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(54) **Silver halide color photosensitive material.**

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Description

FIELD OF THE INVENTION

The present invention relates to a silver halide color photosensitive material containing a dye forming coupler which is little in the drop of color density even when a developing treatment is carried out with a weakly oxidative bleaching bath, bleach-fix bath or fatigued bleaching bath, bleach-fix bath and also is excellent in color image preservability after development; and more particularly, the present invention relates to said photosensitive material which is highly sensitive and excellent in graininess, sharpness and color reproducibility.

BACKGROUND OF THE INVENTION

A color image is formed by reacting a dye forming coupler with an aromatic primary amine developing agent oxidized by color development after light exposure to a silver halide color photosensitive material. Generally in this method, a color reproduction method by a subtractive color process is used, and in order to reproduce blue, green and red, dye images of yellow, magenta and cyan (which are the complement colors of blue, green and red) are formed. For the cyan color image formation, phenol derivatives or naphthol derivatives are mostly employed as a coupler. But it is pointed out that such couplers have defects in that a color image produced by color development is low in fastness to heat or light and the decrease in color density is caused when a developing treatment is carried out with a weakly oxidative bleaching bath or fatigued bleaching bath. In order to improve such defects, a phenol type cyan coupler having a phenylureido group at 2-position and carbonamido group at 5-position has been proposed. These couplers are disclosed in, for example, JP-A-56-65134, JP-A-57-204543, JP-A-57-204544, JP-A-57-204545, JP-A-58-33249 and JP-A-58-33250. (The term "JP-A" as used herein means an "unexamined published Japanese patent -application") Admittedly, the coupler having a phenylureido group at 2-position is excellent in the above respects compared with conventionally known phenol type cyan couplers and naphthol type cyan couplers. But it has become clear that these couplers are low in coupling activity with an oxidation product of a development agent to effect a sufficient color density.

Hereupon, 1-naphthol type cyan couplers having a substituent such as carbonamido group, sulfonamido group and the like at 5-position have been proposed in JP-A-60-237448, JP-A-61-153640 and JP-A-61-145557. Admittedly, these couplers do not decrease in color density when the developing treatment is carried out with a weakly oxidative bleaching (bleach-fix) bath or fatigued bleaching (bleach-fix) bath, are excellent in image preservability after treatment, and are high to some extent in color developability, but are still insufficient in sharpness and graininess.

Further, JP-A-59-149364 discloses a combination of so-called monodispersed emulsion having little fluctuation coefficient in grain diameter of silver halide and a phenol type cyan coupler having phenylureido group at 2-position and acylamino group at 5-position, but it was not satisfactory in respect of sensitivity and graininess.

Furthermore, JP-A-62-79449 proposes a combination of a naphthol type cyan coupler having arylcarbamoyl group at 2-position and a monodispersed emulsion, and it has become possible to provide the photosensitive material which is highly sensitive, is good in graininess and has no fluctuation of cyan density even when the weakly oxidative bleaching (bleach-fix) bath is used. However, it has found that, when these couplers were used, their dye image preservabilities were not satisfactory, and also the hue changes and the color reproducibilities lowered when the used high boiling point organic solvent amount was reduced and the emulsion layer was thinned to improve the sharpness.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide color photosensitive material which is little in the decrease of cyan image density even when a developing treatment is carried out with a weakly oxidative bleaching bath, bleach-fix bath or fatigued bleaching bath, bleach-fix bath.

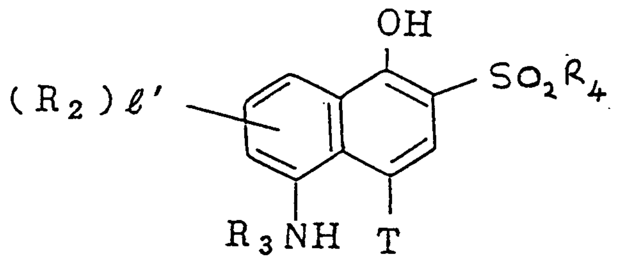
Another object of the present invention is to provide a silver halide color photosensitive material which is highly sensitive and excellent in graininess in all the exposure range.

A further object of the present invention is to provide a silver halide color photosensitive material which is excellent in preservability of cyan image after development treatment.

A still further object of the present invention is to provide a silver halide color photosensitive material which is excellent in sharpness.

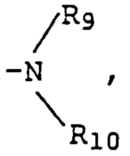
A still further object of the present invention is to provide a silver halide color photosensitive material which is excellent in color reproducibility.

Other objects of the present invention will become apparent from the following detailed description of the invention and examples thereof. These and other objects of the present invention can be accomplished by a silver halide color photosensitive material comprising a support having thereon at least one silver halide emulsion layer, characterized in that the photosensitive material is provided with at least one silver halide emulsion layer containing a substantially monodispersed silver halide grain and contains a cyan dye forming coupler represented by general formula (A):



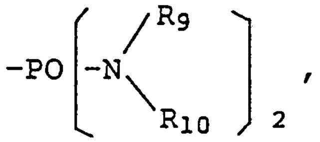
(A)

wherein R_2 represents a halogen atom, hydroxyl group, carboxyl group, sulfo group, amino group, cyano group, nitro group, aliphatic group, aromatic group, carbonamido group, sulfonamido group, carbamoyl group, sulfamoyl group, ureido group, acyl group, acyloxy group, aliphatic oxy group, aromatic oxy group, aliphatic sulfonyl group, aromatic sulfonyl group, aliphatic sulfinyl group, aromatic sulfinyl group, aliphatic oxycarbonyl group, aromatic oxycarbonyl group, aliphatic oxycarbonylamino group, aromatic oxycarbonylamino group, sulfamoylamino group, heterocyclic group or imido group; ℓ' represents an integer of 0 to 3; R_3 represents hydrogen atom or R_6U; T represents hydrogen atom or a group being releasable upon a coupling reaction with an oxidation product of aromatic primary amine developing agent; R_4 represents an aliphatic group, aromatic group, heterocyclic group, amino group, aliphatic oxy group or aromatic oxy group, R_6 represents hydrogen atom, aliphatic group, aromatic group, heterocyclic group, $-OR_7$, $-SR_7$, $-COR_8$,

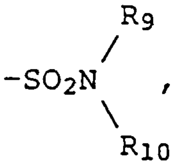


$$-N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix},$$

$-PO(R_7)_2$, $-PO(OR_7)_2$,



$$-PO\left[-N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix}\right]_2,$$



$$-SO_2N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix},$$

$-CO_2R_7$, $-SO_2R_7$, $-SO_2R_7$ or imido group, U represents $>N-R_9$, -CO-, $-SO_2-$, -SO- or a single bond, wherein R_7 represents an aliphatic group, aromatic group or heterocyclic group, R_8 represents hydrogen atom, an aliphatic group, aromatic group or heterocyclic group, R_9 and R_{10} each independently represents hydrogen atom, an aliphatic group, aromatic group, heterocyclic group, acyl group, aliphatic sulfonyl group or aromatic sulfonyl group; when ℓ' is plural, R_2 may be the same or different or may be bonded to each other to form a ring; R_2 and R_3 or R_3 and T may be bonded to each other to respectively form a ring; and R_1, R_2, R_3 or T may be bonded to each other through a divalent or more valent group to form a dimer or higher polymer (oligomer or polymer).

That is, it has been able to found surprisingly in the present invention by containing a specific cyan image forming coupler represented by the general formula (A) in a photosensitive material that not only the color reproducibility is improved when the photosensitive material containing a compound (hereinafter referred to as a bleach accelerator releasing type compound) which reacts with an oxidation product of aromatic primary amine color developing agent to eliminate the bleach accelerator is treated rapidly, but also the obtained minimum density is effectively controlled.

DETAILED DESCRIPTION OF THE INVENTION

The aliphatic group in the present invention indicates a straight, branched or cyclic alkyl group, alkenyl group or alkinyl group, and they may be substituted or unsubstituted.

The aromatic group indicates a substituted or unsubstituted aryl group and may be a condensed ring.

The heterocyclic group indicates a substituted or unsubstituted monocyclic ring or condensed ring type heterocyclic group.

Specific examples of the aliphatic group are methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, t-butyl group, cyclopentyl group, t-pentyl group, cyclohexyl group, n-octyl group, 2-ethylhexyl group, n-decyl group, n-dodecyl group, n-tetradecyl group, n-hexadecyl group, n-octadecyl group, 2-hexyldecyl group, adamantyl group, trifluoromethyl group, carboxymethyl group, methoxyethyl group, vinyl group, allyl group, hydroxyethyl group, heptafluoropropyl group, benzyl group, phenethyl group, phenoxyethyl group, methylsulfonylethyl group, methylsulfonamidoethyl group, 3-(2-ethylhexyloxy)propyl group, 3-n-decyloxypropyl group, 3-n-dodecyloxypropyl group, 3-n-tetradecyloxypropyl group, oleyl group, propargyl group, ethynyl group, 3-(2,4-di-t-pentylphenoxy)propyl group, 4-(2,4-di-t-pentylphenoxy)butyl group, 1-(2,4-di-t-pentylphenoxy)propyl group, 1-(2, 4-di-t-pentylphenoxy) pentyl group, 1-3-tetradecylphenoxy)propyl group, and 2-n-dodecylthioethyl group.

Specific examples of the aromatic group are phenyl group, p-tolyl group, m-tolyl group, o-tolyl group, 4-chlorophenyl group, 4-nitrophenyl group, 4-cyanophenyl group, 4-hydroxyphenyl group, 3-hydroxyphenyl group, 1-naphthyl group, 2-naphthyl group, o-biphenylyl group, p-biphenylyl group, pentafluorophenyl group, 2-methoxyphenyl group, 2-ethoxyphenyl group, 4-methoxyphenyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-carboxyphenyl group, 4-methylsulfonamidophenyl group, 4-(4-hydroxyphenylsulfonyl)-phenyl group , 2-n-tetradecyloxyphenyl group, 4-n-tetradecyloxyphenyl group, 2-chloro-5-n-dodecyloxyphenyl group, 3-n-pentadecylphenyl group, 2-chlorophenyl group, 4-methoxycarbonylphenyl group, 4-methylsulfonylphenyl group, and 2,4-di-t-pentylphenyl group.

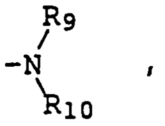
Specific examples of the heterocyclic group are 2-pyridyl group, 3-pyridyl group, 4-pyridyl group, 2-furyl group, 2-thienyl group, 3-thienyl group, 4-quinolyl group, 2-imidazolyl group, 2-benzimidazolyl group, 4-pyrazolyl group, 2-benzothiazolyl group, 2-benzothiazolyl group, 1-imidazolyl group, 1-pyrazolyl group, 5-tetrazolyl group, 1,3,4-thiadiazol-2-yl group, 2-prolyl group, 3-triazolyl group, 4-oxazolyl group, 4-thiazolyl group, 2-pyrimidyl group, 1,3,5-triazin-2-yl group, 1,3,4-oxadiazol-2-yl group, 5-pyrazolyl group, 4-pyrimidyl group, 2-pyrazinyl group, succinimido group, phthalimido group, morpholino group, pyrrolidino group, piperidino group, imidazolidine-2,4-dione-3-yl group, imidazolidine-2,4-dione-1-yl group and oxazolidine-2,4-dione-3-yl group.

Respective substituents in the general formula (A) will be described in detail, as follows.

In the general formula (A), represents an aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms, heterocyclic group having 1 to 30 carbon atoms, amino group having 0 to 30 carbon atoms [e.g., amino, methylamino, dimethylamino, n-butylamino, anilino, N-(2-n-tetradecyloxyphenyl)-amino, pyrrolidino, morpholino, piperidino, 2-ethylhexylamino, n-dodecylamino, N-methyl-N-dodecylamino, 3-dodecyloxypropylamino, 3-(2,4-di-t-pentylphenoxy)propylamino, 4-(2,4-di-t-pentylphenoxy)-butylamino], aliphatic oxy group having 1 to 30 carbon atoms [e.g., methoxy, ethoxy, butoxy, methoxyethoxy, n-dodecyloxy, 3-(2,4-di-t-pentylphenoxy)propoxy] or aromatic oxy group having 6 to 30 carbon atoms [e.g., phenoxy, 4-n-dodecyloxyphenoxy, 4-methoxycarbonylphenoxy].

