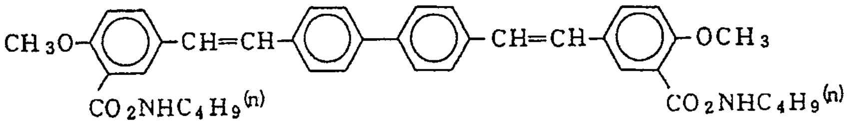

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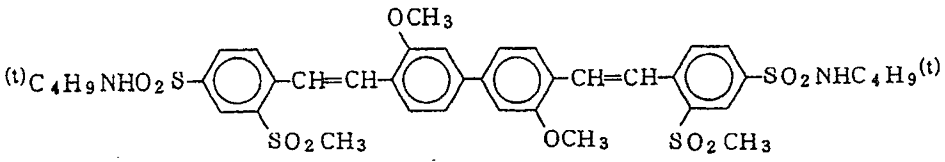
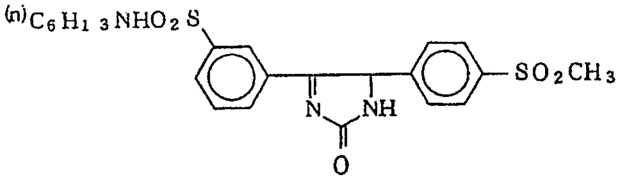


F−20



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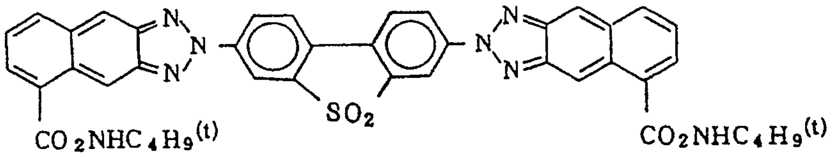

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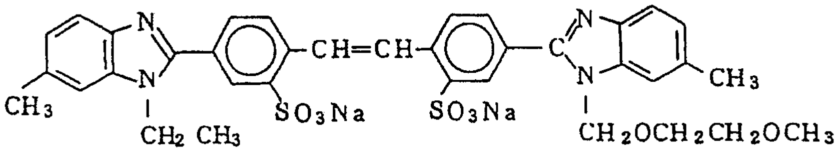

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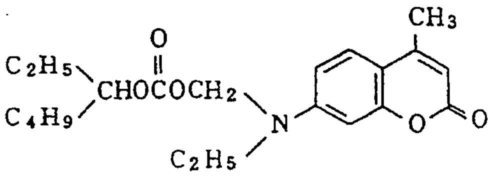

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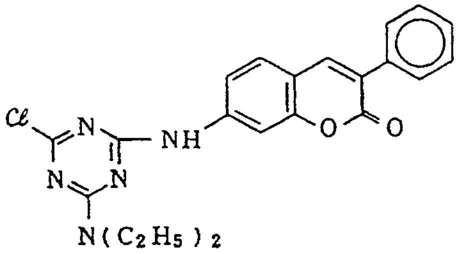
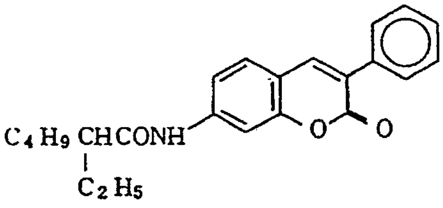
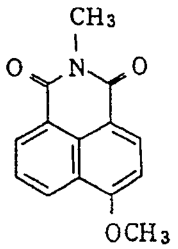


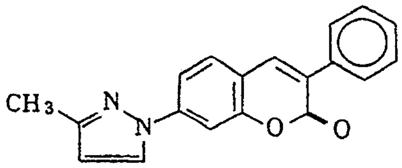
F — 25



F-26



F-27



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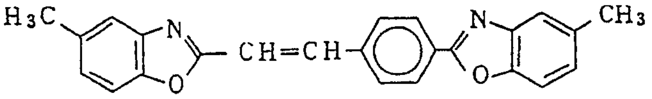

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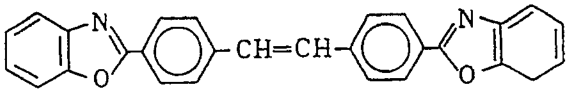

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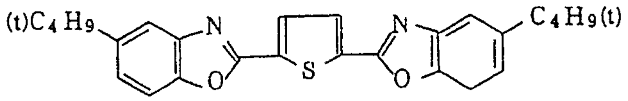

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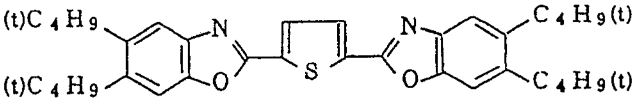

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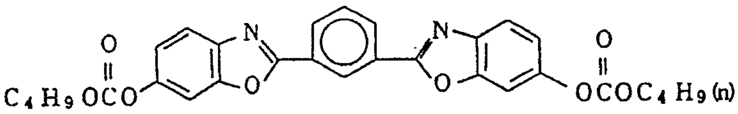


Preferred examples include those of benzoxazole type such as F-10, F-15, F-28, F-29, F-30, F-31, and F-32.

These fluorescent brightening agents may be used either individually or in combinations of two or more thereof.

The fluorescent brightening agent is incorporated into any of layers in a dye fixing material, such as a protective layer, a dye fixing layer, and a subbing layer, and preferably a dye fixing layer. Where a dye fixing layer contains a mordant, the fluorescent brightening agent may be mordanted with the mordant.

The fluorescent brightening agent is preferably present in a dye fixing material in an amount of from 0.1 to 200 mg/m^2, and more preferably of from 5 to 100 mg/m^2.

Incorporation of the oil-soluble fluorescent brightening agent into a dye fixing material can be carried out by a dispersion method using a polymer, a method of finely dispersing in a binder, or, preferably, an oil protection method.

In detail, the method described in U.S. Patent 2,322,027 can be employed. According to this method, the fluorescent brightening agent is dissolved in a high-boiling organic solvent, such as a phthalic ester (e.g., dibutyl phthalate, dioctyl phthalate), a phosphoric ester (e . g., tricresyl phosphate, dioctylbutyl phosphate), a citric ester (e.g., acetyl tributyl citrate), a benzoic ester (e.g., octyl benzoate), an alkylamide (e.g., diethyllaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate), a trimesic ester (e.g., tributyl trimesate), and a chlorinated paraffin (e.g., "Empara 40" produced by Ajinomoto Co., Inc.), with or without a low-boiling organic solvent having a boiling point of from about 30 to 150° C, such as a lower alkyl acetate (e.g., ethyl acetate, butyl acetate), ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone, cyclohexanone, and methyl cellosolve acetate. The solution is then dispersed in a hydrophilic colloid to prepare a dispersion of the oil-soluble fluorescent brightening agent.

In a preferred embodiment of the present invention, the dispersion of the fluorescent brightening agent is prepared by using a phthalic ester or a chlorinated paraffin or a combination of two or more of these and the high-boiling organic solvents described above.

The terminology "a combination of two or more high-boiling organic solvents" as used above means a combination of two or more kinds of high-boiling organic solvents such as those enumerated above (inclusive of two or more isomers thereof). The two or more kinds of solvents combined may be entirely different in structure from each other, but it is more effective to use a mixture of alkyl phosphates, alkyl phthalates, alkyl carboxylates or alkyl oxalates differing in alkyl chain length, a mixture of aryl phosphates differing in position of the substituent, a mixture of halogenated paraffins differing in position of the halogen atom, or a like mixture.

Isomers of the above-described high-boiling organic solvents include those having a double bond in the alkyl chain thereof which form cis-trans isomers, and substituted cyclohexyl phosphates which form structural isomers.

Examples of the combination of solvents include a mixture of the above-mentioned high-boiling organic solvents and a mixture containing isomers.

The inventors have found by study that use of a phthalic ester, a chlorinated paraffin, or a combination of two or more high-boiling organic solvents as a dispersing medium for the oil-soluble fluorescent brightening agent brings about excellent surface gloss, while the reason therefor has not yet been clarified. In many cases, these dispersing media are superior to other media in capability of dissolving an oil-soluble fluorescent brightening agent and are, therefore, considered effective to suppress diffusion of an oil-soluble fluorescent brightening agent. Hence, it is reasonable to consider that these dispersing media inhibit reduction in surface gloss due to diffusion of the fluorescent brightening agent to the surface.

The dye fixing material of the present invention and a light-sensitive material to be combined therewith may be constructed on the same support or separate supports. With respect to the mutual relationship between the light-sensitive material and the dye fixing material, the relationship of these materials to a support, and the relationship of these materials to a white reflecting layer, reference can be made in U.S. Patent 4,500,626, Col. 57. In the present invention, the dye fixing material is preferably provided on a support separate from that for a light-sensitive material.

The dye fixing material comprises a support having thereon a dye fixing layer and, if desired, auxiliary layers, such as a protective layer, a release layer, an anticurling layer, and a backing layer. A protective layer and a backing layer are especially useful. One or more of these layers may contain, in addition to the fluorescent brightening agent, a hydrophilic thermal solvent, a plasticizer, a discoloration inhibitor, a UV absorbent, a slip agent, a matting agent, an antioxidant, a dispersed vinyl compound as a dimensional stabilizer, and the like.

The dye fixing layer contains a polymer mordant capable of fixing a mobile dye released on development.

The polymer mordant includes polymers containing a tertiary amino group, a nitrogen-containing heterocyclic moiety, or a quaternarized cationic group derived therefrom. These polymer mordants are preferably used in admixture with other hydrophilic polymers (e.g., gelatin).

Polymers containing a vinyl monomer carrying a tertiary amino group are described in JP-A-60-60643 and JP-A-60-57836. Polymers containing a vinyl monomer carrying a tertiary imidazole group are described in JP-A-60-118834, JP-A-60- 122941, Japanese Patent Application Nos. 61-87180 and 61-87181, and U.S. Patents 4,282,305, 4,115,124, and 3,148,061.

Examples of suitable polymers containing a vinyl monomer having a quaternary imidazolium salt are described in British Patents 2,056,101, 2,093,041, and 1,594,961, U.S. Patents 4,124,386, 4,115,124, 4,273,853, and 4,450,224, and JP-A-48-28225.

Examples of suitable polymers containing a vinyl monomer having a quaternary ammonium salt are described in US. Patents 3,709,690, 3,898,088, and 3,958,995, JP-A-60-57836, JP-A-60-60643, JP-A-60-122940, JP-A-60-122942, and JP-A-60-235134.

The polymer mordant to be used in the present invention preferably has a molecular weight of from 1,000 to 1,000,000, and particularly from 10,000 to 200,000.

The polymer mordant is used in a mordanted layer of the dye fixing element in combination with a hydrophilic colloid serving as a binder hereinafter described.

A mixing ratio of polymer mordant to hydrophilic colloid and the amount of the polymer mordant to be coated are easily determined by those skilled in the art depending on the amount of a dye to be mordanted, the kind and composition of the polymer mordant, and the image formation system adopted. Usually, the mixing ratio of mordant to hydrophilic colloid ranges from 20/80 to 80/20 by weight, and the amount of the mordant to be coated ranges from about 0.2 to about 15 g/m^2, and preferably from 0.5 to 8 g/m^2.

A combined use of the polymer mordant with a metallic ion in the dye fixing element increases a transferred dye density. The metallic ion can be added to a mordanted layer containing a mordant or a layer adjacent thereto (on the side either nearer to or farther from a support having thereon a mordanted layer, etc.). The metallic ion which can be used is desirably colorless and stable to heat and light and preferably includes polyvalent ions of transition metals, e.g., Cu^{2+}, Zn^{2+} Ni^{2+}, Pt^{2+}, Pd^{2+}, and Co^{3+}, with Zn^{2+} being particularly preferred. These metallic ions are usually added in the form of a water-soluble compound, e.g., $ZnSO_4$ and $Zn(CH_3CO_2)_2$, in an amount of from about 0.01 to about 5 g/m^2, and preferably of from 0.1 to 1.5 g/m^2.

A hydrophilic polymer can be used as a binder in the layer containing the metallic ion. Hydrophilic colloids hereinafter described are useful as a hydrophilic binder for the metallic ion-containing layer.

The mordanted layer containing the polymer mordant may contain various surface active agents for various purposes, for example, for improving coating properties.

The dye fixing material of the present invention may contain a base and/or a precursor thereof.

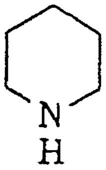
Examples of suitable bases include inorganic bases, e.g., a hydroxide, a carbonate, a bicarbonate, a borate, a secondary or tertiary phosphate, or a metaborate of an alkali metal or a quaternary alkylammonium; and organic bases, e.g., aliphatic amines, aromatic amines, heterocyclic amines, amidines, cyclic amidines, guanidines, cyclic guanidines, etc. and their carbonates, bicarbonates, borates, and secondary or tertiary phosphates.