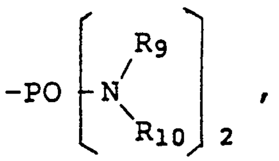
R_2 in the general formula (A) represents halogen atom (e.g., fluorine, chlorine, bromine or iodine), hydroxyl group, carboxyl group, sulfo group, cyano group, nitro group, amino group having 0 to 30 carbon atoms (e.g., amino, methylamino, dimethylamino, pyrrolidino, anilino), aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms, carbonamido group having 1 to 30 carbon atoms (e.g., formamido, acetamido, trifluoroacetamido, benzamido), sulfonamido group having 1 to 30 carbon atoms (e.g., methylsulfonamido, trifluoromethylsulfonamido, n-butylsulfonamido, p-tolylsulfonamido), carbamoyl group having 1 to 30 carbon atoms (e.g., carbamoyl, N,N-dimethylcarbamoyl, N-methylcarbamoyl, pyrrolidinocarbonyl, N-n-hexadecylcarbamoyl), sulfamoyl group having 0 to 30 carbon atoms (e.g., sulfamoyl, N-methylsulfamoyl, N,N-dimethylsulfamoyl, morpholinosulfamoyl, N-n-dodecylsulfamoyl), ureido group having 1 to 30 carbon atoms (e.g., ureido, 3-methylureido, 3-phenylureido, 3,3-dimethylureido), acyl group having 1 to 30 carbon atoms (e.g., acetyl, pivaloyl, benzoyl, dodecanoyl), acyloxy group having 1 to 30 carbon atoms (e.g., acetoxy, benzoyloxy, aliphatic oxy group having 1 to 30 carbon atoms, aromatic oxy group having 6 to 30 carbon atoms, aliphatic thio group having 1 to 30 carbon atoms, aromatic thio group having 6 to 30 carbon atoms, aliphatic sulfonyl group having 1 to 30 carbon atoms, aromatic sulfonyl group having 6 to 30 carbon atoms, aliphatic sulfinyl group having 1 to 30 carbon atoms, aromatic sulfinyl group having 6 to 30 carbon atoms, aliphatic oxycarbonyl group having 2 to 30 carbon atoms, aromatic oxycarbonyl group having 7 to 30 carbon atoms, aliphatic oxycarbonylamino group having 2 to 30 carbon atoms, aromatic oxycarbonylamino group having 7 to 30 carbon atoms, sulfamoylamino group having 0 to 30 carbon atoms (e.g., sulfamoylamino, 3,3-dimethylsulfamoylamino, piperidinosulfonylamino), heterocyclic group having 1 to 30 carbon atoms or imido group having 4 to 30 carbon atoms (e.g., succinimido, maleinimido, phthalimido, diglycolimido, 4-nitrophthalimido).

In the general formula (A), R_3 represents hydrogen atom or R_6U wherein R_6 represents a hydrogen atom, an aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms, heterocyclic group having 1 to 30 carbon atoms, $-OR_7$, $-SR_7$, $-COR_8$,

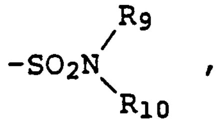


$$-N\begin{matrix} R_9 \\ R_{10} \end{matrix},$$

$-PO(R_7)_2$, $-PO(-OR_7)_2$,



$$-PO\left[-N\begin{matrix} R_9 \\ R_{10} \end{matrix}\right]_2,$$



$$-SO_2N\begin{matrix} R_9 \\ R_{10} \end{matrix},$$

$-CO_2R_7$, $-SO_2R_7$, $-SO_2OR_7$ or imido group having 4 to 30 carbon atoms (e.g., succinimido, maleinimido, phthalimido, diacetylamino), U represents $>N-R_9$, -CO-, $-SO_2-$, -SO- or a single bond, R_7 represents an aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms or heterocyclic group having 1 to 30 carbon atoms, R_8 represents hydrogen atom, an aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms or heterocyclic group having 1 to 30 carbon atoms, R_9 and R_{10} each independently represents a hydrogen atom, an aliphatic group having 1 to 30 carbon atoms, aromatic group having 6 to 30 carbon atoms, heterocyclic group having 1 to 30 carbon atoms, acyl group having 1 to 30 carbon atoms (e.g., acetyl, trifluoroacetyl, benzoyl, p-chlorobenzoyl) or sulfonyl group having 1 to 30 carbon atoms (e.g., methylsulfonyl, n-butylsulfonyl, phenylsulfonyl, p-nitrophenylsulfonyl). R_9 and R_{10} may be bonded to each other to form a ring.

T in the general formula (A) represents hydrogen atom or a group being releaseable upon a coupling reaction with an oxidation product of aromatic primary amine developing agent, and the letter examples are a halogen atom (e.g., fluorine, chlorine, bromine, or iodine), sulfo group, thiocyanato group, isothiocyanato group, selenocyanato group, aliphatic oxy group having 1 to 30 carbon atoms, aromatic oxy group having 6 to 30 carbon atoms, aliphatic thio group having 1 to 30 carbon atoms, aromatic thio group having 6 to 30 carbon atoms, heterocyclic thio group having 1 to 30 carbon atoms, heterocyclic oxy group having 1 to 30 carbon atoms, aromatic azo group having 6 to 30 carbon atoms, heterocyclic group having 1 to 30 carbon atoms, acyloxy group having 1 to 30 carbon atoms (e.g., acetoxy, benzoyloxy), sulfonyloxy group having 1 to 30 carbon atoms (e.g., methylsulfonyloxy, p-tolylsulfonyloxy), carbamoyloxy group having 1 to 30 carbon atoms (e.g., N,N-dimethylcarbamoyloxy, pyridinocarbonyloxy, N-ethylcarbamoyloxy), thiocarbonyloxy group having 2 to 30 carbon atoms (e.g., methylthiocarbonyloxy, phenylthiocarbonyloxy) and carbonyldioxy group having 2 to 30 carbon atoms (e.g., methoxycarbonyloxy, phenoxycarbonyloxy).

R_2 and R_3, R_3 and T or plural R_2's in the general formula (A) may be bonded to each other to form a ring, respectively. Bonded examples of R_2 to R_3 are $-CH_2CO-$, -OCO-, -NHCO-, $-C(CH_3)_2CO-$, -CH=CHCO-, etc. Bonded examples of R_3 to T are $-CH_2C-$, -COO-, etc. Bonded examples of plural R_2's are $-(CH_2)_3-$, $-(CH_2)_4-$, -OCO-, -OCONH-, -NHCONH-, $-(CH=CH)_2-$, $-OCH_2O-$, $-OCH_2CH_20-$ and $-OC(CH_3)_2O-$.

Next, preferable substituents of compounds represented by the general formula (A) will be described below.

Preferably R_4 is an amino group. Examples of $-SO_2R_4$ are sulfamoyl group, N-methylsulfamoyl group, N,N-diethylsulfamoyl group, N,N-di-isopropylsulfamoyl group, N-(3-dodecyloxypropyl)-carbamoyl group, N-[3-(2,4-di-t-pentylphenoxy)propyl]-carbamoyl group, N-[4-(2,4-di-t-pentylphenoxy)butyl]-carbamoyl group, pyrrolidinosulfonyl group, N-phenyl-sulfonyl group, N-(2-butoxyphenyl)carbamoyl group and N-(2-tetradecyloxyphenyl)carbamoyl group.

$(R_2)\ell'$ in the general formula (A) is preferable when ℓ' = 0 and then ℓ' = 1. Preferable R_2 when ℓ' = 1 is a halogen atom, aliphatic group, aliphatic oxy group, carbonamido group, sulfonamido group or a cyano group, and among these, fluorine atom, chlorine atom, trifluoromethyl group, methoxy group or cyano group is particularly preferable. Preferable substitution position of R_2 is 2- or 4-position in terms of the R_3NH-group.

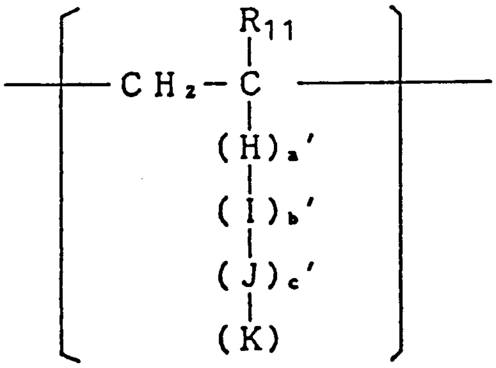
In R_3 in the general formula (A), preferable R_6 is an aliphatic group, aromatic group, $-OR_7$ or $-SR_7$, and preferable U is -CO- or $-SO_2-$. Examples of the aliphatic group are methyl group, trifluoromethyl group, trichloromethyl group, ethyl group, heptafluoropropyl group, t-butyl group, 1-ethylpentyl group, cyclohexyl group, benzyl group, undecyl group, tridecyl group, and 1-(2,4-di-t-pentylphenoxy)propyl group, examples of the aromatic group are phenyl group, 1-naphthyl group, 2-naphthyl group, 2-chlorophenyl group, 4-methoxyphenyl group, 4-nitrophenyl group, and pentafluorophenyl group, examples of $-OR_7$ are methoxy group, ethoxy group, isopropoxy group, n-butoxy group, isobutoxy group, t-butoxy group, n-pentyloxy group, n-hexyloxy group, n-octyloxy group, 2-ethylhexyloxy group, n-decyloxy group, n-dodecyloxy group, 2-methoxyethoxy group, benzyloxy group, trichloroethoxy group, trifluoroethoxy group, phenoxy group, and p-methylphenoxy group, and examples of $-SR_7$ are methylthio group, ethylthio group, allylthio group, n-butylthio group, benzylthio group, n-dodecylthio group, phenylthio group, and p-t-octyloxyphenylthio group. More preferable R_3 is an aliphatic oxycarbonyl group (where R_6 is R_7O- and U is -CO-) and an aliphatic or aromatic sulfonyl group (where R_6 is an aliphatic group or aromatic group and U is $-SO_2-$), and aliphatic oxycarbonyl group is particularly preferable.

In the general formula (A), preferable T is hydrogen atom, a halogen atom, an aliphatic oxy group, aromatic oxy group, aliphatic thio group or heterocyclic thio group. Examples of the aliphatic oxy group are methoxy group, ethoxy group, 2-hydroxyethoxy group, 2-chloroethoxy group, carboxymethoxy group, 1-carboxyethoxy group, methoxyethoxy group, 2-(2-hydroxyethoxy)ethoxy group, 2-methylsulfonylethoxy group, 2-methylsulfonyloxyethoxy group, 2-methylsulfonamidoethoxy group, 2-carboxyethoxy group, 3-carboxypropoxy group, 2-(carboxymethylthio)ethoxy group, 2-(1-carboxytridecylthio)ethoxy group, 1-carboxytridecyl group, N-(2-methoxyethyl) carbamoylmethoxy group, 1-imidazolylmethoxy group, 5-phenoxycarbonylbenzotriazol-1-ylmethoxy group, etc., examples of the aromatic oxy group are 4-nitrophenoxy group, 4-acetamidophenoxy group, 2-acetamidophenoxy group, 4-methylsulfonylphenoxy group, 4-(3-carboxypropanamido)phenoxy group, etc., examples of the aliphatic thio group are methylthio group, 2-hydroxyethylthio group, carboxymethylthio group, 2-carboxyethylthio group, 1-carboxyethylthio group, 3-carboxypropylthio group, 2-dimethylaminoethylthio group, benzylthio group, n-dodecylthio group, 1-carboxytridecylthio group, etc., and examples of the heterocyclic thio group are 1-phenyl-1,2,3,4-tetrazol-5-ylthio group, 1-ethyl-1,2,3,4-tetrazol-5-ylthio group, 1-(4-hydroxyphenyl)-1,2,3,4,-tetrazol-5-ylthio group, 4-phenyl-1,2,4-triazol-3-ylthio group, 5-methyl-1,3,4-oxadiazol-2-ylthio group, 1-(2-carboxyethyl)-1,2,3,4-tetrazol-5-ylthio group, 5-methylthio-1,3,4-thiadiazol-2-ylthio group, 5-methyl-1,3,4-thiadiazol-2-ylthio group, 5-phenyl-1,3,4-oxadiazol-2-ylthio group, 5-amino-1,3,4-thiadiazol-2-ylthio group, benzoxazol-2-ylthio group, 1-methylbenzimidazol-2-ylthio group, 1-(2-dimethylaminophenyl)-1,2,3,4-tetrazol-5-ylthio group, benzothiazol-2-ylthio group, 5-(ethoxycarbonyl-methylthio)-1,3,4-thiadiazol-2-ylthio group, 1,2,4-triazol-3-ylthio group, 4-pyridylthio group or a 2-pyrimidylthio group. More preferable T is hydrogen atom, chlorine atom, an aliphatic oxy group or an aliphatic thio group, and the hydrogen atom or the aliphatic oxy group is particularly preferable.

The coupler shown by the general formula (A) may form a dimer or higher polymer wherein substituent R_4, R_2, R_3 or T is bonded to each other through a divalent or more valent group. In this case, carbon number of the above each substituent can be beyond its specified range.

When the coupler shown by the general formula (A) forms a polymer, its typical example is a homopolymer or copolymer of ethylenic unsaturated addition polymerizable compounds (cyan color forming monomer) having a cyan dye forming coupler residue. In this case, the polymer contains a repeating unit of the following formula (B), one or more kinds of the cyan color forming repeating unit of the general formula (B) may be contained, and the copolymer may contain one or more kinds of non-color-forming ethylenic monomer as a copolymer component.

General formula (B)



$$\left[\begin{array}{c} R_{11} \\ | \\ -CH_2-C- \\ | \\ (H)_{a'} \\ | \\ (I)_{b'} \\ | \\ (J)_{c'} \\ | \\ (K) \end{array}\right]$$

(B)

wherein R_{11} represents hydrogen atom, an alkyl group having 1 to 4 carbon atoms or chlorine atom, H represents -CONH-, -COO- or a substituted or unsubstituted phenylene group, I represents a substituted or unsubstituted alkylene group, phenylene group or aralkylene group, and J represents -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, $-SO_2-$, $-NHSO_2-$ or $-SO_2NH-$. Each of a′, b′ and c′ represents 0 or 1. K represents a cyan coupler residue removing a hydrogen atom other than the hydrogen atom of the hydroxyl group at the 1-position of the compound of the general formula (A).

Copolymers of cyan color forming monomers which provide a coupler unit of general formula (B) and the non-color forming ethylenic monomers indicated below are the preferred polymers.

Examples of the non-color-forming ethylenic monomer which do not couple with the oxidation product of aromatic primary amine developing agent are acrylic acid, α-chloroacrylic acid, α-alkylacrylic acid (e.g., methacrylic acid), esters or amide derived from these acrylic acid (e.g., acrylamide, methacrylamide, n-butylacryamide, t-butylacrylamide, diacetonacrylamide, N-methylolacrylamide, N-(1,1-dimethyl-2-sulfonatoethyl)acrylamide, N-(3-sulfonatopropyl)acrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, acetoacetoxyethyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and β-hydroxy methacrylate), vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and its derivatives such as vinyltoluene, divinylbenzene, styrene sulfinic acid potassium salt, vinyl acetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ether (e.g., vinyl ethyl ether), maleic acid ester, N-vinyl-2-pyrrolidone, N-vinylpyrodine, and 2- or 4-vinylpyridine.

Particularly, acrylic acid esters, methacrylic acid esters and maleic acid esters are preferable. Two or more kinds of the non-color-forming ethylenic monomer used here can be used together. For example, methyl acrylate and butyl acrylate, butyl acrylate and styrene, butyl methacrylate and methacrylic acid, methyl acrylate and diacetonacrylic amide, N-(1,1-dimethyl-2-sulfonatoethyl)acrylic amide and acrylic acid, styrene sulfinic acid potassium salt and N-vinylpyrrolidone can be used.

As well known in the field of polymer coupler, the ethylenic unsaturated monomer to be copolymerized with vinyl type monomer corresponding to the above general formula (B) can be selected in order that the physical property and/or chemical property such as solubility, compatibility with a binding agent (e.g., gelatin) of the photographic colloid composition, flexibility, thermostability, etc. of the copolymer to be formed should favorably be affected.

In order to obtain a lipophilic polymer coupler soluble in an organic solvent, it is preferable to select lipophilic non-color-forming ethylenic monomers as a copolymerization ingredient (e.g., acrylic acid ester, methacrylic acid ester, maleic acid ester vinylbenzenes).

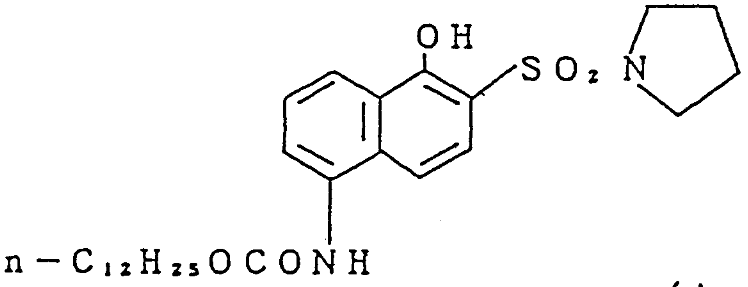
A solution of a lipophilic polymeric coupler obtained by polymerizing a vinyl based monomer which provides a coupler unit which can be represented by the aforementioned general formula (B) in an organic solvent can be prepared by emulsification and dispersion, or by direct emulsification polymerization, in the form of a latex in an aqueous gelation solution.

The method disclosed in U.S. Patent 3,451,820 can be used for the emulsification and dispersion of a lipophilic polymeric coupler in the form of a latex in an aqueous gelatin solution, and the method disclosed in U.S. Patents 4,080,211 and 3,370,952 can be used for emulsion polymerization.

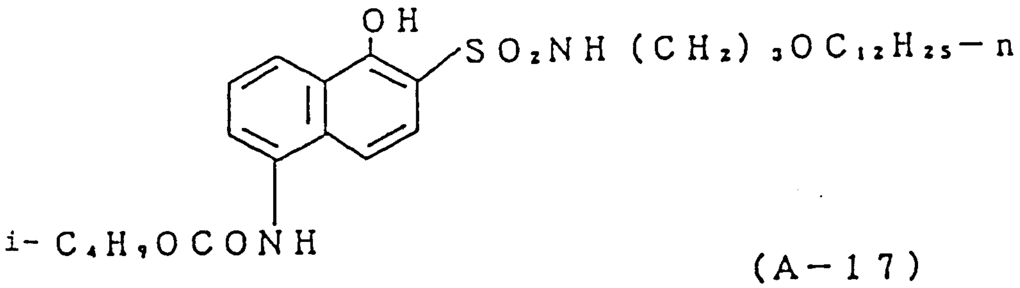
Also, in order to obtain a hydrophilic polymer coupler soluble in neutral or alkaline water, it is preferable to use hydrophilic non-color-forming ethylenic monomer as a copolymerization ingredient [e.g., N-(1,1-dimethyl-2-sulfonatoethyl)acrylic amide, 3-sulfonatopropyl acrylate, styrene sulfonic acid sodium salt, 2-styrene sulfinic acid potassium salt, acrylic amide, methacrylic amide, acrylic acid, methacrylic acid, N-vinyl-pyrrolidone and N-vinylpyridine].

The hydrophilic polymer coupler can be added, in the form of aqueous solution, to a coating solution, and also can be added by dissolving into a mixed solvent comprising water and a water-miscible organic solvent (e.g., a lower alcohol, tetrahydrofuran, acetone, ethyl acetate, cyclohexane, ethyl lactate, dimethylformamide, dimethylacetamide). Moreover, they can be dissolved in aqueous alkaline solutions or in alkali containing organic solvents and added in this form. Also, a small amount of surface active agent can be added.

Specific examples of the coupler represented by the general formula (A) in the present invention will be hereinafter be shown, but the present invention is not limited thereto.



(A−16)



(A−17)

Examples other than the above examples of the coupler represented by the general formula (A) used in the present invention are described in JP-A-60-237448, JP-A-61-153640, and JP-A-61-145557. Synthesis of these couplers can also be carried out according to the methods described in JP-A-62-123157, and JP-A-123158 in addition to the methods according to the above patent specifications.

These couplers used in the present invention can be added to any layer in the photosensitive materials, but it is preferable to add them to a monodispersed emulsion containing layer. When the emulsion layer is divided into two or more layers having same color sensitivities and different photographic sensitivities, it is preferable to add 4-equivalents of the coupler to the layer of the lowest sensitivity and 2-equivalents of the coupler to the layer of the highest sensitivity.

The coupler amount to be added is 5 x 10^{-6} to 3 x 10^{-3} mol/m^2, preferable 1 x 10^{-5} to 2 x 10^{-3} mol/m^2, and more preferably 3 x 10^{-5} to 1 x 10^{-3} mol/m^2.

When the coupler employed in this invention is used in a layer other than the layer of the highest sensitivity, a usable weight ratio of the below mentioned high boiling point organic solvent for coupler dispersion to the coupler is usually 1/1 or below but 1/2 or below is more preferable, and 1/3 or below is particularly preferable.

The substantially monodispersed emulsion employed in the present invention is an emulsion which has a grain diameter distribution such that the fluctuation coefficient $S/\bar{r}$ in the grain diameter of silver halide is 0.25 or less, wherein $\bar{r}$ is a mean grain diameter and S is a standard deviation. That is, when respective grain diameters are ri and grain number is ni, the mean grain diameter $\bar{r}$ is defined as

$$\bar{r} = \frac{\Sigma ni.ri}{\Sigma ni}$$

and the standard deviation S is defined as

$$S = \sqrt{\frac{\Sigma(\bar{r} - ri)^2.ni}{\Sigma ni}}$$

The respective grain diameters mean a diameter corresponding to a projected area which occurs when the silver halide emulsion is subjected to a photographing according to a method (normally an electron microscope photographing) well known in this field as described in T.H. James: The Theory of the Photographic Process, 3ed., pages 36-43 (1966) published by McMillan Publishing Co., Inc. The silver halide grain diameter corresponding to the projected area is defined as a diameter of circle which area is equal to the projected area of silver halide grain, as shown in the above literature. Accordingly, the mean grain diameter $\bar{r}$ and its deviation S can also be obtained even when the grain form of silver halide is other than sphere, that is, for example, when the form is a cube, octahedron, tetradecahedron, tabular form, potato-like form or the like.

The fluctuation coefficient in the grain diameter of silver halide is 0.25 or less, preferably 0.20 or less and more preferably 0.18 or less.

The size of the silver halide grain is not particularly limited, but it is preferably 0.1 µm to 3,0 µm, more particularly 0.3 µm to 2.0 µm, and most preferably 0.5 µm to 1.2 µm.

The form of the silver halide grain can be either a regular crystal form (normal crystal grain) such as hexahedron, octahedron, dodecahedron or tetradecahedron, or an irregular crystal form such as sphere, potato-like form, tabular form or the like, but a particularly desirable form is a normal crystal grain.

The normal crystal grain having 50% or more of (111) face is particularly preferable. Even the irregular crystal form having 50% or more of (111) face is particularly preferable. A face ratio of the (111) face can be determined by a dye adsorption method of Kubelka Munk wherein the dye is preferentially adsorbed on either one of (111) face and (100) face and the dye associated states on (111) face and (100) face select respectively different dyes spectrometrically. The face ratio of (111) face can be determined by adding such a dye to an emulsion and examining in detail the spectrograph corresponding to the added amount of the dye. Reference of details of the above dye adsorption method can be made to Tadaaki Tani, Nihon Kagakukaishi ("Journal of Japan Chemical Society"), page 942 (1984).

With reference to the halogen composition of the silver halide grain, it is preferable that 60 mol % or more of silver bromide is contained and 10 mol % or less of silver chloride is contained. More preferable grain contains 2 mol % to 40 mol % of silver iodide and particularly preferable one contains 5 mol % to 20 mol % of silver iodide. The halogen composition distribution of the grains is preferably uniform.

Most preferably halogen composition of the monodispersed emulsion used in the present invention is a grain which has substantially a clear layer structure having two layers comprising a core portion of high iodine content layer and a shell portion of low iodine content layer. This layer structure grain will hereinafter be illustrated.

The core portion is silver halide of high iodine content, and preferable content of the iodine is between 10 mol % and 40 mol % of solid solution limit, that is, preferably 10 to 40 mol % and more preferably 15 to 40 mol %. The silver halide other than silver iodide in the core portion can be either one of silver chlorobromide and silver bromide, but it is preferable that the silver bromide ratio is high.

Outermost layer composition is silver halide containing 8 mol % or less of silver iodide, more preferably 5 mol % or less of silver iodide.

A silver halide other than silver iodide in the outermost layer can be any one of silver chloride, silver chlorobromide and silver bromide, but it is preferable that the silver bromide ratio is high.

The above said clear layer structure can be decided by a method of X-ray diffraction. The example of application of the method of X-ray diffraction is described in H. Hirsh, Journal of Photographic Science, Vol. 10, pages 129 et seq. (1962) and the like. Determination of a lattice constant according to the halogen composition gives rise to a diffraction peak by a diffraction angle satisfying a Bragg condition ($2d\sin\theta = n\lambda$).