Suitable base precursors include precursors of the above-mentioned organic bases. The terminology "base precursor" as used herein means a compound capable of releasing a basic component on thermal decomposition or electrolysis. Examples of such base precursors include salts of a thermally decomposable organic acid, e.g., trichloroacetic acid, cyanoacetic acid, acetoacetic acid, and α-sulfonylacetic acid, and the above-mentioned organic base, or 2-carboxycarboxamide described in U.S. Patent 4,088,496. In addition, the base precursors described in British Patent 998,945, U.S. Patent 3,220,846, and JP-A-50-22625 are also employable.

Examples of compounds capable of forming a base on electrolysis include those capable of forming a base on electrolytic oxidation, such as various fatty acid salts which are electrolytically decomposed to produce a carbonate of an alkali metal, a guanidine, an amidine, etc. with high efficiency; and those capable of forming a base on electrolytic reduction, such as nitro or nitroso compounds which are reduced to produce an amine, nitriles which are reduced to produce an amine, and nitro, azo or azoxy compounds which are reduced to produce a p-aminophenol, a p-phenylenediamine or a hydrazine. P-aminophenols, p-phenylenediamines, and hydrazines can be used not only as a base but a dye image forming substance. It is also useful to electrolytically decompose water in the presence of various inorganic salts to form an alkali component.

Specific but non-limiting examples of suitable bases or precursors thereof which can be used in the present invention are shown below.

Lithium hydroxide, sodium hydroxide, sodium carbonate, cesium carbonate, sodium hydrogencarbonate, potassium carbonate, potassium hydrogencarbonate, sodium quinolinate, sodium secondary phosphate, potassium secondary phosphate, sodium tertiary phosphate, potassium tertiary phosphate, potassium pyrophosphate; sodium metaborate, borax, aqueous ammonia, tetramethylammonium hydroxide, tetraethylammonium hydroxide, $(CH_3)_2NH$, $(C_2H_5)_2NH$, $C_3H_7NH_2$, $HOC_2H_4NH_2$, $(HOC_2H_4)_2NH$, $(HOC_2H_4)_3N$, $H_2NC_2H_4NH_2$, $H_2NC_4H_8NH_2$, $CH_3NHC_2H_4NHCH_3$, $(CH_3)_2NC_3H_6N(CH_3)_2$,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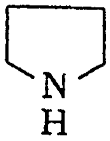
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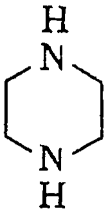
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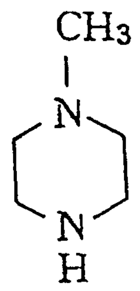

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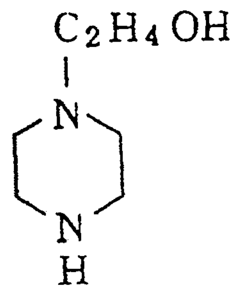

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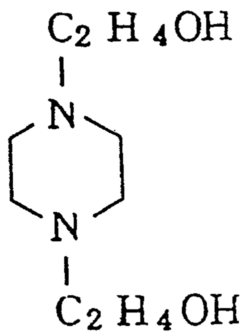

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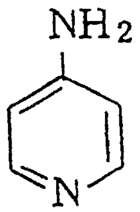

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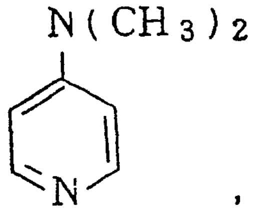

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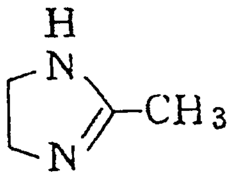

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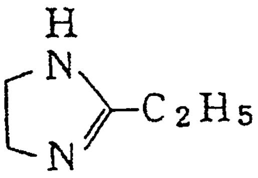

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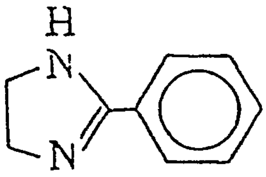

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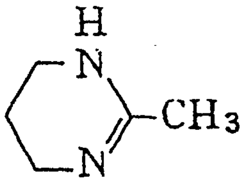

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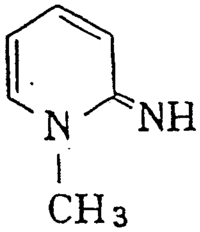

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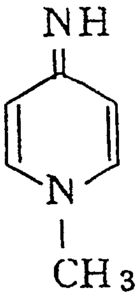

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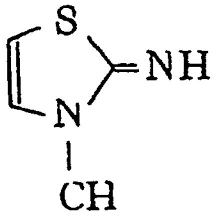

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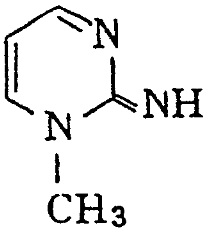

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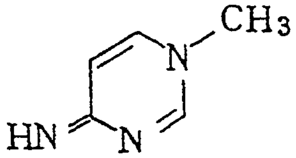
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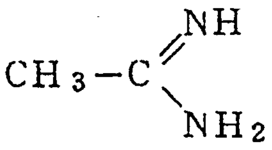
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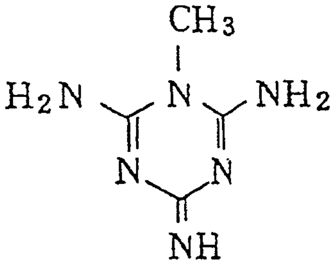
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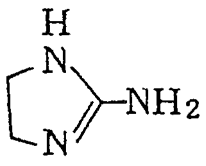
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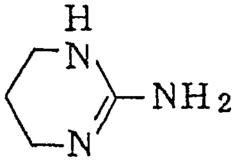
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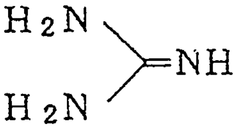
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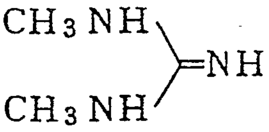
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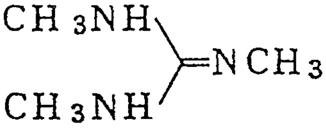
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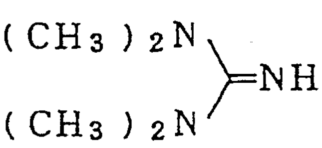
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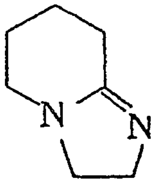
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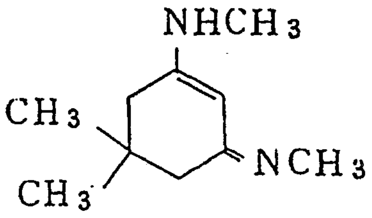
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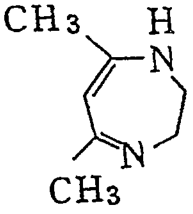


guanidinotrichloroacetic acid, piperidinotrichloroacetic acid, morpholinotrichloroacetic acid, p-toluidinotrichloroacetic acid, 2-picolinotrichloroacetic acid, guanidine carbonate, piperidine carbonate, morpholine carbonate, and tetramethylammonium trichloroacetate.

Further, a method in which a sparingly soluble metallic salt (e.g., zinc oxide, basic zinc carbonate, calcium carbonate) and a complexing compound capable of complexing with a metal ion constituting the metallic salt (e.g., a picolinic acid salt) are reacted in the presence of water as a medium to produce a water-soluble base can also be used. According to this method, a dispersion of the sparingly soluble metallic salt is incorporated in a light-sensitive material, while a water-soluble compound capable of complexing with the metal ion is incorporated into a dye fixing material as a base precursor, and they are reacted in the presence of water on intimate contact under heating to produce a base. Therefore, this method is particularly effective from the viewpoint of preservability of a light-sensitive material and a dye fixing material.

The above-described bases and/or base precursors can be used either individually or in combination of two or more thereof.

The base and/or precursor thereof is used in an amount of from 5×10^{-4} to 5×10^{-1} mol/m^2, and preferably from 2.5×10^{-3} to 2.5×10^{-2} mol/m^2.

The heat developable light-sensitive material which can be used in combination with the dye fixing material according to the present invention essentially comprises a support having thereon a light-sensitive silver halide, a binder, and a dye donating compound capable of releasing or forming a diffusible dye upon heat development (the dye donating compound sometimes serves as a reducing agent as hereinafter described). If desired, the light-sensitive material may contain an organic metal salt oxidizing agent, a reducing agent, and the like. These components are usually incorporated into the same layer, but they may be incorporated separately into different layers as far as they are in a reactive state. For example, presence of a colored dye donating compound in a layer beneath a silver halide emulsion layer prevents reduction in sensitivity. A reducing agent is preferably incorporated into a heat developable light-sensitive material. It may also be externally supplied through, for example, diffusion from a dye fixing material as hereinafter described.

To obtain colors of broad range of a chromaticity diagram by using three primary colors of yellow, magenta, and cyan, at least three silver halide emulsion layers differing in spectral sensitivity should be used in combination. For example, a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer are combined; or a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive layer are combined. The order of providing these layers is arbitrarily selected from those known for general color light-sensitive materials. If desired, each light-sensitive layer may be composed of two or more divided layers.

The heat developable light-sensitive material can further contain auxiliary layers, such as a protective layer, a subbing layer, an intermediate layer, a yellow filter layer, an antihalation layer, a backing layer, etc.

Silver halide grains which can be used in the present invention may be, for example, any of silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodide, and silver chloroiodobromide.

Silver halide emulsions may be either of a surface latent image type emulsion or an internal latent image type emulsion. The internal latent image type emulsion is used as a direct reversal emulsion in combination with a nucleating agent or light fog. The emulsion may be a so-called core/shell emulsion having different phases between the inside of the grains and the surface layer thereof. The silver halide emulsions may be either mono-dispersed or poly-dispersed. A mixture of mono-dispersed emulsions may also be used.

Silver halide grains have a mean grain size of from 0.1 to 2 µm, and preferably from 0.2 to 1.5 µm. The grains may have a regular crystal form, such as a cubic form, an octahedral form, and a tetradecahedral form, or an irregular crystal form, such as a tubular form having a high aspect ratio.

Specific examples of suitable silver halide emulsions are described in U.S. Patents 4,500,626 (Col. 50) and 4,628,021, Research Disclosure 17029 (1978), and JP-A-62-253159.

Silver halide emulsions may be used in the primitive (unripened) state but are usually used after being chemically sensitized by known techniques, such as sulfur sensitization, reduction sensitization, and novel metal sensitization, either alone or in combination thereof. Chemical sensitization may be performed in the presence of a nitrogen-containing heterocyclic compound as suggested in JP-A-62-253159.

The light-sensitive silver halide emulsion is usually coated on a support to a silver coverage of from 1 mg to 10 g/m^2.

As stated above, an organic metal salt can be used as an oxidizing agent in combination with light-sensitive silver halide emulsions. Of organic metal salts, organic silver salts are particularly preferred.

Organic compounds forming organic silver salt oxidizing agents include benzotriazoles, fatty acids, and other compounds as described in U.S. Patent 4,500,626, Cols. 52-53. In addition, silver salts of alkynyl-containing carboxylic acids, e.g., silver phenylpropiolate, as described in JP-A-60-113235 and acetylene silver as described in JP-A-61-249044 are also useful. These organic silver salts may be used either individually or in combination of two or more thereof.

The organic silver salt is usually used in an amount of from 0.01 to 10 mols, and preferably from 0.01

to 1 mol, per mol of light-sensitive silver halide. The total silver coverage of the light-sensitive silver halide and the organic silver salt suitably ranges from 50 mg to 10 g/m^2.

In the heat-developable light-sensitive material, various antifoggants or stabilizers can be used. Examples of these compounds include azoles or azaindenes described in Research Disclosure 17643, pp. 24-25 (1978), nitrogen-containing carboxylic acids or phosphoric acids described in JP-A-59-168442, mercapto compounds and metal salts thereof described in JP-A-59-111636, and acetylene compounds described in JP-A-62-87957.

Silver halides which can be used in the present invention may be spectrally sensitized with methine dyes or other sensitizing dyes. Usable sensitizing dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. Specific examples of these sensitizing dyes are described in U.S. Patent 4,617,257, JP-A-59-180550, JP-A-60-140335, and Research Disclosure 17029 (1978), pp. 12-13.

The sensitizing dyes may be used either individually or in combination thereof. Combinations of sensitizing dyes are often used for the purpose of supersensitization.