A method of X-ray diffraction measurement is described in detail in Kisobunsekikagaku Koza 24, (X-ray analysis) ("Lecture of Fundamental Analytical Chemistry") published by Kyoritsu Shuppan, A guide to X-ray diffraction published by Rigakudenki Co., Ltd. and the like. Standard measuring method is that Cu is used as a target and a diffraction curve on (220) face of silver halide is generated using Kβ ray of Cu as a ray source (tube voltage of 40 KV, tube current of 60 mA). In order to improve the resolving power of the measuring apparatus, it is necessary that the width of slits (diverging slit, receiving slit, etc.), time constant of the apparatus, and scanning speed and recording speed of the goniometer be suitably selected and a measuring accuracy be confirmed by using a standard sample such as silicon, etc.

When the emulsion grain has a clear two layer structure, two peaks appear on the diffraction curve, that is, one diffraction maximum due to silver halide of high iodine content layer and the other diffraction due to silver halide of low iodine content layer.

The substantially clear two layer structure means that, when a curve relating between a diffraction strength and a diffraction angle on (220) face of silver halide is obtained by using Kβ ray of Cu in the range of 38° to 42° of diffraction angle (2θ), two diffraction maximums of a diffraction peak corresponding to a high iodine content layer containing 10 to 45 mol % of silver iodide and a diffraction peak corresponding to a low iodine content layer containing 5 or less mol % of silver iodide, and one minimum therebetween appear, and a ratio of the diffraction strength corresponding to the high iodine content layer peak to the diffraction strength corresponding to the low iodine content layer peak becomes 1/10 to 3/1, more preferably 1/5 to 3/1, and most preferably 1/3 to 3/1.

With reference to the emulsion having substantially clear two layer structure, it is more preferable that the diffraction strength of minimum value between two peaks is 90% or less, more preferably 80% or less, most preferably 60% or less of weaker strength peak between two diffraction maximums (peaks). The technical method for analyzing a diffraction curve consisting of two diffraction components is well known as explained in, for example, Jikken Butsurigaku Koza (Lecture of Experimental Physics"), No. 11 (Lattice Flaw), published by Kyoritsu Shuppan. It is useful that the diffraction curve is analyzed by the use of a curve analyzer made by Du Dont de Nemours and Company assuming that the curve is a function such as Gauss function, Lorentz function or the like.

Even in the case of an emulsion wherein different two kinds of silver halide grains having no clear layer structures respectively coexist, the two peaks appear in the above mentioned X-ray diffraction. It becomes possible to distinguish whether the silver halide emulsion is an emulsion having a layer structure or an emulsion wherein two kinds of silver halide grains co-exist as stated above, by using an EPMA method (Electron-Probe Michro Analyzer method) besides the X-ray diffraction method. In the EPMA method, a sample well dispersed in order that the emulsion grains are not contacted with one another is prepared and an electron beam is applied. Elementary analysis of very minute portion becomes possible by means of an X-ray analysis according to the electron beam excitation. According to this method wherein characteristic X-ray strangths of silver and iodine radiated from respective grains are obtained, the halogen compositions of respective grains can be determined.

It can be determined whether the emulsion has a layer structure, when the halogen compositions in at least 50 grains are confirmed according to the EPMA method. The emulsions having a layer structure are preferable when the iodine contents of grains are uniform. Relative standard deviation when the iodine content distribution of granules is measured according to EPMA method, is preferably 50% or less, more preferably 35% or less and most preferably 20% or less.

In order to obtain a preferable photographic property of emulsion of silver halide grain having clearly layer structure, the high iodine content silver halide in the core must sufficiently be covered by low iodine content silver halide in the shell. Necessary widths of the shell are different depending upon the grain size, but 0.1 µm or more width is desirable when the grain has a large size of 1.0 µm or more, and 0.05 µm or more width is desirable when the grain has a small size of less than 1.0 µm. In order to obtain an emulsion having a clear layer structure, the silver content ratio of shell portion to core portion is preferably in the range of 1/5 to 5, more preferably 1/5 to 3, most preferably 1/5 to 2.

That the silver halide grain substantially has clearly two layer structures is explained as that two regions different in halogen composition substantially exist in the grain wherein the central portion is a core portion and a surface portion is a shell portion. Substantially two layers means that the third region (for example, a layer existing between central core portion and outermost shell portion) may be exist. However, it also means that, even if such third region might be exist, the configurations of two peaks (corresponding to high iodine content portion and low iodine content portion) must not substantially be affected by the third region when the X-ray diffraction pattern is made as above. It is the same when the third region exists in the core portion.

It is also preferable in the present invention to employ a layer structure grain, the so-called three fold grain having a core of high silver halide content, a shell of low silver halide content and an intermediate layer therebetween, as proposed in, for example, JP-A-61-275741, JP-A-61-250643, JP-A-61-250645, JP-A-61-246747, JP-A-61-246739, etc.

The photographic emulsion of silver halide usable in the present invention can be prepared by the use of methods as described in, for example, Research Disclosure, No. 17643, pages 22-23 (Dec., 1978), I. Emulsion preparation and types", ibid No. 18716, page 648 (Nov., 1979) P. Glafkides, Chemie et Phisique published by Focal Press (1967), V.L. Zelikman et al, Making and Coating Photographic Emulsion published by Focal Press (1964), etc.

A tabular grain having an aspect ratio of about 5 or more can be used in the present invention. The tabular grain can be simply prepared according to the methods as described in Gutoff, Photographic Science and Engineering, Vol. 14, pages 248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520, British Patent 2,112,157, etc.

The crystal structure can be uniform ones or those having inner and outer halogen compositions different from each other, those having layer structures or those wherein silver halides of different compositions are joined with one another by an epitaxial junction or with the compounds such as silver rhodanide, lead oxide, etc. other than the silver halide. Further, mixtures of various crystal system grains can also be used.

The silver halide emulsions are usually used after physical ripening, chemical ripening and spectral sensitization. Additives used in such steps are described in Research Disclosure Nos. 17643 and 18716 and the relevant places are summarized in the following table. Well known additives for photography usable in the present invention are also described in the above mentioned two Research Diusclosure literatures and the relevant places are shown in the following table.

Kind of Additive	RD 17643	RD 18716
1. Chemical sensitizer	Pages 23	Page 648, right column
2. Sensitivity improver		ditto
3. Spectral sensitizer, Color sensitizer	Pages 23-24	Page 648, right column to page 649, right column
4. Whitening agent	Page 24	
5. Antifoggant and Stabilizer	Pages 24-25	Page 649, right column
6. Light absorber Filter dye, Ultraviolet absorber	Pages 25-26	Page 649, right column to page 650, left column
7. Stain inhibitor	Page 25, right column	Page 650, left column to right column
8. Dye image stabilizer	Page 25	
9. Hardening agent	Page 26	Page 651, left column
10.Binder	Page 26	ditto
11.Plasticizer, Lubricant	Page 27	Page 650, right column
12.Coating aid, Surface active agent	Pages 26 to 27	ditto
13.Antistatic agent	Page 27	ditto

Various color couplers can be used in the present invention and their specific examples are shown in patents described in the above mentioned Research Disclosure, No. 17643, VII-C to G.

As a yellow coupler, those described in, for example, U.S. Patents 3,933,501, 4,022,620, 4,326,024, and 4,401,752, JP-B-58-10739 (the term "JP-B" as used herein means an "examined Japanese patent publication"), British Patents 1,425,020 and 1,476,760, etc. are preferble.

As a magenta coupler, 5-pyrazolone type or pyrazoloazol type compounds are preferable, and those described in U.S. Patents 4,310,619, 4,351,897, European Patent 73,636, U.S. Patents 3,061,432, 3,725,067, Research Disclosure, No. 24220 (June, 1984), JP-A-60-33552, Research Disclosure No. 24230 (June, 1984), JP-A-60-43659, U.S. Patents 4,500,630, 4,540,654, etc. are particularly preferable.

As a cyan coupler, phenol type or naphthol type couplers are given, and those described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, European Patent 121,365A, U.S. Patents 3,446,622, 4,333,999, 4,451,559, and 4,427,767 are preferable.

As a colored coupler for correcting useless absorption of coupler dye, those described in Research Disclosure, No. 17643, VII-G, U.S. Patents 4,163,670, JP-B-57-39413, U.S. Patents, 4,004,929, 4,138,258, and British Patent 1,146,368 are preferable.

As a coupler having an appropriate diffusion property, those described in U.S. Patents 4,336,237, British Patent 2,125,570, European Patent 96,570 and West German Patent Application (OLS) No. 3,234,533.

Typical examples of a polymerized dye forming coupler are described in U.S. Patents 3,451,820, 4,080,211, 4,367,282, British Patent 2,102,173, etc.

A coupler which releases a photographically useful residue with coupling is also used preferably in the present invention. As a DIR coupler which releases a development inhibitor, those described in patents described in the above Research Disclosure, No. 17643, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248 and U.S. Patent 4,248,962 are preferable.

As a coupler which imagewisely releases a nucleating agent or development accelerator when developed, those desdribed in British Patent 2,097,140, 2,131,188, JP-A-59-157638 and JP-A-59-170840 are preferable.

The other couplers usable as a photosensitive material other than the above ones are competing couplers described in U.S. Patent 4,130,427, etc., multiequivalent couplers described in U.S. Patents 4,238,472, 4,338,393, 4,310,618, etc., DIR redox compound releasing couplers described in JP-A-60-185950, etc., couplers which release dyes for recoloration after being released as described in European Patent 173,302A, and the like.

As a yellow coupler used for silver halide color photographic materials in the present invention, benzoylacetanilide type 2-equivalent coupler is preferable, and as a magenta coupler, 1-phenyl-5-pyrazolone type 2-equivalent coupler is preferable.

The couplers used in the present invention can be introduced into the photosensitive materials by various known dispersion methods.

Examples of high boiling point solvent used for oil in water droplet dispersion method are described in U.S. Patent 2,322,027, etc.

Actual examples of the high boiling point organic solvents which have a boiling point of 175°C or higher at atmospheric pressure and are used for the oil in water droplet dispersion method are phthalic acid esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate), phosphoric or phosphonic acid esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, di-2-ehylhexylphenyl phosphonate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxy benzoate), amides (e.g., N,N-diethyl-dodecanamide, N,N-diethyllaurylamide, N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), hydrocarbons (e.g., paraffin, dodecylbenzene, di-isopropylnaphthaline) and the like. Further, as an auxiliary solvent, organic solvents having a boiling point of about 30°C or higher, preferably 50°C or higher and not higher than about 160°C can be used, and typical examples thereof are ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate, dimethylformamide).

Actual examples of process and effect of latex dispersion method as well as latex for use of impregnation are described in U.S. Patent 4,199,363, West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230 and the like.

The present invention can be applied to various types of color photographic materials. Color negative film for general or movie purpose, color reversal film for slide or television, color paper, color positive film, color reversal paper and the like can be given as typical examples.

The suitable supports usable in the present invention are described in the above described Research Disclosure, No. 17643, pages 28 to 29 and ibid. No. 18716, page 647, right column to page 648, left column.

The color photographic materials according to the present invention can be subjected to a development treatment by a usual methods as described in the above described Research Disclosure, No. 17643, pages 28-29 and ibid. No. 18716, page 651, left column to right column.

The color developer employed in development treatment of photosensitive material in the present invention is preferably an alkaline aqueous solution mainly composed of aromatic primary amine type color developing agent. As the color agent, aminophenol type compounds are useful, but p-phenylenediamine type compounds are preferably used and typical examples thereof are 3-methyl-4-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesuylfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline and sulfates, hydrochlorides or p-toluenesulfonates thereof. Two or more kinds of these compounds can be jointly used depending upon the purposes.

The color developers, in general, contain a pH buffer agent such as carbonate, borate or phosphate of an alkali metal and also contain a development inhibitor or an antifoggant such as bromide salt, iodide salt, benzimidazoles, benzothiazoles or mercapto compounds. If necessary, they contain, as a typical example, various preservatives such as hydroxylamine, diethylhydroxylamine, hydrazine sulfites, phenylsemicarbazides, triethanolamine, catecholsulfonic acids and triethylenediamine-(1,4-diaza-bicyclo[2,2,2]octane), organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salt and amines, fogging agents such as dye forming coupler, competing coupler and sodiumboron hydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone; viscosity imparting agent, various chelating agents represented by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylsulfonic acid and phosphonocarboxylic acid, e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof.

Further, when the reversal process is carried out, the color development is made after the black and white development was made. In this black and white development bath, well known black and white developing agents (e.g., dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyirazolidone or amino phenols such as N-methyl-p-aminophenol) can be used individually or jointly.