Photographic emulsions may contain a compound which exhibits no spectral sensitizing effect by itself or absorbs substantially no visible light but which shows supersensitizing effect in combination with the sensitizing dye. Examples of such a compound are described, e.g., in U.S. Patent 2,615,641 and JP-A-63-23145.

The sensitizing dyes may be added to an emulsion during, before or after chemical ripening. They may also be added before or after nucleation of silver halide grains as taught in U.S. Patents 4,183,756 and 4,225,666 The amount of the sensitizing dye to be added generally ranges from about 1 x 10^{-8} to 1 x 10^{-2} mol, per mol of silver halide.

Binders to be used in layers constituting each of the light-sensitive material and the dye fixing material are preferably hydrophilic. Examples of suitable hydrophilic binders are described in JP-A-62-253159, pp. 26-28. In particular, transparent or semi-transparent binders are preferred. Included in such hydrophilic binders are naturally occurring compounds, such as proteins (e.g., gelatin and derivatives thereof), cellulose derivatives, and polysaccharides (e.g., starch, gum arabic, dextran, and pullulan); and synthetic high polymers, such as polyvinyl alcohol, polyvinylpyrrolidone, and acrylamide polymers. Also useful as a binder are highly water-absorbing polymers described in JP-A-62-245260 including homo- or copolymers of a vinyl monomer(s) having -COOM or -SO$_3$M (wherein M is a hydrogen atom or an alkali metal) and copolymers of such a vinyl monomer and other vinyl monomer(s) (e.g. - sodium methacrylate, ammonium methacrylate, and Sumikagel L-5H (produced by Sumitomo Chemical Co., Ltd.)). These binders may be used in combinations of two or more thereof.

In a system wherein heat development is effected by supplying a small amount of water, use of the above-described highly water-absorbing polymer expedites absorption of water. Further, use of the highly water-absorbing polymer in a dye fixing layer or a protective layer thereof is effective to prevent the transferred dye from being re-transferred from the dye fixing material to other materials.

In the present invention, the binder is preferably coated in an amount of not more than 20 g/m^2, more preferably not more than 10 g/m^2, and most preferably not more than 7 g/m^2.

Layers constituting the light-sensitive material or dye fixing material inclusive of a backing layer may contain various polymer latices for improvement of film properties, for example, improvement in dimensional stability, prevention of curling, blocking or cracking, and prevention of pressure sensitization or desensitization. To this effect, any of the polymer latices described in JP-A-62-245258, JP-A-62-136648, and JP-A-62-110066 can be used. In particular, incorporation of a polymer latex having a low glass transition point (e.g., 40 °C or lower) into a mordanted layer is effective to prevent cracking of the mordanted layer, while incorporation of a polymer latex having a high glass transition point into a backing layer produces anticurling effects.

Reducing agents which can be used in the heat-developable light-sensitive material are selected from those conventional in the field of heat developable light-sensitive materials. Reducing dye donating compounds hereinafter described are also included in reducing agents. The reducing dye donating compound may be used in combination with other reducing agents. In addition, reducing agent precursors which have no reducing effect per se but are capable of exhibiting a reducing effect on reaction with a nucleophilic reagent or on heating at the time of development can also be used.

Specific examples of suitable reducing agents inclusive of precursors thereof which can be used in this invention are described in U.S. Patents 4,500,626 (Cols. 49-50), 4,483,914 (Cols. 30-31), 4,330,617, and 4,590,152, JP-A-60-140335 (pp. 17-18), JP-A-57-40245, JP-A-56-138736, JP-A-59-178458, JP-A-59-53831, JP-A-59-182449, JP-A-59-182450, JP-A-60-119555, JP-A-60-128436 to 128439, JP-A-60-198540, JP-A-60-181742, JP-A-61-259253, JP-A-62-244044, JP-A-62-131253 to 131256, and EP 220,746A2 (pp. 78-96).

Combinations of various reducing agents as disclosed in U.S. Patent 3,039,869 can also be used.

If desired, where a non-diffusible reducing agent is employed, an electron transfer agent and/or a precursor thereof may be used in combination to thereby accelerate electron transfer between the non-diffusible reducing agent and the developable silver halide.

Such an electron transfer agent or a precursor thereof can be selected from the above-described reducing agents or precursors thereof. It is desirable that the electron transfer agent or its precursor has greater mobility than the non-diffusible reducing agent (i.e., electron donor). Particularly useful electron transfer agents are 1-phenyl-3-pyrazolidones or aminophenols.

The non-diffusible reducing agent (electron donor) to be combined with the electron transfer agent is selected from the above-described reducing agents as long as it is substantially immobile in the layer where they belong. Suitable examples of such a non-diffusible reducing agent include hydroquinones, sulfonamidophenols, sulfonamidonaphthols, compounds described as electron donors in JP-A-53-110827, and non-diffusible reducing dye donating compounds as hereinafter described.

The amount of the reducing agent to be used in the present invention usually ranges from 0.001 to 20 mols, and preferably from 0.01 to 10 mols, per mol of silver.

Typical examples of the dye donating compounds which can be used in the present invention include 2-equivalent couplers having a non-diffusion group as a releasable group and capable of forming a diffusible dye on coupling reaction with an oxidation product of a color developing agent. The non-diffusion group may comprise a polymer chain.

Specific examples of color developing agents and couplers are described in T.H. James, The Theory of the Photographic Process (4th Ed.)1 pp. 291-334 & 354-361, JP-A-58-123533, JP-A-58-149046, JP-A-58-149047, JP-A-59-111148, JP-A-59-124399, JP-A-59-174835, JP-A-59-231539, JP-A-59-231540, JP-A-60-2950, JP-A-60-2951, JP-A-60-14242, JP-A-60-23474, and JP-A-60-66249.

Further included in the dye donating compounds are compounds having a function of imagewise releasing or diffusing a diffusible dye. Such compounds can be represented by formula (LI):

$(Dye\text{-}Y)_n\text{-}Z$ (LI)

wherein Dye represents a dye group, a dye group which has been temporarily shifted to a short wavelength region, or a dye precursor group; Y represents a mere bond or a linking group; Z represents a group which produces a difference in diffusibility of the compound represented by $(Dye\text{-}Y)_n\text{-}Z$ or releases Dye to produce a difference in diffusibility between the thus released Dye and $(Dye\text{-}Y)_n\text{-}Z$ in correspondence or counter-correspondence to light-sensitive silver salts having an imagewise distributed latent image; and n represents 1 or 2. When n is 2, two Dye-Y moieties may be the same or different.

Specific examples of the dye donating compounds represented by formula (LI) include the following compounds (i) to (v). Compounds (i) to (iii) form a diffusible dye image (positive dye image) in counter-correspondence to development of silver halide, while compounds (iv) and (v) form a diffusible dye image (negative dye image) in correspondence to development of silver halide.

(i) Dye developing agents comprising a hydroquinone developing agent bound to a dye component as described in U.S. Patents 3,134,764, 3,362,819, 3,597,300, 3,544,545, and 3,482,972. The compounds of this type are diffusible in alkaline conditions but become non-diffusible on reaction with silver halide.

(ii) Non-diffusion compounds which release a diffusible dye in alkaline conditions but lose their function on reaction with silver halide as described in U.S. Patent 4,503,137. Examples of such compounds include compounds which undergo intramolecular nucleophilic substitution to release a diffusible dye as described in U.S. Patent 3,980,479, and compounds which undergo intramolecular rewinding of the isooxazolone ring to release a diffusible dye as described in U.S. Patent 4,199,354.

(iii) Non-diffusion compounds which react with a reducing agent remaining non-oxidized after development to release a diffusible dye as described in U.S. Patent 4,559,290, EP 220,746A2, U.S. Patent 4,783,396, and Technical Disclosure Bulletin 87-6199. Examples of such compounds include compounds which undergo intramolecular nucleophilic substitution after being reduced to release a diffusible dye as described in U.S. Patents 4,139,389 and 4,139,379, JP-A-59-185333, and JP-A-57-84453, compounds which undergo intramolecular electron transfer after being reduced to release a diffusible dye as described in U.S. Patent 4,232,107, JP-A-59-101649, JP-A-61-88257, and Research Disclosure 24025 (1984), compounds whose single bond is cleaved after being reduced to release a diffusible dye as described in West German Patent 3,008,588A, JP-A-56-142530, and U.S. Patents 4,343,893 and 4,619,884, nitro compounds which receive electrons to release a diffusible dye as described in U.S. Patent 4,450,223, and compounds which receive electrons to release a diffusible dye as described in U.S. Patent 4,609,610.

Preferred examples of the compounds of this type include compounds having an N-X bond (wherein X represents an oxygen, sulfur or nitrogen atom) and an electrophilic group per molecule as described in EP

220,746A2, Technical Disclosure Bulletin 87-6199, U.S. Patent 4,783,396, JP-A-63-201653, and JP-A-63-201654, compounds having an SO_2-X (wherein X is as defined above) and an electrophilic group per molecule as disclosed in U.S. Patent 4,840,887 (corresponding to Japanese Patent Application No. 62-106885), compounds having a PO-X bond (wherein X is as defined above) and an electrophilic group per molecule as disclosed in JP-A-63-271344, and compounds having a C-X' bond (wherein X' has the same meaning as X or represents -SO_2-) and an electrophilic group per molecule as disclosed in JP-A-63-271341.

Further, compounds in which after reduction by a π-bond conjugated with an electron accepting group, a single bond is cleaved to release a diffusible dye, as described in JP-A-1-161237 and JP-A-1-161342, can also be used.

Especially preferred of these compounds are the compounds having an N-X bond and an electrophilic group per molecule. Specific examples of the compounds are Compound Nos. (1) to (3), (7) to (10), (12), (13), (15), (23) to (26), (31), (32), (35), (36), (40), (41), (44), (53) to (59), (64), and (70) described in EP 220,746A2 or U.S. Patent 4,783,396 and Compound Nos. (11) to (23) described in Technical Disclosure Bulletin 87-6199.

(iv) Compounds having a diffusible dye as a releasable group which are capable of releasing a diffusible dye on reaction with an oxidation product of a releasing agent (DRR couplers). Specific examples of the DRR couplers are described in British Patent 1,330,524, JP-B-48-39165 (the term "JP-B" as used herein means an "examined published Japanese patent application"), and U.S. Patents 3,443,940, 4,474,867, and 4,483,914.

(v) Compounds having a reducing effect on a silver halide or an organic silver salt which release a diffusible dye upon exerting the reducing effect (DRR compounds). Since the compounds of this type do not need other reducing agents, image staining due to oxidative decomposition products of reducing agents can be eliminated. Typical examples of these compounds are described in U.S. Patents 3,928,312, 4,053,312, 4,055,428, and 4,336,322, JP-A-59-65839, JP-A-59-69839, JP-A-53-3819, JP-A-51-1043431 Research Disclosure 17465, U.S. Patents 3,725,062, 3,728,113, and 3,443,939, JP-A-58-116537, JP-A-57-179840, and U.S. Patent 4,500,626. Specific examples of the DRR compounds include the compounds of Cols. 22 to 44 of U.S. Patent 4,500,626 supra . Among them, particularly preferred are compound Nos. (1) to (3), (10) to (13), (16) to (19), (28) to (30), (33) to (35), (38) to (40), and (42) to (64). The compounds described in U.S. Patent 4,639,408, Cols. 37 to 39 are also useful.

In addition to the above-described couplers and the compounds of formula (LI), dye donating compounds which can be used in the present invention include silver dye compounds comprised of an organic silver salt bound to a dye as disclosed in Research Disclosure , Issue of May, 1978, pp. 54-58; azo dyes for use in heat development silver dye bleach process as disclosed in U.S. Patent 4,235,957 and Research Disclosure , Issue of Apr., 1976, pp. 30-32; and leuco dyes as described in U.S. Patents 3,985,565 and 4,022,617.

Hydrophobic additives such as dye donating compounds and non-diffusible reducing agents can be introduced into layers of light-sensitive materials by known techniques as described in U.S. Patent 2,322,027. In this case, high-boiling organic solvents, e.g., those described in JP-A-59-83154, JP-A-59-178451 to 178455, and JP-A-59-178457, may be used either alone or, if desired, in combination with low-boiling organic solvents having a boiling point of from 50 to 160° C.

The high-boiling organic solvent is usually used in an amount not more than 10 g, and preferably not more than 5 g, per gram of the dye donating compound; and not more than 1 mℓ, preferably not more than 0.5 mℓ, and more preferably not more than 0.3 mℓ, per gram of the binder.

The dispersion method using polymerization products as described in JP-B-51-39853 and JP-A-51-59943 is also employed for incorporation of the hydrophobic additives.

Where the additive to be introduced is substantially water-insoluble, it may be incorporated into the binder in the form of a finely divided dispersion as well.

To disperse hydrophobic additives in a hydrophilic colloid, various surface active agents can be made use of. For example, surface active agents described in JP-A-59-157636, pp. 37-38 as well as the above-described anionic surface active agents are suitably used.

In the present invention, the light-sensitive material can contain a compound which serves both to accelerate development and to stabilize an image. Examples of such a compound which can be preferably used are described in U.S. Patent 4,500,626, Cols. 51-52.

Constituent layers of the light-sensitive material and dye fixing material may contain a high-boiling organic solvent as a plasticizer, a slip agent, or an agent for improving releasability between the light-sensitive material and the dye fixing material. Specific examples of suitable high-boiling organic solvents are described in JP-A-62-253159 (p. 25) and JP-A-62-245253. For the same purposes, various kinds of silicone oils (inclusive of from dimethyl silicone oil to modified silicon oils comprising dimethylsiloxane having introduced thereinto various organic groups) can also be used. Examples of effective silicone oils are modified silicone oils of various kinds, and particularly carboxyl-modified silicone oil ("X-22-3710" produced by Shin-Etsu Silicone Co., Ltd.) described in pp. 6-8 of "Modified Silicone Oil", technical data reported by Shin-Etsu Silicone Co., Ltd. Silicone oils described in JP-A-62-215953 and JP-A-63-46449 are also effective.

The light-sensitive material and dye fixing material may further contain a discoloration inhibitor, such as antioxidants, ultraviolet absorbents, and a certain kind of metal complexes.

Examples of suitable antioxidants include chroman compounds, coumaran compounds, phenol compounds (e . g., hindered phenols), hydroquinone derivatives, hindered amine derivatives, and spiroindane compounds. Compounds described in JP-A-61-159644 are also effective.

Examples of suitable ultraviolet absorbents include benzotriazole compounds (e.g., those described in U.S. Patent 3,533,794), 4-thiazolidone compounds (e.g., those described in U.S. Patent 3,352,681), benzophenone compounds (e.g., those described in JP-A-46-2784), and compounds described in JP-A-54-48535, JP-A-62-136641, and JP-A-61-88256. Ultraviolet absorbing polymers as described in JP-A-62-260152 are also effective.

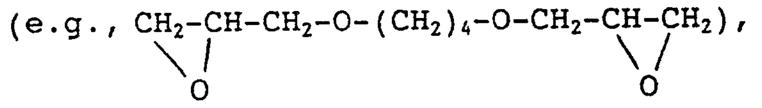
Metal complexes useful as discoloration inhibitors include compounds described in U.S Patents 4,241,155, 4,245,018 (Cols. 3-36), and 4,254,195 (Cols. 3-8), JP-A-62-174741, JP-A-61-88256 (pp. 27-29), JP-A-63-199248, JP-A-1-75568, and JP-A-1-74272.

Examples of useful discoloration inhibitors are described in JP-A-62-215272, pp. 125-137.

The discoloration inhibitor for preventing the dye transferred to a dye fixing material from discoloring may be previously incorporated into the dye fixing material or may be supplied to the dye fixing material externally from, for example, a light-sensitive material.

The above-described antioxidants, ultraviolet absorbents and metal complexes may be used in combinations thereof.

Hardening agents which can be used in layers constituting the light-sensitive material or dye fixing material include those described in U.S. Patent 4,678,739 (Col. 41), JP-A-59-116655, JP-A-62-245261, and JP-A-61-18942. Specific examples of suitable hardening agents are aldehyde hardening agents (e.g., formaldehyde), aziridine hardening agents, epoxy hardening agents



$$(\text{e.g.,}\ \underbrace{CH_2-CH}_{O}-CH_2-O-(CH_2)_4-O-CH_2-\underbrace{CH-CH_2}_{O}),$$

vinylsulfone hardening agents (e.g., N,N′-ethylenebis(vinylsulfonylacetamido)ethane), N-methylol hardening agents (e.g., dimethylolurea), and high-molecular weight hardening agents (e.g., the compounds described in JP-A-62-234157).

Layers constituting the light-sensitive material or dye fixing material can contain various surface active agents for the purpose of coating aid, improvement of release, improvement of slip properties, prevention of static charge, and acceleration of development. However, the amount of the anionic surface active agent is adjusted based on the description described above in the present invention.

Layers constituting the light-sensitive material or dye fixing material can further contain organofluoro compounds for the purpose of improvement of slip properties, prevention of static charge, and improvement of release. Typical examples of the organofluoro compounds are fluorine-containing surface active agents as described in JP-B-57-9053 (Cols. 8-17), JP-A-61-20944, and JP-A-62-135826, and hydrophobic fluorine compounds, such as oily fluorine compounds (e.g., fluorine oil) and solid fluorine compound resins (e.g., tetrafluoroethylene resin). However, the amount of the organofluoro compounds which have an anionic residue and an ability of surface activity is adjusted based on the definition described above in the present invention.

The light-sensitive material or dye fixing material may also contain a matting agent, such as the compounds described in JP-A-61-88256 (p. 29) (e.g., silicon dioxide, polyolefins, and polymethacrylates), and the compounds described in JP-A-63-274944 and JP-A-63-274952 (e.g., benzoguanamine resin beads, polycarbonate resin beads, and AS resin beads).

Layers constituting the light-sensitive material or dye fixing material may further contain other additives, such as thermal solvents, defoaming agents, antiseptic biocides, and colloidal silica. Specific examples of these additives are described in JP-A-61-88256, pp. 26-32.

The light-sensitive material or dye fixing material may furthermore contain image formation accelerators. Image formation accelerators have functions to accelerate reduction-oxidation reaction between a silver salt oxidizing agent and a reducing agent, to accelerate dye formation, dye decomposition or release of a diffusible dye from a dye donating compound, and to accelerate transfer of a dye from a light-sensitive layer to a dye fixing layer. From the viewpoint of physicochemical functions, image formation accelerators are classified into bases or base precursors, nucleophilic compounds, high-boiling organic solvents (oils), thermal solvents, surface active agents, and compounds interacting with silver or silver ion. Note that these groups of substances generally have composite functions to exhibit some of the above-described accelerating effects combined. For details, reference can be made in U.S. Patent 4,678,739, Cols. 38-40.

The light-sensitive material and/or dye fixing material may contain various development stopping agents for the purpose of obtaining images of constant quality irrespective of variations in temperature and time of development. The terminology "development stopping agent" as used herein means a compound which, after proper development, rapidly neutralizes a base or reacts with a base to reduce the base concentration in the film to thereby stop development or a compound which, after proper development, interacts with silver or a silver salt to inhibit development. Examples of such a development stopping agent include acid precursors which release an acid on heating, electrophilic compounds which undergo substitution reaction with a co-existing base on heating, and nitrogen-containing heterocyclic compounds, mercapto compounds and precursors thereof. For details, reference can be made to JP-A-62-253159 pp. 31-32.

Supports which can be used in the light-sensitive material and/or dye fixing material should withstand a processing temperature and generally include paper and synthetic resin films. Specific examples of suitable supports are films of polyethylene terephthalate, polycarbonate, polyvinyl chloride, polystyrene, polypropylene, polyimide, and cellulose derivatives (e.g., triacetyl cellulose), films of these synthetic resins having incorporated therein pigments, e.g., titanium oxide, synthetic paper films made of polypropylene, etc., mixed paper prepared from a synthetic resin pulp (e.g., polyethylene) and a natural pulp, Yankee paper, baryta paper, coated paper (particularly cast coat paper), metals, fabrics, glass, and the like.

These supports may be used either alone or in the form of a sheet laminated with a synthetic high polymer, e.g., polyethylene, on one or both sides thereof.

In addition, the supports described in JP-A-62-253159 (pp. 29-31) may also be employed.

The surfaces of the support may be coated with a hydrophilic binder and a semiconducting metal oxide (e.g., alumina sol and tin oxide), carbon black or other antistatic agents.

Image formation or recording on the light-sensitive material by exposure is performed by a process comprising directly photographing scenery or persons with a camera, etc., a process comprising exposing the light-sensitive material to light through a reversal film or a negative film by using a printer or an enlarger, a process comprising exposing an original by scanning through a slit by using an exposing means of a copying machine, etc., a process comprising exposing the light-sensitive material to light emitted from a light-emitting diode (LED) or a laser by electrical signals converted from image information, and a process comprising putting image information into an image display device, e.g., a CRT, a liquid crystal display, an electroluminescence display, and a plasma display, and exposing the light-sensitive material to light emitted therefrom directly or via an optical system.

Light sources for recording images on the light-sensitive material include natural light, a tungsten lamp, an LED, a laser light source, and a CRT light source as described in U.S. Patent 4,500,626, Col. 56.

Imagewise exposure may also be carried out by using a wavelength conversion element comprising a combination of a nonlinear optical material and a coherent light source such as a laser. The terminology "nonlinear optical material" as used herein means a material capable of exhibiting nonlinearity between polarization and an electrical field when a strong opto-electrical field, such as a laser beam, is applied thereto. Suitable examples of such a material include inorganic compounds, e.g., lithium niobate, potassium dihydrogenphosphate (KDP), lithium iodate, and BaB_2O_4; urea derivatives; nitroaniline derivatives; nitropyridine-N-oxide derivatives, e.g., 3-methyl-4-nitropyridine-N-oxide (POM), and compounds described in JP-A-61-53462 and JP-A-62-210432. Known wavelength conversion elements include a single crystal optical waveguide mode and a fiber mode, both of which can be used in the present invention.

Image information which can be recorded on the light-sensitive material includes picture signals obtained from a video camera, an electron still camera, etc., TV signals according to Nippon Television Signal Code (NTSC), picture signals obtained by dividing an original into many pixels, and picture signals produced by means of a computer represented by CG or CAD.

The light-sensitive material and/or dye fixing material may have an electrically conductive heating element layer as a heating means for heat development or dye diffusion transfer. In this case, transparent or opaque heating elements described in JP-A-61-145544 can be utilized. The electrically conductive layer also serves as an antistatic layer.

The heating temperature for heat development is from about 50 °C to about 250 °C and preferably from about 80 °C to about 180 °C. The dye diffusion transfer process may be carried out simultaneously with or after heat development. In the latter case, transfer can be effected at a temperature of from room temperature up to the heat developing temperature, particularly from 50° C to a temperature about 10° C lower than the heat developing temperature.

Migration of a dye can be effected only by heat application. A solvent may be used to accelerate migration of a dye. In a preferred embodiment of an image formation system, the light-sensitive material is heated, either after or simultaneously with imagewise exposure, in the presence of a small amount of water as a solvent and a base and/or a base precursor thereby to conduct development and simultaneously or successively transfer a dif fusible dye formed on the area corresponding or counter-corresponding to a developed silver image to the dye fixing layer. According to this image formation system, a dye image of high density can be obtained in a short time since formation or release of a diffusible dye proceeds very rapidly, and transfer of the formed or released diffusible dye to a dye fixing layer also proceeds rapidly.

The amount of water to be used in the above-described embodiment is at least 1/10 the weight of the total coated films of the light-sensitive material and dye fixing material and preferably as small as not more than the weight of water corresponding to the maximum swollen volume of the total coated films, particularly not more than the amount obtained by subtracting the weight of the total coated films from the weight of water corresponding to the maximum swollen volume of the total coated films.

The coated films become very labile on swelling and are likely to cause local smearing under some conditions. To avoid this, the amount of water supplied is preferably not more than the weight corresponding to the water volume of the total coated films of both the light-sensitive material and the dye fixing material swollen to the maximum degree. More specifically, water is preferably used in an amount of from 1 to 50 g, more preferably from 2 to 35 g, and most preferably from 3 to 25 g, per m^2 of the total area of the light-sensitive material and the dye fixing material.

The base and/or base precursor which can be used in this embodiment may be incorporated into either of the light-sensitive material and the dye fixing material. It may also be supplied as dissolved in water to be supplied.

In the above-described embodiment, it is preferable that a combination of a sparingly water soluble basic metallic compound and a compound capable of complexing with a metallic ion constituting said metallic compound in a water medium is made to exist in the image formation reaction system as a base precursor. These two compounds are allowed to react on heating to increase a pH of the system. The terminology "image formation reaction system" as herein referred to means a region where an cage formation reaction takes place and includes layers belonging to each of the light-sensitive material and the dye fixing material. When there are two or more layers, any of these layers may be called "image formation reaction system".

In order to prevent reaction between the sparingly soluble metallic compound and the complexing compound before development processing, it is necessary to incorporate these compounds at least into separate layers. For example, in the case of mono-sheet materials comprising a light-sensitive material and a dye fixing material on the same support, these two compounds should be added to different layers preferably with at least one layer being interposed therebetween. In a more preferred embodiment, the two compounds are added to different layers each separately provided on the respective support. For instance, it is desirable to add a sparingly soluble metallic compound to a light-sensitive material, while adding a complexing compound to a dye fixing element having its own support. The complexing compound may be supplied as dissolved in water which is supplied as a solvent for image formation. The sparingly soluble metallic compound is preferably added as a finely divided dispersion prepared by the method described in JP-A-56-174830 and JP-A-53-102733. The dispersion preferably has an average particle size of 50 µm or less, and more preferably 5 µm or less. The sparingly soluble metallic compound may be added to any one or more layers of the light-sensitive material, such as a light-sensitive layer, an intermediate layer, and a protective layer.