The pH values of the color developer and black and white developer are generally 9 to 12. Replenishing amount of these developers depends on the color photosensitive material but in general, it is 3 liters or less per 1 m^2 of the photosensitive material, and it can be decreased to 500 ml or less by lowering the ion concentration of bromide in the replenish solution. When the replenishing amount is decreased, it is preferable that an area contacting with air in the processing tank is reduced to prevent an evaporation of the replenish solution and also avoid an air oxidation. It is also possible to reduce the replenishing amount by means of controlling an accumulation of bromide ion concentration in the developers.

The phototographic emulsion layer after color development is usually treated with bleaching agent. The bleaching treatment can be made simultaneously with fixing treatment (bleach-fix treatment) or can also be made individually. In order to further quicken the treatment, the bleach-fix treatment after bleaching treatment can also be employed. Furthermore, a treatment in continuous two bleach-fix baths, a fix treatment before bleach-fix treatment or a bleaching treatment after bleach-fix treatment can also be carried out optionally according to the purposes. Examples of bleaching agent to be used are, for example, multivalent metal compounds of iron (III), cobalt (III), chrome (VI), copper (II), peracids, quinones, and nitro compounds. Typical bleaching agents to be used are ferricyanide compounds; dichromates; organic complex salts of iron (III) or cobalt (III) (e.g., aminocarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid, or complex salts such as citric acid, tartaric acid, and malic acid.; persulfates; bromates; permanganates; nitrobenzenes and the like. Among these, iron (III) complex salts of aminopolycarboxylic acid including the iron (III) complex salt of ethylenediaminetetraacetic acid, and peracid salts are preferable from viewpoints of quick treatment and prevention of environmental pollution. Further, the ion (III) complex salt of aminopolycarboxylic acid is especially useful as both the bleaching solution and bleach-fix solution. The pH value of bleaching solution or bleach-fix solution using such iron (III) complex salt of aminopolycarboxylic acid is usually 5.5 to 8, and the lower pH value can be employed for quickening the treatment. In bleaching bath, bleach-fix bath and prebath thereof, a bleach accelerator can be used, if necessary. Actual examples of the useful bleach accelerator are described in the following specifications: compounds having mercapto group or disulfide group as described in U.S. Patent 3,893,858, West German Patents 1,290,812, and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, Research Disclosure, No. 17129 (July 1978), etc., thiazolidine derivatives as described in JP-A-50-140129, thiourea derivatives as described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,701,561, iodine salts as described in West German Patent 1,127,715 and JP-A-58-16235, polyoxyethylene compounds as described in West German Patents 966,410 and 2,748,430, polyamines as described in JP-B-45-8836, the other compounds as described in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940, bromide ion and the like can be used. Among these, the compounds having mercapto group or disulfide group are preferable because of those having much accelerating effect, and particularly, compounds as described in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 and also compounds as described in U.S. Patent 4,552,834 are preferable. These bleach accelerators can be added to the photosensitive material. These bleach accelerators are especially effective when the color photosensitive material for photographic use is bleach-fixed.

As a fixing agent, thiosulfates, thiocyanates, thioether type compounds, thioureas, iodide salts, etc. can be given, and generally the thiosulfates are used and particularly, ammonium thiosulfate is used most widely. As a preservative of bleach-fix bath, sulfites, bisulfites or carbonyl bisulfite addition compounds are preferable.

In general, the silver halide color photosensitive material in the present invention is subjected to washing and/or stabilizing step after desilvering treatment. The amount of washing water in the washing step can be determined in the wide range according to photosensitive material (characteristic of, for example, used material such as coupler, etc.), use, temperature of washing water, number of washing tank (number of steps), replenishing systems such as counter current, forward current, etc. and the other various conditions. Among these, a relation between washing tank number and water amount in multistage counter current system can be obtained by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pages 248-253 (May 1955).

According to the multistage countercurrent system described in the above literature, water amount of washing step can be much reduced, but owing to a much increased residence time of water in the tank, problems that bacteria propagate and produce floating matters attach to the photosensitive material arise. In order to solve such problems in the photosensitive material treatment in the present invention, a method for reducing calcium ion and magnesium ion as described in JP-A-62-288838 can be used very effectively. Also, chlorine type sterilizers such as isothiazolone compounds as described in JP-A-57-8542, thiabendazoles and chlorinated isocyanuric acid sodium salt, the other sterilizers such as benzotriazole as described in Hiroshi Horiguchi, Bokin Bobai no Kagaku ("Chemistry of Bactericides and Fungicides"), Eisei Gijutukai ("Sanitary Technology Society") ed., : Biseibutsu no Mekkin, Sakkin, Bobai Gijutsu ("Techniques of Sterilization, Pasteurization, and Fungicides of Microoganisms") and Nippon Bokinbobaigakkai ("Japan Bactericide and Fungicide Society") ed., Bokin Bobaizai Jiten ("Dictionary of Bactericides and Fungicides") can be used.

The pH value of washing water in the photosensitive material treatment of the present invention is 4 to 9, preferably 5 to 8. Washing water temperature and washing time can be determined variously according to characteristics, uses, etc. and generally ranges of 20 seconds to 10 minutes at 15 °C to 45 °C, preferably 30 seconds to 5 minutes at 25 °C to 40 °C are chosen. Further, the photosensitive material of the present invention can be treated directly with a stabilizing solution in place of the above water washing. In such a stabilizing treatment, all the well known methods as described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be used.

Also, subsequenhtly to the above washing treatment, there is a case where further stabilizing treatment is made, and as its example, a stabilizing bath containing formalin and a surface active agent which is used as a last bath for the color photosensitive material for photographic use can be given. Various chelating agent and fungicides can also be added to this stabilizing bath.

Overflown solution accompanied by replenishing of washing water and/or stabilizing solution can be utilized again in the other steps such as desilvering step, etc.

In the silver halide color photosensitive material of the present invention, a color developing agent can be included for the purpose of simplification and speed up of the treatment. The preferable inclusion is to use various precursors of the color developing agent. As the precursors, indoaniline type compounds described in U.S. Patent 3,342,597, Schiff base type compounds described in U.S. Patent 3,342,599 and Research Disclosure No. 14850, ibid. No. 15159, aldol compounds described in Research Disclosure, No. 13924, metal salt complexes described in U.S. Patent 3,719,492 and urethane type compounds described in JP-A-53-135628.

In the silver halide color photosensitive material of the present invention, various 1-phenyl-3-pyrazolidones can be included, if necessary, for the purpose of accelerating the color development. Typical examples thereof are described in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

The various processing solutions in the present invention are used at 10°C to 50°C. Usually, the temperature at 33°C to 38°C is standard, but it is possible that the processing can be accelerated at higher temperature to shorten the processing time, while an image quality improvement and an improvement of processing solution stability can be attained at lower temperature. Further, in order to save silver in the photosensitive material, a treatment using a cobalt intensification or hydrogen peroxide intensification as described in West German Patent 2,267,770 or U.S. Patent 3,674,499 can be carried out.

Furthermore, the silver halide photosensitive material of the present invention can also be applied to heat developable photosensitive materials as described in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and EP-A-0, 210, 660.

The present invention will hereinafter be illustrated in detail with reference to Examples.

EXAMPLE

Emulsions A to K used in the following Examples were prepared as follows:

Emulsion A

To 12.0 ℓ of an aqueous solution dissolving 240 g of inert gelatin, 950 g of potassium bromide and 48.0 g of potassium iodide with stirring at 65°C, was added 7.0 ℓ of an aqueous solution dessolving 1000g of silver nitrate over 50 minutes to obtain a 5.0 mol % emulsion of silver iodide. After desalting the emulsion in a usual manner, 18 mg of sodium thiosulfate and 14 mg of chloroauric acid were added to the emulsion which was ripened at 60°C for 50 minutes and chemically sensitized to obtain an Emulsion A having a mean grain diameter $\bar{r}$ of 0.7 µm and a fluctuation coefficient $S/\bar{r}$ of 0.40.

Emulsion B, C and D

According to a control double jet method in the presence of ammonia, octahedron emulsions having 10 mol % of silver iodide contents, a mean grain diameter of 0.55 µm and respective fluctuation coefficients of 0.26, 0.23 and 0.19 were prepared as a core emulsion. After washing these core emulsions with water, a shell attaching with pure silver bromide was caried out in such a manner that silver content of the core portion became equal to that of the shell portion. After desalting the respective emulsions in a usual manner, 30 mg of sodium thiosulfate and 15 mg of chloroaurate were added to the respective emulsions which were ripened at 60°C for 60 minutes and chemically sensitized to obtain respective Emulsions B, C and D having respective mean grain diameters of 0.7 µm and respective fluctuation coefficients of 0.24, 0.21 and 0.16.

Emulsions E, F

According to the preparation method of the Emnulsion A, Emulsion E having 2 mol % of silver iodide content, mean grain diameter ($\bar{r}$) of 0.7 µm and fluctuation coefficient ($S/\bar{r}$) of 0.39, and Emulsion F having 6 mol % of silver iodide content, $\bar{r}$ of 1.4 µm and $S/\bar{r}$ of 0.45 were prepared.

Emulsion G, H

According to a control double jet method in the presence of ammonia, Emulsion G and Emulsion H as a chemical sensitizer respectively having 2 mol % of silver iodide content, $\bar{r}$ of 0.7 µm, $S/\bar{r}$ of 0.17 and 6 mol % of silver iodide content, $\bar{r}$ of 0.7 µm, $S/\bar{r}$ of 0.20 were prepared.

Emulsion I, J, K

According to the preparation method of the Emulsion B, the shell attaching was carried out with pure silver bromide. Emulsion I having core/shell ratio of 1/1, 4 mol % silver iodide in core, $\bar{r}$ of 0.7 µm, $S/\bar{r}$ of 0.16; Emulsion J having core/shell ratio of 1/1, 12 mol % of silver iodide in core, $\bar{r}$ of 0.7 µm, $S/\bar{r}$ of 0.19; and Emulsion K having core/shell ratio of 1/2, 18 mol % of silver iodide in core, $\bar{r}$ of 0.7 µm, $S/\bar{r}$ of 0.19

were prepared. According to a X-ray diffraction, AgI contents in the core portions of these emulsions corresponded to those of prescription and AgI contents in the shell portion were 0 %. Further, according to the results of X-ray microanalyser measurement whereby iodine distribution of about 100 grains of these emulsions was observed, all the grains showed AgI contents being within ±15% range of total AgI contents of prescription. From these results, it was confirmed that the respective grains were fairly uniform and had a clear layer structure.

Emulsion L

According to a method as described in JP-A-61-246739, Emulsion L having core/intermediate/shell ratio of 1/1/1, respective silver iodide content ratio of 15/5/1, $\bar{r}$ of 0.7 µm, S/$\bar{r}$ of 0.16 was prepared.

EXAMPLE 1

On a cellulose triacetate film support provided with a subbing layer were coated layers having the compositions set forth below to prepare a multilayer color photosensitive material as Sample 101.

(Photosensitive layer composition)

The figures corresponding to respective ingredients show coating amounts represented by unit of g/m^2, the silver halide and colloidal silver are shown by coating amount of silver as converted, and the sensitizing dye is shown by coating amount of mol unit per 1 mol of silver halide in the same layer.

The first layer (Antihalation layer)	
Black colloidal silver	0.2
Gelatin	1.0
Ultraviolet absorber UV-1	0.05
Ultraviolet absorber UV-2	0.1
Ultraviolet absorber UV-3	0.1
Dispersion oil OIL-1	0.02

The second layer (Intermediate layer)	
Fine grain silver halide (Mean grain diameter 0.07 µm)	0.15
Gelatin	1.0

The third layer (The first red-sensitive emulsion layer)	
Emulsion A	1.42
Gelatin	0.9
Sensitizing dye A	2.0×10^{-4}
Sensitizing dye B	1.0×10^{-4}
Sensitizing dye C	0.3×10^{-4}
Cp-b	0.35
Cp-c	0.052
Cp-d	0.047
D-1	0.023
D-2	0.035
HBS-1	0.10
HBS-2	0.10

The fourth layer (Intermediate layer)	
Gelatin	0.8
Cp-b	0.10
HBS-1	0.05

The fifth layer (The second red-sensitive emulsion layer)	
Emulsion A	1.38
Gelatin	1.0
Sensitizing dye A	1.5×10^{-4}
Sensitizing dye B	2.0×10^{-4}
Sensitizing dye C	0.5×10^{-4}
Cp-b	0.150
Cp-d	0.027
D-1	0.005
D-2	0.010
HBS-1	0.50
HBS-2	0.060

The sixth layer (The third red-sensitive emulsion layer)	
Emulsion E	2.08
Gelatin	1.5
Cp-a	0.060
Cp-c	0.024
Cp-d	0.038
D-1	0.006
HBS-1	0.12

The seventh layer (Intermediate layer)	
Gelatin	1.0
Cpd-A	0.05
HBS-2	0.05

The eighth layer (The first green-sensitive layer)	
Monodispersed silver iodobromide emulsion (Silver iodide 3 mol %, Mean grain diameter 0.4 µm, Fluctuation coefficient 19 %)	0.64
Monodispersed silver iodobromide emulsion (Silver iodide 6 mol %, Mean grain diameter 0.7 µm, Fluctuation coefficient 18 %)	1.12
Gelatin	1.0
Sensitizing dye D	1×10^{-4}
Sensitizing dye E	1×10^{-4}
Sensitizing dye F	1×10^{-4}
Cp-h	0.20
Cp-f	0.61
Cp-g	0.084
Cp-k	0.035
Cp-ℓ	0.036
D-3	0.041
D-4	0.018
HBS-1	0.25
HBS-2	0.45

The nineth layer (The second green-sensitive emulsion layer)	
Monodispersed silver iodobromide emulsion (Silver iodide 7 mol %, Mean grain diameter 1.0 µm, Fluctuation coefficient 18 %)	2.07
Gelatin	1.5
Sensitizing dye D	1.5×10^{-4}
Sensitizing dye E	2.3×10^{-4}
Sensitizing dye F	1.5×10^{-4}
Cp-f	0.007
Cp-h	0.012
Cp-g	0.009
HBS-2	0.088

The tenth layer (The intermediate layer)	
Yellow colloidal silver	0.06
Gelatin	1.2
Cpd-A	0.30
HBS-1	0.3

The eleventh layer (The first blue-sensitive emulsion layer)	
Monodispersed silver iodobromide emulsion (Silver iodide 6 mol%, Mean grain diameter 0.4 µm, Fluctuation coefficient 20%)	0.31
Monodispersed silver iodobromide emulsion (Silver iodide 5 mol%, Mean grain diameter 0.9 µm, Fluctuation coefficient 17%)	0.38
Gelatin	2.0
Sensitizing dye G	1×10^{-4}
Sensitizing dye H	1×10^{-4}
Cp-i	0.63
Cp-j	0.57
D-1	0.020
D-4	0.015
HBS-1	0.05

The twelfth layer (The second blue-sensitive emulsion layer)	
Monodispersed silver iodobromide emulsion (Silver iodide 8 mol%, Mean grain diameter 1.3 µm, Fluctuation coefficient 18 %)	0.77
Gelatin	0.5
Sensitizing dye G	5×10^{-5}
Sensitizing dye H	5×10^{-5}
Cp-i	0.10
Cp-j	0.10
D-4	0.005
HBS-2	0.10

The thirteenth layer (Intermediate layer)	
Gelatin	0.5
Cp-m	0.1
UV-1	0.1
UV-2	0.1
UV-3	0.1
HBS-1	0.05
HBS-2	0.05

The fourteenth layer (Protective layer)	
Monodispersed silver iodobromide emulsion (Silver iodide 4 mol%, Mean grain diameter 0.05 µm, Fluctuation coefficient 10 %)	0.1
Gelatin	1.5
Poly(methyl methacrylate) grain (Mean diameter 1.5 µm)	0.1
S-1	0.2
S-2	0.2

The other surface active agent K-1, gelatin hardener H-1 were added.

(Samples 102, 103 and 105)

Samples 102, 103 and 105 were prepared similarly to the Sample 101 except that the couplers Cp-b in the third, fourth and fifth layers of the Sample 101 were replaced by the couplers Cp-c, Cp-n and the coupler (A-17) of the present invention respectively in an equimolar amount.

(Samples 106-108, 110-113, 115-118 and 120)

Samples 106-108, 110-113, 115-118 and 120 were prepared by replacing the Emulsion A in the third, and fifth layers of the Samples 101 to 103 and 105 with the Emulsions B, C and D, respectively.

(Samples 121 to 123 and 125)

Samples 121 to 123 and 125 were prepared similarly to the samples 111 to 113 and 115 except that in the third layer the HBS-1 was decreased to 0.02, the HBS-2 to 0.02, the gelatin to 0.6; in the fourth layer the HBS-1 was decreased to 0.01, the gelatin to 0.5; and in the fifth layer the HBS-1 was decreased to 0.01, the HBS-2 to 0.02, the gelatin to 0.7.

(Sample 126)

Sample 126 was prepared similarly to the Sample 125 except that the Cp-h in the eighth layer and ninth layer were replaced with 1.5 time mol of Cp-e; and the coating amount of the gelatin in the eighth layer and ninth layer were replaced with 1.2 and 1.8, respectively.

(Sample 127)

Sample 127 was prepared by replacing the Cp-i in the eleventh and twelfth layers of the Sample 125 with 1.6 time mol of Cp-o; and the coating amount of the gelatin with 2.4 and 0.8, respectively.

After adjusting color temperature to 4800 °K by filtering a light source A and giving an imagewise exposure of 10 CMS as maximum exposure, these Samples were subjected to a color development processing using the following bleaching solution A at 38 °C.

Also, the color development processing using the following bleaching solution B was caried out and Table 1 shows cyan densities of the bleaching solution B in the exposure in the case where the cyan density was 1.0 when processed with the bleaching solution A.

Further, cyan color image MTF value was measured by exposing with white light and developing a MTF measuring pattern. The MTF measurement was carried out according to the method as described in Mees, The Theory of the Photographic Process, 3rd ed., published by Macmillan Publishing Co., Inc.

Furthermore, Table 1 shows a color turbidity which was obtained by subtracting a fog density from a magenta density in the exposure wherein cyan density became (photographic fog + 1.5).

Also, after the Samples was subjected to (Condition A) white light imagewise exposure and development processing, (Condition B) it was left for 14 days as it is at 60 °C and relative humidity of 70 %. Table 1 shows a forced fastness which is a cyan density on Condition B by an exposure giving cyan density of 1.5 on Condition A.

The results are shown in Table 1

Processing Step	Time
Color development	2 min. 45 sec.
Bleaching-A (or Bleaching-B)	6 min. 30 sec.
Washing	2 min. 10 sec.
Fixing	4 min. 20 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 0.5 sec.

Processing compositions used in respective steps are as follows:

Color developer	
Diethylenetriaminepentaacetic acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Sodium sulfite	4.0 g
Patassium carbonate	30.0 g
Potassium bromide	1.4 g
Potassium iodide	1.3 mg
Hydroxylamine sulfuric acid salt	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino) -2-methylaniline sulfuric acid salt	4.5 g
Water to make	1.0 ℓ
	pH 10.0

Bleaching-A solution	
Ammonium ethylenediamine tetraacetato ferrate	100.0 g
Disodium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Ammonium nitrate	10.0 g
Water to make	1.0 ℓ
	pH 6.6

Fixing solution	
Disodium ethylenediaminetetraacetate	1.0g
Sodium sulfite	4.0 g
Ammonium thiosulfate solution (70%)	175.0 ml
Sodium bisulfite	4.6 g
Water to make	1.0 ℓ
	pH 6.6

Stabilizing solution	
Formalin (40 %)	2.0 ml
Polyoxyethylene-p-monononylphenyl ether (Mean polymerization degree: ca. 10)	0.3 g
Water to make	1.0 ℓ

Next, a development processing was carried out similarly except that the Bleaching-A solution was changed to Bleaching-B solution as prescribed below. This Bleaching-B solution was prepared as a forced deterioration solution to model a state which is fatigued by the processing of a large amount of photosensitive materials.

The Bleaching-B solution is a mixture of 900 ml (B-1) solution and 100 ml (B-2) solution.

Composition of Bleachinkg solution	
(B-1):	
Ammonium bromide	160.0 g
Ammonia water (28%)	7.1 ml
Sodium ethylenediaminetetraacetato ferrate	117 g
Glacial acetic acid	14 ml
Water to make	900 ml
(B-2′)	
Sodium ethylenediaminetetraacetate ferrate	130 g
Water to make	1 ℓ

Steel wool was added to the (B-2′) solution. The resulting solution was corked tightly and left as it is to change Fe(III)-EDTA to Fe(II)-EDTA. This solution is the (B-2) solution.

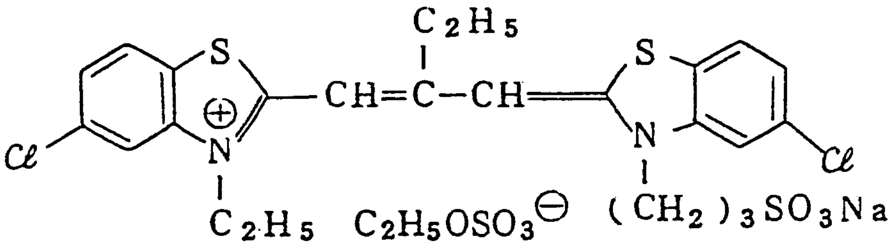
Table 1

Sample	Emulsion of 3rd and 4th layer	Coupler of 3rd, 4th and 5th layer	Relative Sensitivity 1)	Density on Bleaching-B solution	Forced fastness test value	Color turbidity	MTF Value 25 cycle/mm
101 (Comparison)	A	Cp-b	0	0.96	0.78	0.04	0.40
102 "	"	Cp-c	0.01	1.35	1.21	0.07	0.39
103 "	"	Cp-n	-0.01	1.34	1.08	0.04	0.40
105 "	"	A-17	0	1.36	1.22	0.04	0.40
106 "	B	Cp-b	0.01	0.97	0.77	0.04	0.41
107* "	"	Cp-c	0.01	1.34	1.20	0.07	0.40
108** "	"	Cp-n	0	1.34	1.07	0.04	0.41
110 (Invention)	"	A-17	0.01	1.35	1.21	0.04	0.41
111 (Comparison)	C	Cp-b	-0.01	0.97	0.78	0.03	0.42
112* "	"	Cp-c	0	1.35	1.21	0.06	0.41
113** "	"	Cp-n	-0.01	1.35	1.07	0.03	0.42
115 (Invention)	"	A-17	0	1.36	1.22	0.03	0.42
116 (Comparison)	D	Cp-b	0	0.96	0.78	0.04	0.42
117* "	"	Cp-c	0.01	1.34	1.22	0.03	0.40
118** "	"	Cp-n	0	1.34	1.07	0.06	0.42
120 (Invention)	"	A-17	0	1.35	1.22	0.03	0.42
121 (Comparison)	C	Cp-b	-0.01	0.97	0.77	0.03	0.44
122* "	"	Cp-c	-0.05	1.36	1.26	0.08	0.40
123** "	"	Cp-n	-0.09	1.36	1.17	0.08	0.40
125 (Invention)	"	A-17	0	1.36	1.24	0.03	0.44
126 "	"	"	0	1.36	1.24	0.03	0.45
127 "	"	"	-0.01	1.36	1.24	0.03	0.45

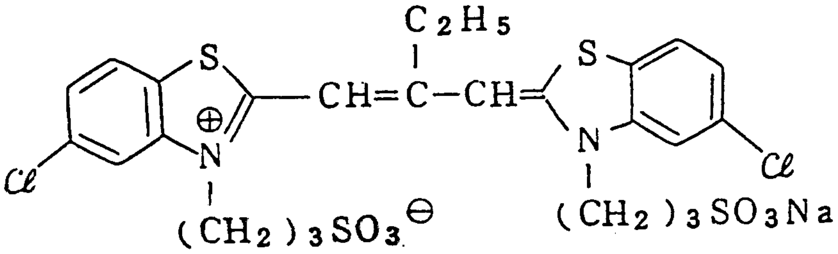
* : Combination sample proposed in JP-A-59-149364
** : Combination sample proposed in JP-A-62-79449
1) : Logarithmic relative value of the reciprocal of an exposure for giving a density of (photographic fog +0.3).

As is clear from the Table 1, the Samples of the present invention are fast in cyan color image, little in density lowering caused by forced Bleaching-B, and excellent in color reproducibility and also in sharpness expressed by MTF value.