The amount each of the sparingly soluble metallic compound and complexing compound to be added depends on the kind of the compound, the particle size of the sparingly soluble metallic compound, the rate of complexing, and the like. Usually, it is not more than 50% by weight, preferably from 0.01 to 40% by weight, based on the weight of the coating. Where the complexing compound is supplied as dissolved in water, a preferred concentration ranges from 0.005 to 5 mol/ℓ, and particularly from 0.05 to 2 mol/ℓ. The ratio of complexing compound to sparingly soluble metallic compound in the reaction system usually ranges from 1/100 to 100, and preferably from 1/10 to 20, by mole.

Water can be supplied to a light-sensitive layer or a dye fixing layer in accordance with the method described in JP-A-61-147244.

Heating for development and/or dye transfer can be carried out by using a heating means, e.g., a heated block or plate, a heating plate, a hot presser, a heat roller, etc., as described in JP-A-61-147244.

The light-sensitive element and/or dye fixing element may be directly heated by providing a conductive layer made of a conductive material, e.g., graphite, carbon black, and a metal, and passing electricity through the conductive layer.

With respect to pressure conditions and processes of pressure application in bringing the light-sensitive material and the dye fixing material into intimate contact, the disclosure of JP-A-61-147244 can be referred to.

Any of various heat developing apparatus can be employed for photographic processing of the photographic element of the present invention. Examples of suitable apparatus are described in JP-A-59-75247, JP-A-59-177547, JP-A-59-181353, JP-A-60-18951, and JP-A-U-62-25944 (the term "JP-A-U" as used herein means an "unexamined published Japanese utility model application").

The present invention is now illustrated in greater detail by way of Examples, but it should be understood that the present invention is not deemed to be limited thereto. In Examples, all the parts, percents, and ratios are by weight unless otherwise indicated.

EXAMPLE 1

Preparation of Dye Fixing Materials

Preparation of Dye Fixing Material (5):

Dye Fixing Material (5) having the following layer structure was prepared.

3rd Layer:	
Gelatin	0.05 g/m^2
Silicone oil (1)	0.04 g/m^2
Surface active agent (2)	0.03 g/m^2
Surface active agent (3)	0.10 g/m^2
Surface active agent (4)	0.08 g/m^2
Matting agent (1)	0.02 g/m^2
Guanidine picolinate	0.45 g/m^2
Water-soluble polymer (1)	0.24 g/m^2

2nd Layer:	
Mordant (1)	2.35 g/m^2
Water-soluble polymer (1)	0.20 g/m^2
Gelatin	1.40 g/m^2
Water-soluble polymer (2)	0.60 g/m^2
High-boiling solvent (2)	1.40 g/m^2
Guanidine picolinate	2.25 g/m^2
Fluorescent brightening agent F-30	0.05 g/m^2
Surface active agent (1)	0.10 g/m^2
Surface active agent (5)	0.01 g/m^2

1st Layer:	
Gelatin	0.45 g/m^2
Surface active agent (3)	0.01 g/m^2
Water-soluble polymer (1)	0.04 g/m^2
Hardening agent (1)	0.30 g/m^2

Support (1):

Shown in Table 1 below.

1st Backing Layer:	
Gelatin	3.25 g/m^2
Hardening agent (1)	0.25 g/m^2

2nd Backing Layer:	
Gelatin	0.44 g/m^2
Silicone oil (1)	0.08 g/m^2
Surface active agent (4)	0.04 g/m^2
Surface active agent (5)	0.01 g/m^2
Matting agent (2)	0.03 g/m^2

TABLE 1

Structure of Support (1):		
Layer	Composition	Film Thickness (µm)
Surface subbing layer	Gelatin	0.1
Surface PE layer (glossy)	Low-density polyethylene (density: 0.923) : 89.2 parts Surface-treated titanium oxide: 10.0 parts Ultramarine : 0.8 part	45.0
Pulp layer	Fine paper (LBKP/NBKP = 1:1; density: 1.080)	96.2
Back PE layer (matte)	High-density polyethylene (density: 0.960)	36.0
Back subbing layer	Gelatin Colloidal silica	0.05 0.05
	Total:	173.8

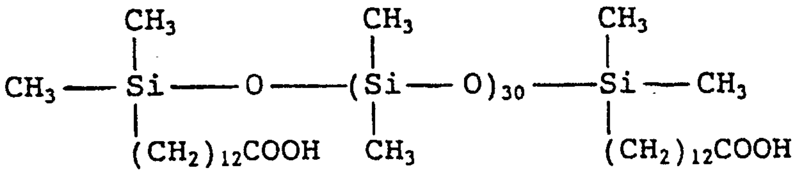
Physical properties of Support (1) are shown in Table 2 below.

TABLE 2

Physical Properties	Measured Value	Method of Measurement
Stiffness (longitudinal direction/width direction)	4.40/3.15 (unit; g)	Taber stiffness tester
Whiteness	L* 94.20 a* +0.12 b* -2.75	CIE L*a*b*

Compounds used in sample preparation were as follows.

Silicone Oil (1):

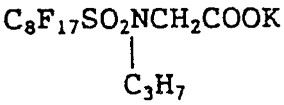


$$CH_3-\underset{(CH_2)_{12}COOH}{\overset{CH_3}{Si}}-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_{30}-\underset{(CH_2)_{12}COOH}{\overset{CH_3}{Si}}-CH_3$$

Surface Active Agent (1):

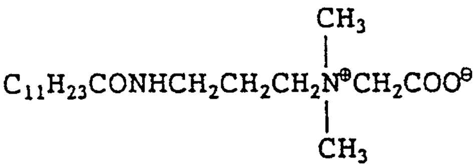
(n: about 12.6)

Surface Active Agent (2):



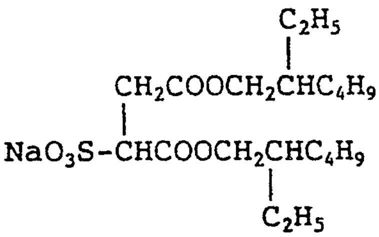
$$C_8F_{17}SO_2\underset{C_3H_7}{N}CH_2COOK$$

Surface Active Agent (3):



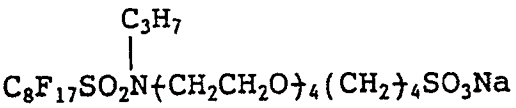
$$C_{11}H_{23}CONHCH_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}CH_2COO^{\ominus}$$

Surface Active Agent (4):



$$\begin{array}{l} CH_2COOCH_2\overset{C_2H_5}{C}HC_4H_9 \\ | \\ NaO_3S-CHCOOCH_2\underset{C_2H_5}{C}HC_4H_9 \end{array}$$

Surface Active agent (5):



$$C_8F_{17}SO_2\overset{C_3H_7}{\overset{|}{N}}\!\!-\!(CH_2CH_2O)_4(CH_2)_4SO_3Na$$

Fluorescent Brightening Agent F-30:

2,5-Bis(5-t-butylbenzoxazole(2))thiophene

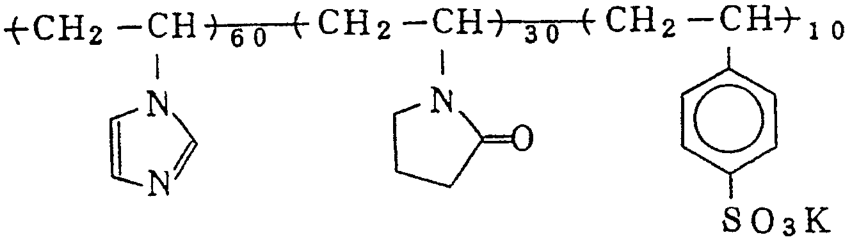
Water-Soluble Polymer (1):

Sumikagel L5-H (produced by Sumitomo Chemical Co., Ltd.)

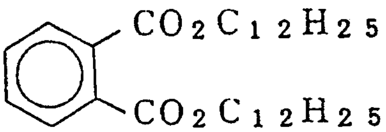
Water-Soluble Polymer (2):

Dextran (molecular weight: 70,000)

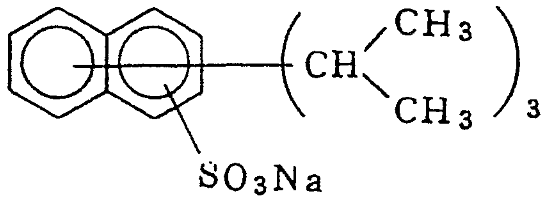
Mordant (1):



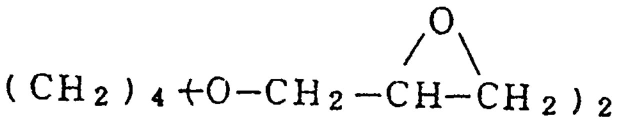
High-Boiling Solvent (1):



Surface Active Agent (6):



Hardening Agent (1):



$(CH_2)_4(O-CH_2-\overset{\diagup O \diagdown}{CH-CH_2})_2$

Matting Agent (1):

Silica

Matting Agent (2):

Benzoguanamine resin (average particle size: 15 µm)

The fluorescent brightening agent was used in the form of a gelatin dispersion prepared as follows.

Five grams of Fluorescent brightening agent (1) was dissolved in 140 g of High-boiling organic solvent (2) and 50 mℓ of ethyl acetate under heating to prepare a uniform solution. The resulting solution was mixed with 300 g of a 20% aqueous solution of lime-processed gelatin and 10.0 g of Surface active agent (1) with stirring, and the mixture was dispersed by means of a ultrasonic dispersing machine.

Dye fixing materials (1) to (4) and (6) to (37) were prepared in the same manner as for Dye fixing material (5), except that the gelatin dispersion of Fluorescent brightening agent F-30 was replaced with a dispersion prepared in the same manner as described above by using each of the fluorescent brightening agents and high-boiling organic solvents shown in Table 3 below and Surface active agent (1), (4) or (6) for the 2nd layer of the amount shown in Table 3.

TABLE 3

Dye Fixing Material	Fluorescent Brightening Agent Dispersion			3rd Layer		2nd Layer	Total Amount of Anionic Surface Active Agents (mg/m^2)	Remark
	Fluorescent Brightening Agent	High-Boiling Organic Solvent	Surface Surface Active Agent (mg/m^2)	Surface Active Agent (4) (mg/m^2)	Surface Active Agent (2) (mg/m^2)	Surface Active Agent (5) (mg/m^2)		
(1)	F-30	(2)	-	15	-	-	15	Comparison
(2)	F-30	(2)	-	30	-	-	30	Invention
(3)	F-30	(2)	(1) 30	50	30	-	110	"
(4)	F-30	(2)	(1) 60	80	30	10	180	"
(5)	F-30	(2)	(1) 100	80	30	10	220	Comparison
(6)	F-30	(3)	(1) 30	50	30	-	110	Invention
(7)	F-30	(4)	(1) 30	50	30	-	110	"
(8)	F-30	(5)	(1) 30	80	-	-	110	"
(9)	F-30	(5)	(1) 100	80	40	-	220	Comparison
(10)	F-30	(1)	(1) 30	80	-	-	110	Invention
(11)	F-10	(1)	(1) 30	80	-	-	110	"
(12)	F-16	(1)	(1) 30	80	-	-	110	"

TABLE 3 (cont'd.)

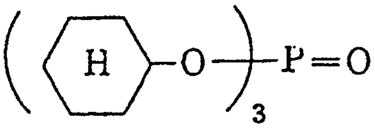
Dye Fixing Material	Fluorescent Brightening Agent Dispersion			3rd Layer		2nd Layer	Total Amount of Anionic Surface Active Agents (mg/m²)	Remark
	Fluorescent Brightening Agent	High-Boiling Organic Solvent	Surface Surface Active Agent (mg/m²)	Surface Active Agent (4) (mg/m²)	Surface Active Agent (2) (mg/m²)	Surface Active Agent (5) (mg/m²)		
(13)	F-30	(1)	(1) 60	80	40	-	180	Invention
(14)	F-30	(6)	(1) 60	80	40	-	180	"
(15)	F-30	(6)	(1) 100	80	30	10	220	Comparison
(16)	F-10	(6)	(1) 100	80	40	-	220	"
(17)	F-30	(7)	(1) 30	50	-	-	80	Invention
(18)	F-30	(8)	(1) 30	50	-	-	80	"
(19)	F-30	(9)	(1) 30	50	-	-	80	"
(20)	F-30	(9)	(1) 60	80	40	-	180	"
(21)	F-30	(9)	(1) 100	80	40	-	220	Comparison
(22)	F-30	(10)	(1) 30	80	30	10	150	Invention
(23)	F-30	(11)	(1) 30	80	30	10	150	"
(24)	F-30	(13)	(1) -	15	-	-	15	Comparison

TABLE 3 (cont'd.)

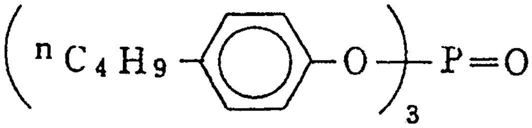
Dye Fixing Material	Fluorescent Brightening Agent Dispersion: Fluorescent Brightening Agent	Fluorescent Brightening Agent Dispersion: High-Boiling Organic Solvent	Fluorescent Brightening Agent Dispersion: Surface Surface Active Agent (mg/m²)	3rd Layer: Surface Active Agent (4) (mg/m²)	3rd Layer: Surface Active Agent (2) (mg/m²)	2nd Layer: Surface Active Agent (5) (mg/m²)	Total Amount of Anionic Surface Active Agents (mg/m²)	Remark
(25)	F-30	(13)	(1) -	30	-	-	30	Invention
(26)	F-30	(13)	(1) 30	80	40	-	150	"
(27)	F-30	(12)	(1) 30	50	-	-	80	"
(28)	F-10	(12)	(1) 30	50	-	-	80	"
(29)	F-16	(12)	(1) 30	50	-	-	80	"
(30)	F-30	(12)	(1) 30	80	40	-	150	"
(31)	F-30	(12)	(1) 60	80	40	10	180	"
(32)	F-30	(14)	(1) 30	50	-	-	80	"
(33)	F-30	(15)	(1) 30	80	30	10	150	"
(34)	F-30	(2)	(6) 30	80	-	-	110	"
(35)	F-30	(1)	(6) 30	80	-	-	110	"
(36)	F-30	(12)	(6) 30	80	40	-	150	"
(37)	F-30	(14)	(6) 30	50	-	-	80	"

Compounds used in the preparation of Dye fixing materials (1) to (4) and (6) to (37) are as follows.

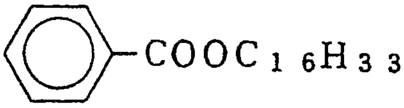
High-Boiling Organic solvent (2):



High-Boiling Organic Solvent (3):



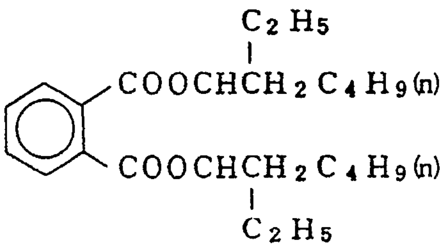
High-Boiling Organic Solvent (4):



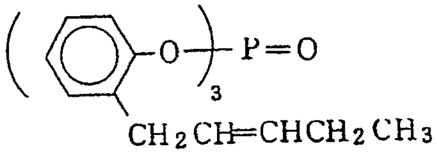
High-Boiling Organic Solvent (5):

$nC_{11}H_{23}CON{(}C_2H_5)_2$

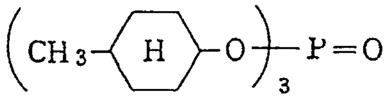
High-Boiling Organic Solvent (6):



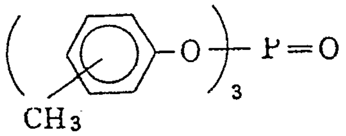
High-Boiling Organic Solvent (7):



High-Boiling Organic Solvent (8):

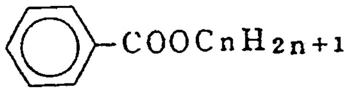


High-Boiling Organic Solvent (9):



Ratio of positional isomers (o:m:p) = 40:12:48

High-Boiling Organic Solvent (10):



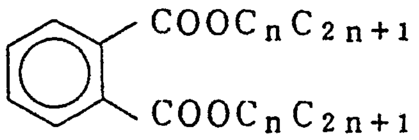
Ratio of alkyl chain length (n=10:n=12:n=14:n=16) = 0.4:5:17:78

High-Boiling Organic Solvent (11):

$(C_nH_{2n+1}O)P=O$

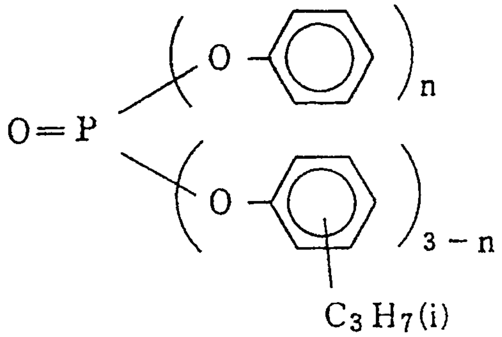
Ratio of alkyl chain length (n=6:n=8:n=9) = 2:11:87

High-Boiling Organic Solvent (12):



Ratio of alkyl chain length (n=10:n=12) = 5:95

High-Boiling Organic Solvent (13):



(n: about 1.7)

High-Boiling Organic Solvent (14):

$C_{26}H_{43.5}Cl_{6.5}$ (Cℓ content: about 41%)

High-Boiling Organic Solvent (15):

$C_{14}H_{25.9}Cl_{4.1}$ (Cℓ content: about 43%)

The multilayer light-sensitive material prepared in Reference Example was exposed to light of a tungsten lamp (5,000 lux) through a gray filter having a continuously varying density.

The exposed light-sensitive material was forwarded on a line at a linear speed of 20 mm/sec while supplying water to the emulsion surface thereof at a rate of 15 mℓ/m^2 with a wire bar and, immediately thereafter, each of Dye fixing materials (1) to (37) was brought into intimate contact with the light-sensitive material in such a manner that the coated surfaces faced to each other.

The film unit was heated for 15 seconds by means of a heat roller set at such a temperature that the film having absorbed water was heated to 80° C. The light-sensitive material was then stripped off the dye fixing material to thereby obtain a gray image on the dye fixing material.

Specular gloss of the Dye fixing material at an angle of incident of 20° was measured with a glossmeter manufactured by Nihon Densoku Kogyo K.K.. Then, the dye fixing material was allowed to stand at 50° C and 80% RH for 40 hours, and the specular gloss was measured again.

The maximum density D_{max} of the image formed on the dye fixing material was measured with a densitometer ("FCD-3" manufactured by Fuji Photo Film Co., Ltd.). Then, the dye fixing material was allowed to stand under a fluorescent lamp (15,000 lux) for 4 weeks, and the maximum density D'_{max} was measured again. A D'_{max} to D_{max} ratio was obtained.

Releasability between the light-sensitive material and dye fixing material was systemically evaluated from how much force was required for releasing, whether or not the surface of the dye fixing material suffered from peeling on releasing, or whether or not the film of the light-sensitive material remained on the dye fixing material after releasing.

The results of these measurements and evaluations are shown in Table 4 below.

TABLE 4

Dye Fixing Material	Surface Gloss Before Preservation	Surface Gloss After Preservation	D'_{max}/D_{max} Ratio	Releasability	Remark
(1)	58	35	0.93	Poor	Comparison
(2)	61	54	0.92	Medium	Invention
(3)	63	57	0.93	Good	"
(4)	65	56	0.91	"	"
(5)	61	37	0.83	"	Comparison
(6)	63	57	0.93	"	Invention
(7)	64	57	0.92	"	"
(8)	63	54	0.84	"	"
(9)	60	31	0.91	"	Comparison
(10)	75	70	0.95	"	Invention
(11)	73	68	0.90	"	"
(12)	73	67	0.94	"	"
(13)	69	61	0.95	"	"
(14)	66	59	0.93	"	"

TABLE 4 (Cont'd.)

Dye Fixing Material	Surface Gloss		D'_{max}/D_{max} Ratio	Releasability	Remark
	Before Preservation	After Preservation			
(15)	67	32	0.85	Good	Comparison
(16)	67	34	0.80	Medium	"
(17)	74	69	0.92	Good	Invention
(18)	72	68	0.91	"	"
(19)	73	68	0.94	"	"
(20)	74	66	0.92	"	"
(21)	72	30	0.83	"	Comparison
(22)	71	64	0.91	"	Invention
(23)	72	65	0.92	"	"
(24)	60	35	0.92	Poor	Comparison
(25)	66	64	0.92	Good	Invention
(26)	73	66	0.93	"	"
(27)	83	80	0.95	"	"
(28)	76	72	0.91	"	"

TABLE 4 (Cont'd.)

Dye Fixing Material	Surface Gloss		D'_{max}/D_{max} Ratio	Releasability	Remark
	Before Preservation	After Preservation			
(29)	77	74	0.95	Good	Invention
(30)	79	73	0.94	"	"
(31)	77	71	0.94	"	"
(32)	81	78	0.96	"	"
(33)	82	76	0.97	"	"
(34)	64	58	0.92	"	"
(35)	76	72	0.91	"	"
(36)	80	76	0.95	"	"
(37)	78	75	0.90	"	"

As is apparent from Tables 3 and 4, the dye fixing materials according to the present invention in which a total amount of anionic surface active agents used falls within a specific range exhibit satisfactory releasability and surface gloss. To the contrary, when the total amount of surface active agents is less than the specified range (Sample Nos. 1 and 24), although the initial surface gloss is satisfactory, the dye fixing materials have deteriorated releasability. Moreover, the surface gloss of these samples is reduced with time. The reason to which these results are ascribed is not clear, but it is believed that the stability of the fluorescent brightening agent dispersion is reduced thereby to accelerate precipitation of oil-soluble components.

When the total amount of surface active agents is more than the specified range, surface gloss is poor and also subject to deterioration with time. Besides, the dye image exhibits slightly deteriorated light stability. It is believed, while not clear, that the anionic surface active agents undergo mutual action with a cationic mordant to reduce image stability.

Further, when in using a phthalic ester (Sample Nos. 10 to 14) or a combination of two or more kinds of high-boiling organic solvents (Sample Nos. 17 to 20, 23 to 26) in the preparation of a fluorescent brightening agent dispersion, satisfactory surface gloss can be obtained, and changes during preservation can be reduced. The dye images formed on the dye fixing materials of the present invention have satisfactory stability.

From all these considerations, the effects of the present invention are obvious.

The construction of the light-sensitive material (1) used in the present examples are illustrated below.

The preparation of the light-sensitive silver halide emulsion in each layer is described.

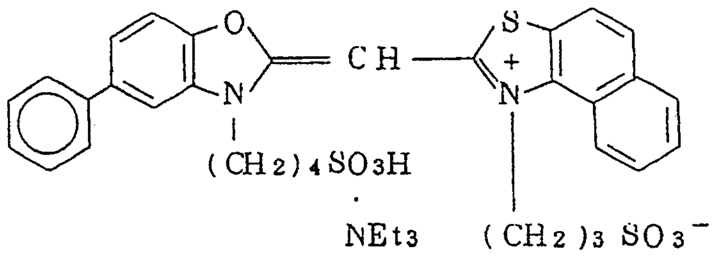
Preparation of Emulsion (I)

A gelatin aqueous solution was prepared from 800 mℓ of water, 20 g of gelatin, 3 g of potassium bromide, and 0.3 g of $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$, and the solution was kept at 55°C with stirring. Solutions (I) and (II) shown below were simultaneously added to the gelatin aqueous solution over 30 minutes. Then, Solutions (III) and (IV) shown below were added thereto over 20 minutes. After 5 minutes from the start of the addition of Solutions (III) and (IV), a dye solution prepared by dissolving 0.12 g each of Dyes (a) and (b) shown below in 160 mℓ of methanol was added thereto over 18 minutes.

After washing with water and desalting, 20 g of lime-processed osseous gelatin was added thereto, and the emulsion was adjusted to a pH of 6.2 and a pAg of 8.5. To the emulsion were added sodium thiosulfate, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, and chloroauric acid to conduct optimal chemical sensitization to prepare 600 g of a mono-dispersed tetradecahedral silver iodobromide emulsion having a mean grain size of 0.40 µm. The resulting emulsion was designated Emulsion (I).