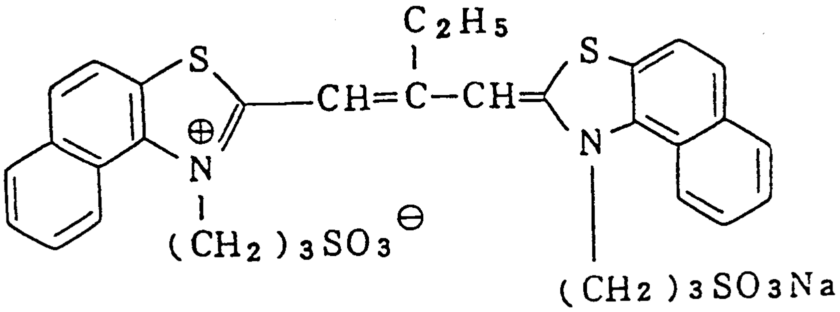
Sensitizing dye A



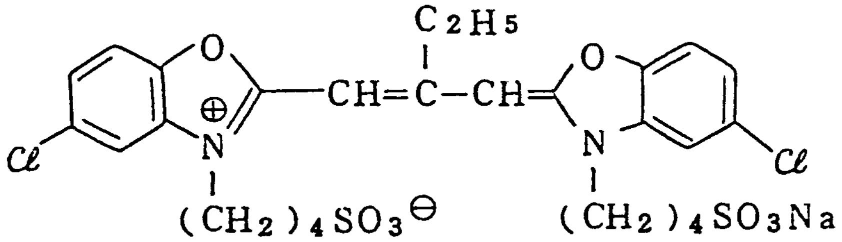
Sensitizing dye B



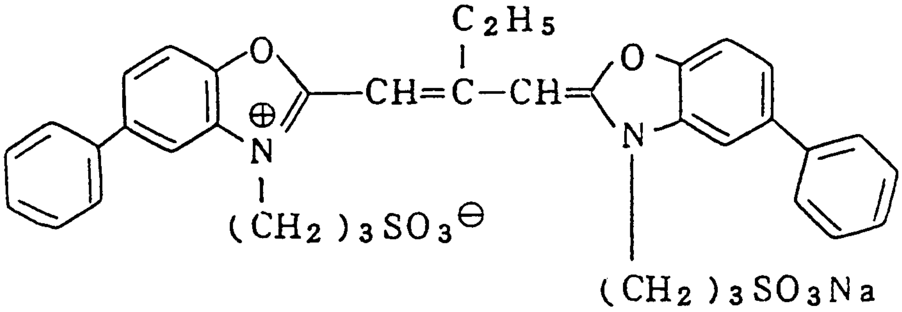
Sensitizing dye C



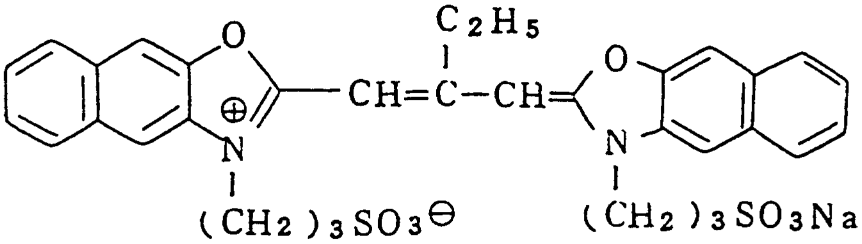
Sensitizing dye D



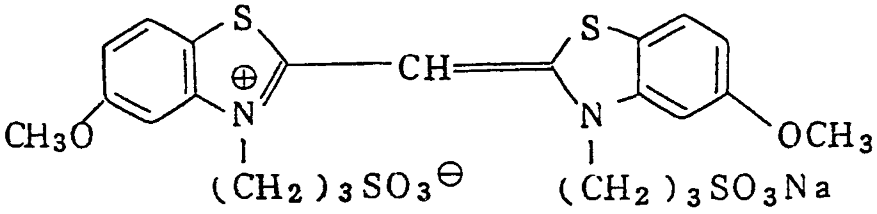
Sensitizing dye E



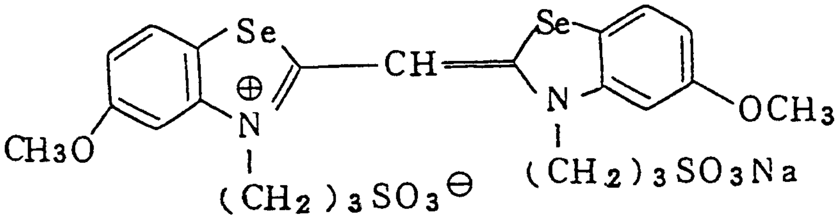
Sensitizing dye F



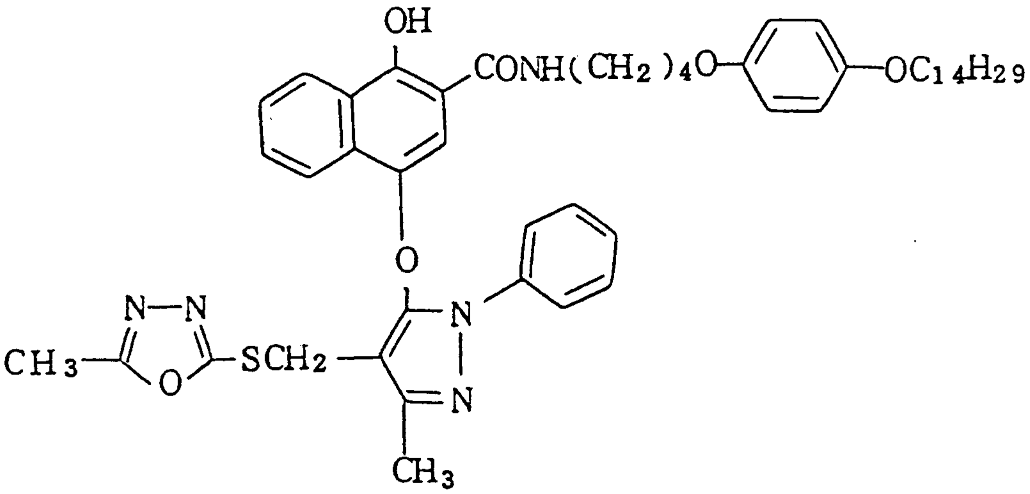
Sensitizing dye G



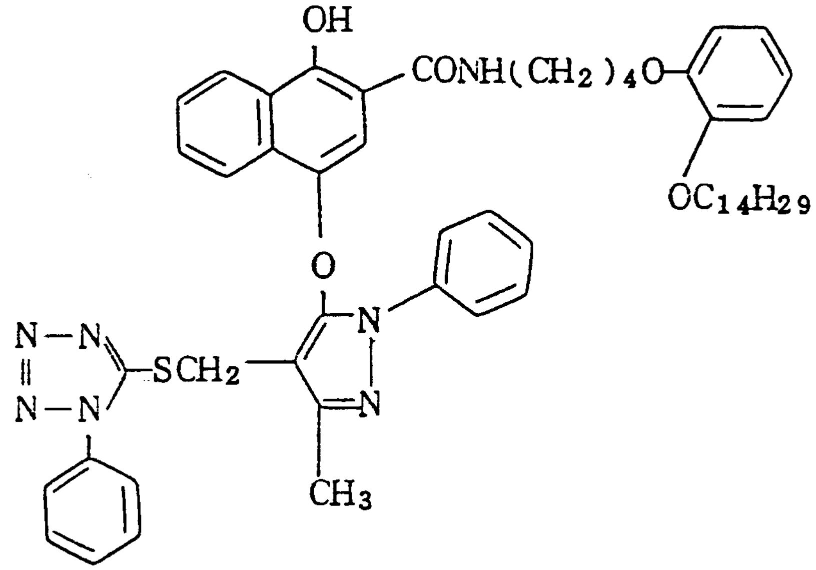
Sensitizing dye H



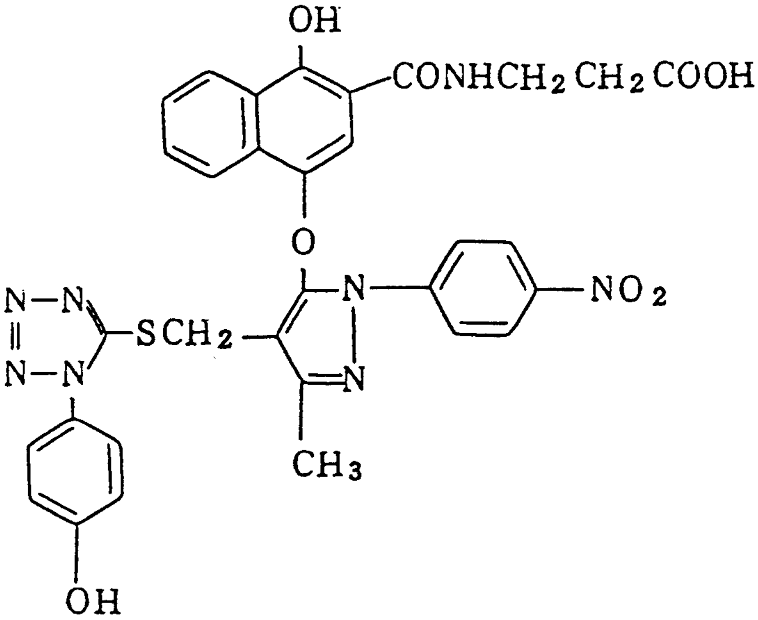
D − 1



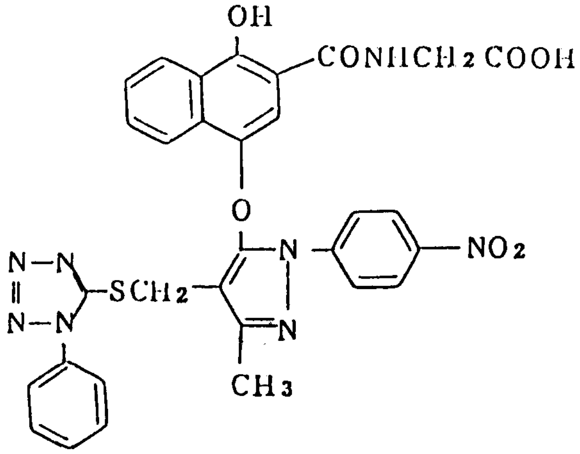
D − 2


OH
CONH(CH2)4O
OC14H29
O
N
N
N−N
N−N
SCH2
CH3

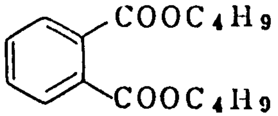
D − 3


OH
CONHCH2CH2COOH
O
N
N
NO2
N−N
N−N
SCH2
CH3
OH

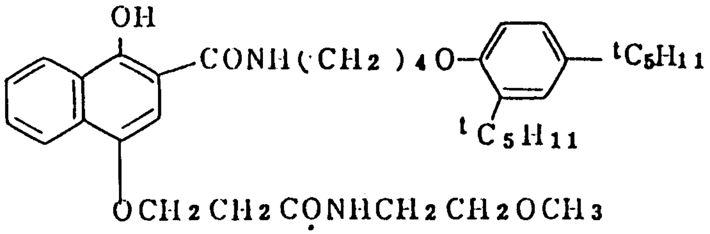
D — 4



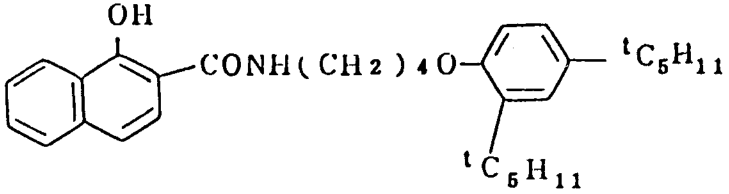
OIL — 1



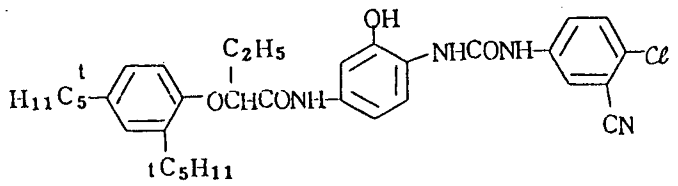
Cp — a



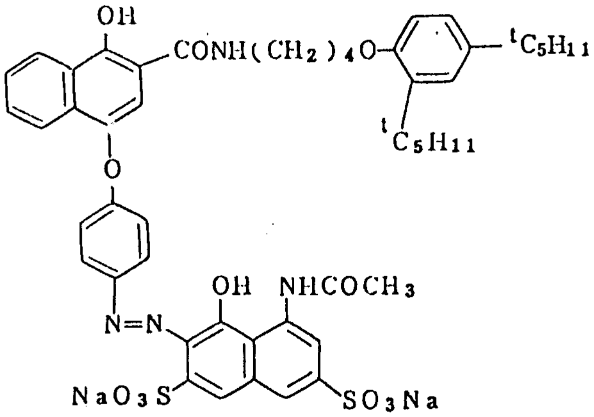
Cp — b



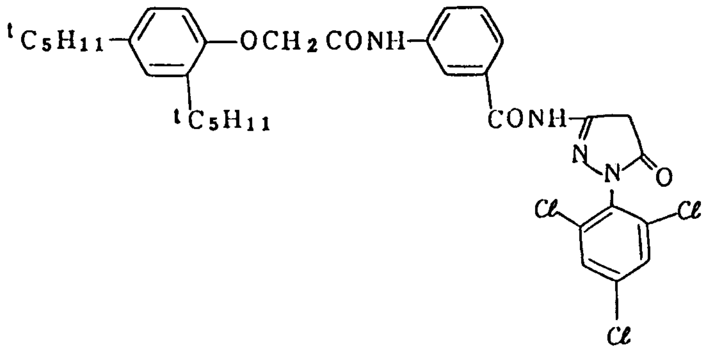