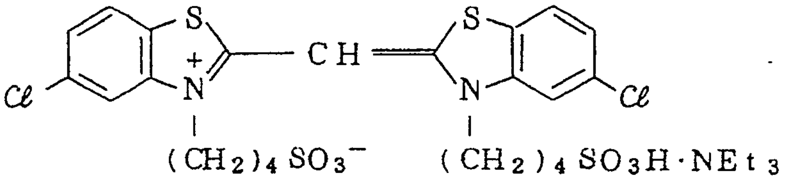
	Solution I	Solution II	Solution III	Solution IV
$AgNO_3$	30 g	-	70 g	-
KBr	-	20 g	-	49 g
KI	-	1.8 g	-	-
Water to make:	180 mℓ	180 mℓ	350 mℓ	350 mℓ

Dye (a):



0.12g

Dye (b):

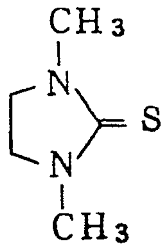


Preparation of Emulsion (II):

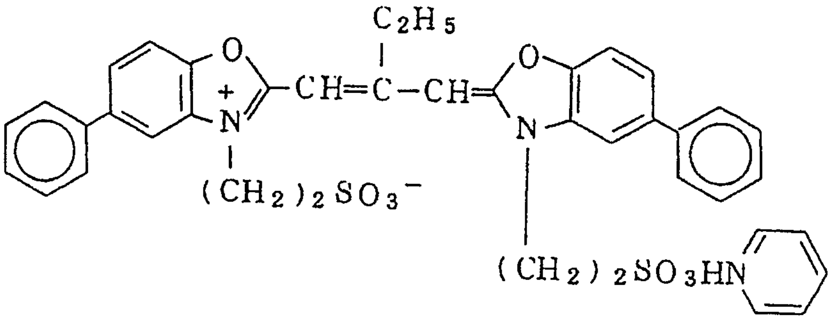
An aqueous gelatin solution was prepared from 730 mℓ of water, 20 g of gelatin, 0.30 g of potassium bromide, 6 g of sodium chloride, and 0.015 g of Compound (A) shown below, and the solution was kept at 60.0° C under stirring. To the gelatin aqueous solution were added simultaneously Solutions (I) and (II) shown below at constant flow rates over 60 minutes. After the addition of Solutions (I) and (II), 77 mℓ of a methanol solution containing 0.23 g of Sensitizing Dye (c) shown below was added thereto to obtain a mono-dispersed cubic grain emulsion having a mean grain size of 0.45 µm.

After washing with water and desalting, 20 g of gelatin was added to the emulsion, and the emulsion was adjusted to a pH of 6.4 and a pAg of 7.8. The emulsion was then chemically sensitized with 1.6 mg of triethylthiourea and 100 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 60.0° C for 55 minutes to obtain 635 g of an emulsion designated Emulsion (II).

Compound (A):



Dye (c):



	Solution I	Solution II
$AgNO_3$	100.0 g	-
KBr	-	56.0 g
NaCℓ	-	7.2 g
Water to make	400 mℓ	400 mℓ

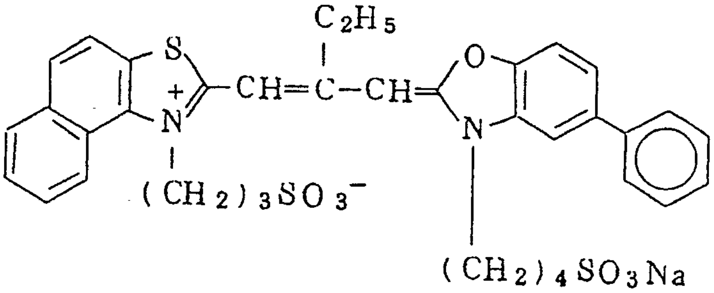
Preparation of Emulsion (III):

A gelatin aqueous solution was prepared from 800 mℓ of water, 20 g of gelatin, 1 g of potassium bromide, and 0.5 g of $OH(CH_2)_2S(CH_2)_2OH$, and the solution was kept at 50° C under stirring. To the gelatin aqueous solution were simultaneously added Solutions (I), (II), and (III) shown below at constant feed rates over a period of 30 minutes to prepare a mono-dispersed emulsion of silver bromide grains having a mean grain size of 0.42 µm having dyes adsorbed thereon.

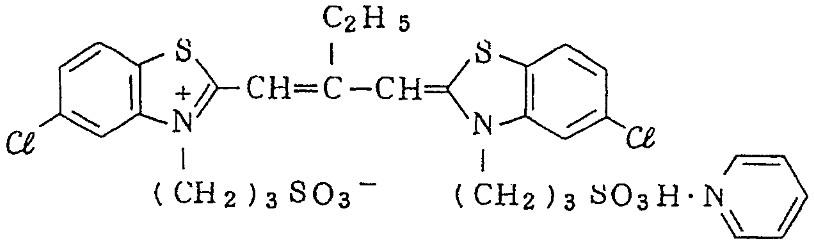
After washing with water and desalting, 20 g of lime-processed osseous gelatin was added to the emulsion, and the emulsion was adjusted to a pH of 6.4 and a pAg of 8.2. To the emulsion kept at 60° C were added 9 mg of sodium thiosulfate, 190 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, and 6 mℓ of a 0.01% aqueous solution of chloroauric acid to conduct chemical sensitization for 45 minutes. The yield of the emulsion was 635 g. The resulting emulsion was designated Emulsion (III).

	Solution I	Solution II	Solution III
$AgNO_3$	100 g	-	-
KBr	-	70 g	-
Dye (d)	-	-	40 mg
Dye (e)	-	-	80 mg
Water to make	450 mℓ	400 mℓ	-
Methanol to make	-	-	60 mℓ

Dye (d):



Dye (e):

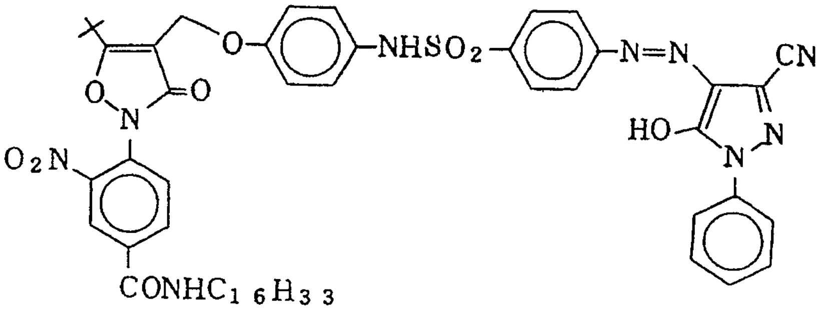


Preparation of Dye Donating Substance Dispersion:

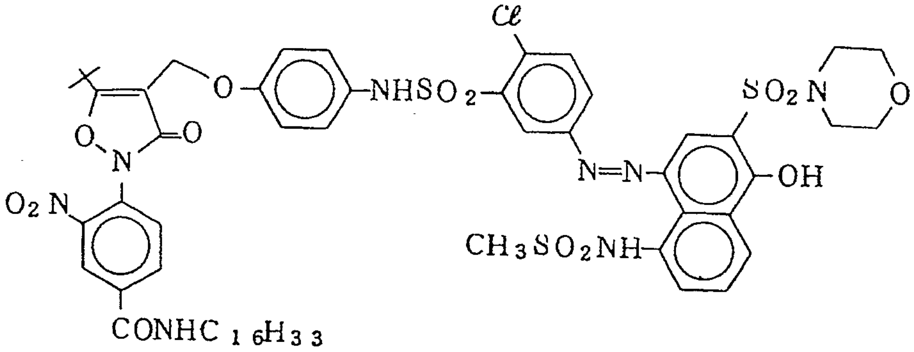
A mixture of a yellow, magenta or cyan dye donating compound, an electron donor, a high-boiling organic solvent, and an electron transfer agent precursor as formulated below was dissolved in 50 mℓ of ethyl acetate under heating at about 60° C to form a uniform solution. The resulting solution was mixed with 100 g of a 10% aqueous solution of lime-processed gelatin, 50 mℓ of water, and 0.6 g of sodium dodecylbenzenesulfonate by stirring, and the mixture was dispersed in a homogenizer at 10,000 rpm for 10 minutes to prepare a gelatin dispersion of the respective dye donating compound.

	Yellow	Magenta	Cyan
Dye donating compound	(1) 13.0 g	(2) 15.5 g	(3) 16.6 g
Electron donor (1)	10.2 g	8.6 g	8.1 g
High-boiling solvent (2)	6.5 g	7.8 g	8.3 g
Electron transfer agent precursor (3)	0.4 g	0.7 g	0.7 g

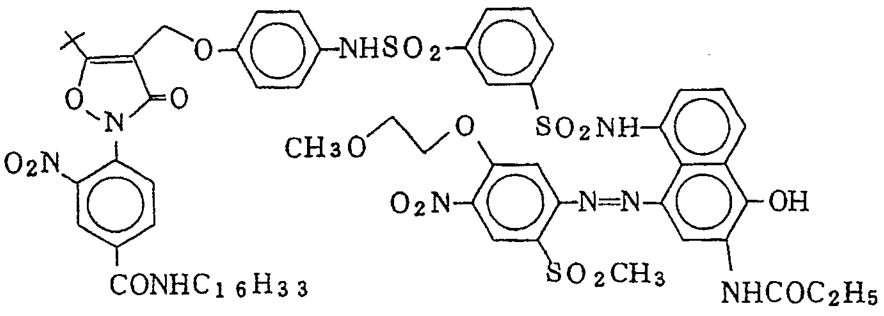
Dye Donating Compound (1):



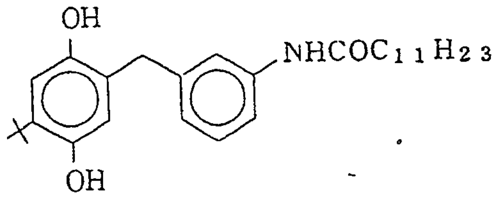
Dye Donating Compound (2):



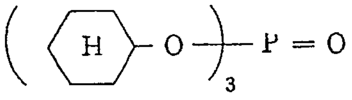
Dye Donating Compound (3):



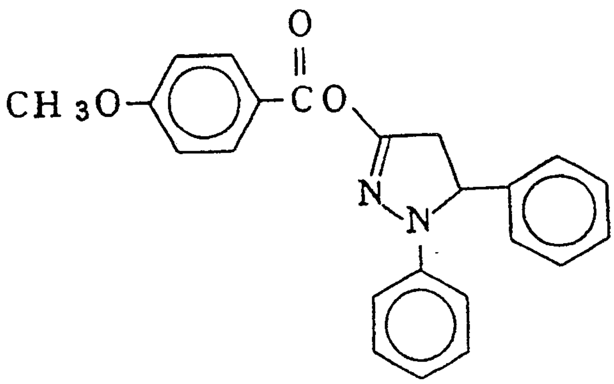
Electron Donor (1):



High-Boiling Solvent (2):



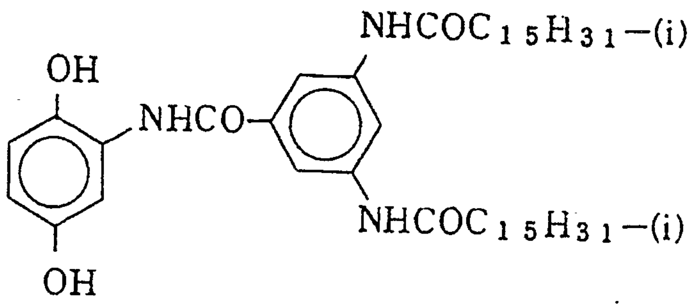
Electron Transfer Agent Precursor (3):



Preparation of Gelatin Dispersion of Electron Donor (4):

To 30 mℓ of ethyl acetate were added 23.6 g of Electron donor (4) shown below and 8.5 g of High-boiling solvent (2) shown above to form a uniform solution. The resulting solution was mixed with 100 g of a 10% aqueous solution of lime-processed gelatin, 0.25 g of sodium hydrogensulfite, 0.3 g of sodium dodecylbenzenesulfonate, and 30 mℓ of water with stirring, and the mixture was dispersed in a homogenizer at 10,000 rpm for 10 minutes.

Electron Donor (4):



Preparation of Zinc Hydroxide Dispersion:

To 100 mℓ of a 4% gelatin aqueous solution were added 12.5 g of zinc hydroxide having an average particle size of 0.2 µm, 1 g of carboxymethyl cellulose as a dispersing agent, and 0.1 g of sodium polyacrylate, and the mixture was ground in a mill by using glass beads of 0.75 mm in diameter as a grinding medium for 30 minutes. The glass beads were separated to obtain a dispersion of zinc hydroxide.

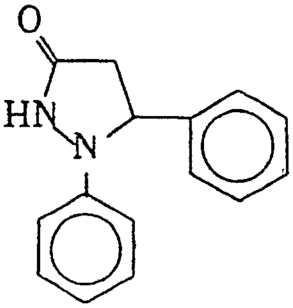
Preparation of Activated Carbon Dispersion:

To 100 mℓ of a 5% gelatin aqueous solution were added 2.5 g of an activated carbon powder (guaranteed reagent produced by Wako Pure Chemical Industries, Ltd.), 1 g of Demol N (a dispersing agent produced by Kao Soap Co., Ltd.), and 0.25 g of polyethylene glycol nonylphenyl ether, and the mixture was ground in a mill by using glass beads of 0.75 mm in average particle size for 120 minutes. The glass beads were separated to obtain a dispersion of activated carbon having an average particle size of 0.5 µm.

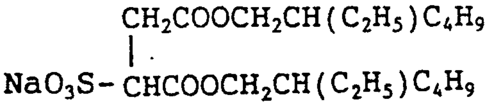
Preparation of Electron Transfer Agent (8):

To a 5% gelatin aqueous solution were added 10 g of Electron transfer agent (8) shown below, 0.5 g of polyethylene glycol nonylphenyl ether as a dispersing agent, and 0.5 g of Anionic surface active agent (6) shown below, and the mixture was ground in a mill by using glass beads of 0.75 mm in diameter for 60 minutes. The glass beads were separated to obtain a dispersion of the electron transfer agent having an average particle size of 0.3 µm.

Electron Transfer Agent (8):



Anionic Surface Active Agent (6):



$$\begin{array}{l} \quad\quad\quad\; CH_2COOCH_2CH(C_2H_5)C_4H_9 \\ \quad\quad\quad\; | \\ NaO_3S-CHCOOCH_2CH(C_2H_5)C_4H_9 \end{array}$$

A heat developable color light-sensitive material having the following layer structure was prepared by using the above prepared silver halide emulsions and dispersions of various additives.

Layer Structure:

6th Layer (Protective Layer):	
Gelatin	900 mg/m^2
Silica (particle size: 4 μm)	40 mg/m^2
Zinc hydroxide	600 mg/m^2
Surface active agent (5)	130 mg/m^2
Surface active agent (6)	26 mg/m^2
Water soluble polymer	8 mg/m^2

5th Layer (Blue-Sensitive Layer):	
Emulsion (I)	380 mg of Ag/m^2
Yellow dye donating compound (1)	400 mg/m^2
Gelatin	600 mg/m^2
Electron donor (1)	308 mg/m^2
High-boiling solvent (2)	200 mg/m^2
Electron transfer agent precursor (3)	15 mg/m^2
Zinc hydroxide	330 mg/m^2
Antifoggant (6)	0.6 mg/m^2
Surface active agent (7)	18 mg/m^2
Water-soluble polymer	13 mg/m^2

4th Layer (Intermediate Layer):	
Gelatin	700 mg/m^2
Electron donor (4)	130 mg/m^2
High-boiling solvent (2)	48 mg/m^2
Surface active agent (6)	15 mg/m^2
Surface active agent (8)	61 mg/m^2
Surface active agent (7)	2 mg/m^2
Electron transfer agent (8)	27 mg/m^2
Electron transfer agent (9)	36 mg/m^2
Water-soluble polymer	19 mg/m^2
Hardening agent (10)	37 mg/m^2

3rd Layer (Green-Sensitive Layer):	
Emulsion (II)	220 mg of Ag/m^2
Magenta dye donating substance (2)	365 mg/m^2
Gelatin	310 mg/m^2
Electron donor (1)	158 mg/m^2
High-boiling solvent (2)	183 mg/m^2
Electron transfer agent precursor (3)	15 mg/m^2
Electron transfer agent (8)	27 mg/m^2
Surface active agent (7)	13 mg/m^2
Water-soluble polymer	11 mg/m^2
Antifoggant (6)	0.8 mg/m^2

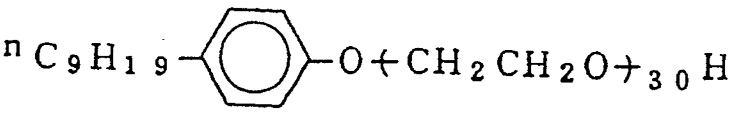
2nd Layer (Intermediate Layer):	
Gelatin	790 mg/m^2
Zinc hydroxide	300 mg/m^2
Electron donor (4)	130 mg/m^2
High-boiling solvent (2)	73 mg/m^2
Surface active agent (7)	2 mg/m^2
Surface active agent (8)	100 mg/m^2
Surface active agent (6)	11 mg/m^2
Water-soluble polymer	12 mg/m^2
Activated carbon	25 mg/m^2

1st Layer (Red-Sensitive Layer):	
Emulsion (III)	230 mg of Ag/m^2
Cyan dye donating compound (3)	343 mg/m^2
Gelatin	330 mg/m^2
Electron donor (1)	163 mg/m^2
High-boiling solvent (2)	172 mg/m^2
Electron transfer agent precursor (3)	17 mg/m^2
Electron transfer agent (8)	28 mg/m^2
Surface active agent (7)	10 mg/m^2
Water-soluble polymer	5 mg/m^2
Antifoggant (11)	0.7 mg/m^2

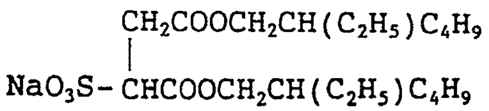
Support:

96 µm thick polyethylene terephthalate film having carbon black on its back.
Compounds used in the preparation of the light-sensitive material are shown below.

Surface Active Agent (5):

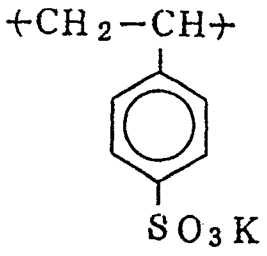


Surface Active Agent (6):

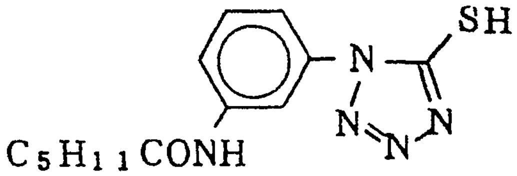


$$\begin{array}{l} \quad CH_2COOCH_2CH(C_2H_5)C_4H_9 \\ \quad | \\ NaO_3S-CHCOOCH_2CH(C_2H_5)C_4H_9 \end{array}$$

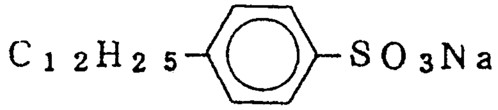
Water-Soluble Polymer:



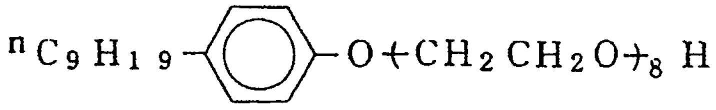
Antifoggant (6):



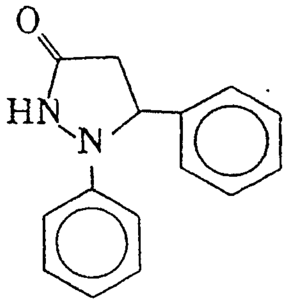
Surface Active Agent (7):



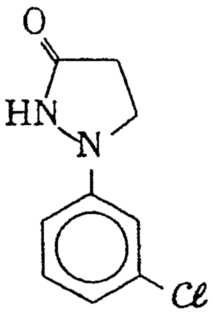
Surface Active Agent (8):



Electron Transfer Agent (8):



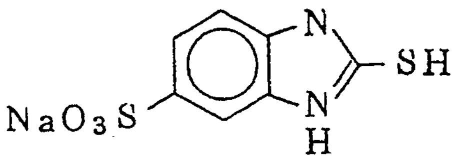
Electron Transfer Agent (9):



Hardening Agent (10):

1,2-Bis(vinylsulfonylacetamido) ethane

Antifoggant (11):



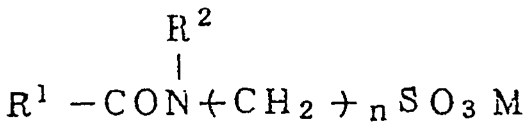
EXAMPLE 2

The dye fixing materials obtained in Example 1 were tested in the same manner as in Example 1, except for replacing the light-sensitive material of Reference Example with the light-sensitive material of Example 1 of JP-A-63-316848. As a result, substantially the same results as in Example 1 were obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

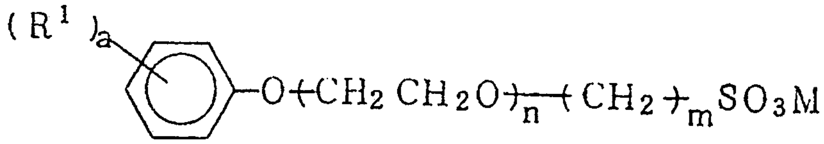
Claims

1. A dye fixing material having a dye fixing layer capable of receiving a diffusible dye formed in a heat developable light-sensitive material by heat development, said dye fixing material containing an oil-soluble fluorescent brightening agent on the side of the dye fixing layer, with a total amount of an anionic surface active agent or agents present on the side of the dye fixing layer falling within the range of from 20 to 200 mg/m^2.
2. A dye fixing material as in claim 1, wherein said oil-soluble fluorescent brightening agent is provided in the form of a dispersion in a dispersing medium comprising a high boiling organic solvent.
3. A dye fixing material as in claim 2, wherein said dispersing medium comprises two or more high boiling organic solvents.
4. A dye fixing material as in claim 2, wherein said high boiling organic solvent comprises phthalic esters or chlorinated paraffins.
5. A dye fixing material as in claim 1, wherein said fluorescent brightening agent is present in the dye fixing material in an amount of from 0.1 to 200 mg/m^2.
6. A dye fixing material as in claim 1, wherein said fluorescent brightening agent is selected from the group consisting of stilbene compounds, coumarin compounds, biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazoline compounds and carbostyril compounds.
7. A dye fixing material as in claim 1, wherein said anionic surface active agent or agents are represented by at least one of formulae (I) to (IX):



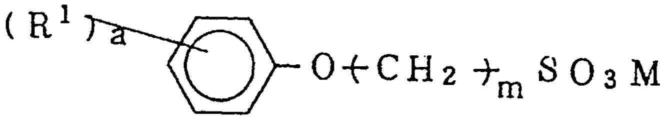
$$R^1-CO\overset{\displaystyle R^2}{\overset{|}{N}}\!-(CH_2)_n SO_3M \qquad (I)$$

wherein R^1 represents a fluorine-substituted or unsubstituted saturated or unsaturated hydrocarbon group having from 3 to 20 carbon atoms; R^2 represents a hydrogen atom or hydrocarbon group having from 1 to 3 carbon atoms; n represents an integer of from 1 to 20; M represents a monovalent alkali metal:



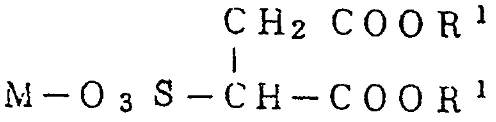
(II)

wherein R^1, M, and n are as defined above; a represents 0, 1 or 2; and m represents an integer of from 1 to 6:



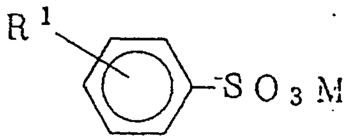
(III)

wherein R^1, M, m and a are as defined above:



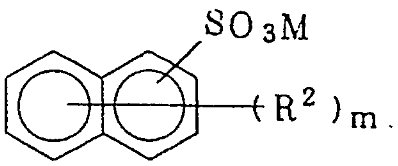
$$M-O_3S-\overset{CH_2COOR^1}{\overset{|}{C}}H-COOR^1 \qquad (IV)$$

wherein R^1 and M are as defined above and the two R^1 groups may be the same or different:
R^1 -O-SO_3M (V)
wherein R^1 and M are as defined above:



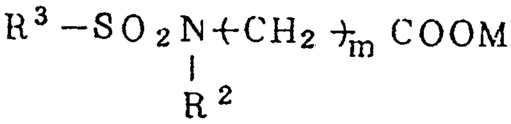
(VI)

wherein R^1 and M are as defined above:



(VII)

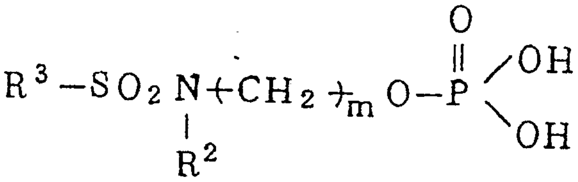
wherein R^2, M and m are as defined above:



$$R^3-SO_2\underset{\substack{|\\R^2}}{N}\left(CH_2\right)_m COOM$$

(VIII)

wherein R^2, M and m are as defined above: R^3 represents a saturated or unsaturated hydrocarbon group having from 3 to 22 carbon atoms which may be partially or completely fluorinated:



$$R^3-SO_2\underset{\substack{|\\R^2}}{N}\left(CH_2\right)_m O-\overset{\substack{O\\ \|}}{P}\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}$$

(IX)

wherein R^2, R^3, and m are as defined above.