C p — c



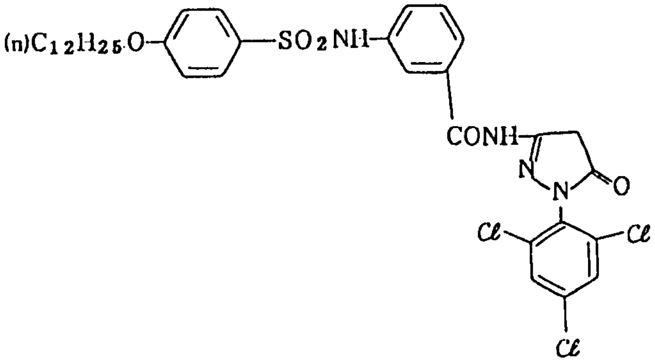
C p — d



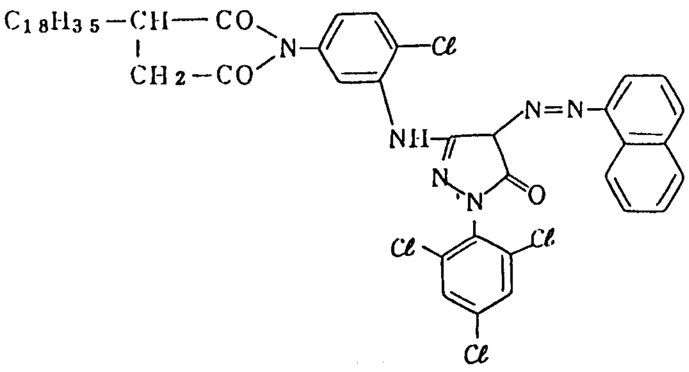
C p — e



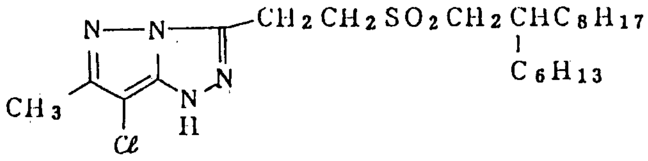
C p — f



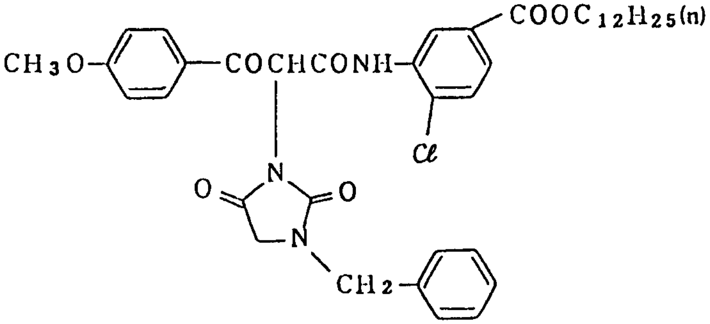
Cp — g



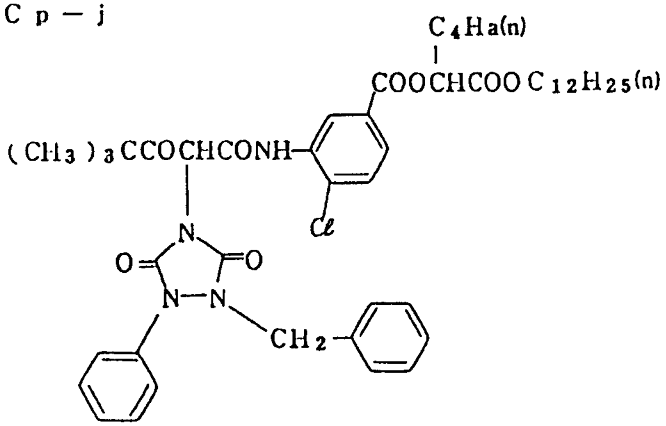
Cp — h



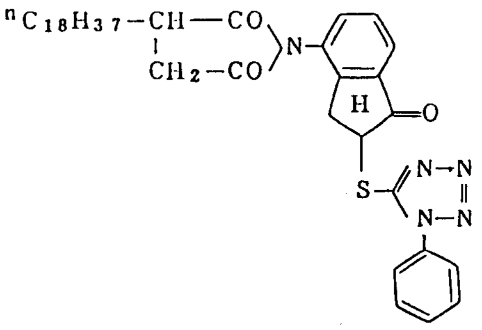
Cp — i



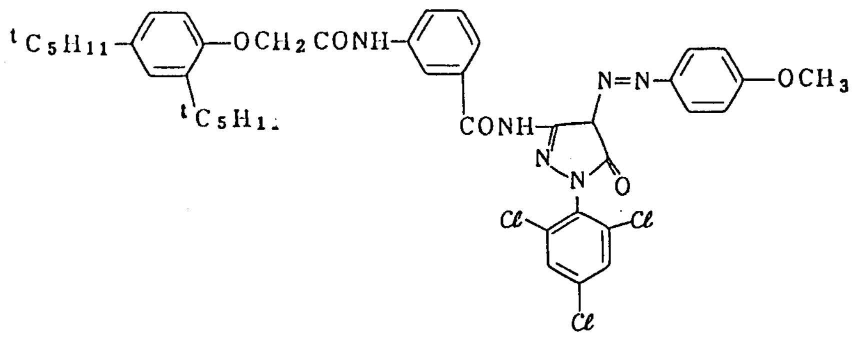
Cp — j



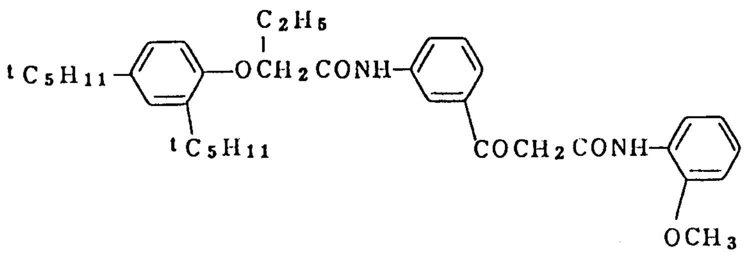
Cp — k



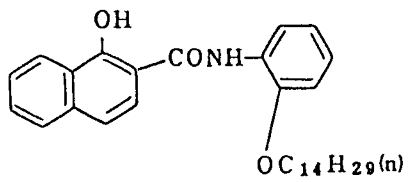
Cp — ℓ



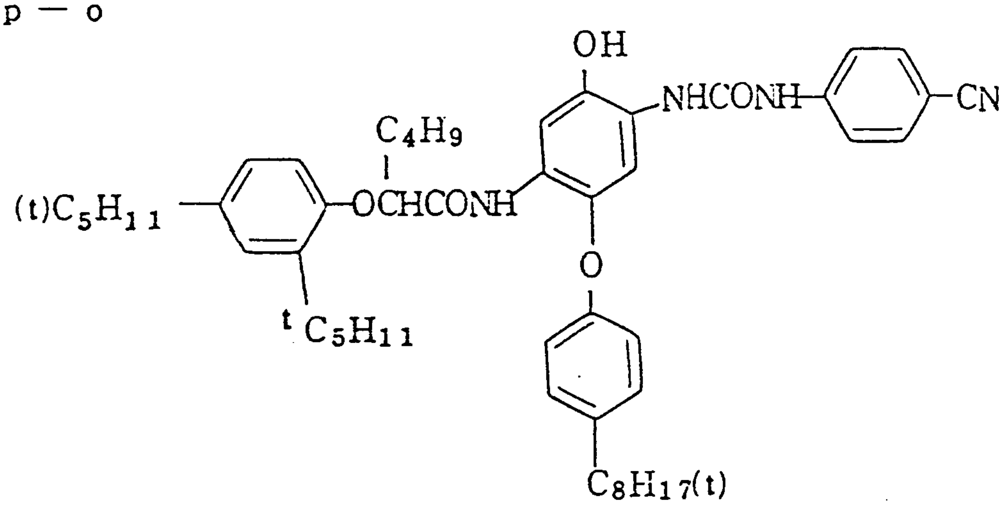
Cp — m



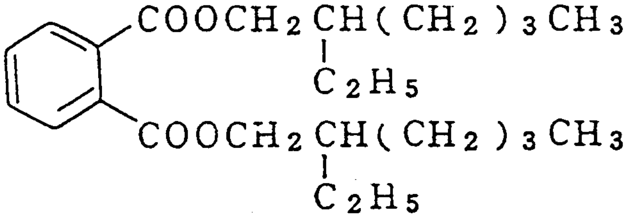
Cp — n



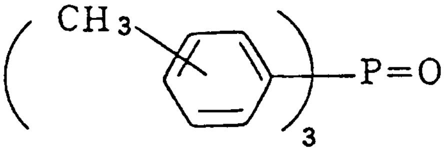
Cp—o



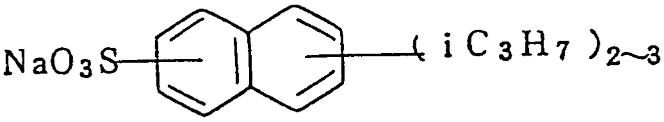
HBS—1



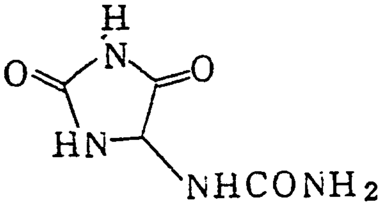
HBS—2



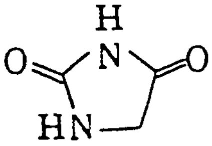
K－1



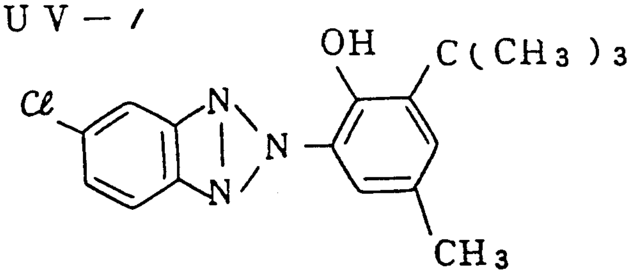
S－1



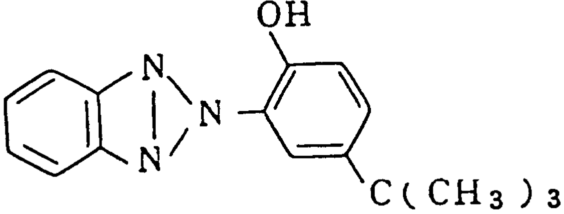
S－2



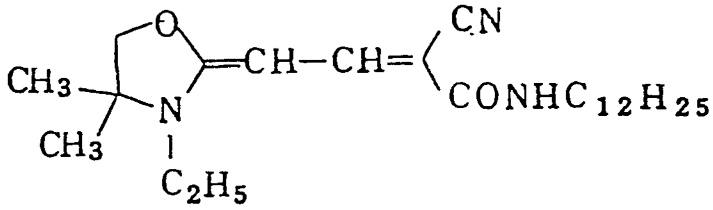
UV－1



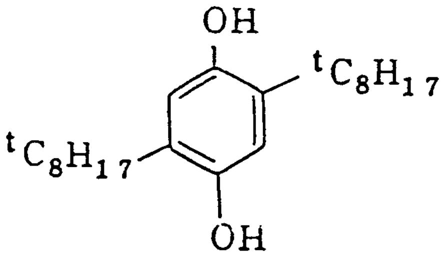
UV－2



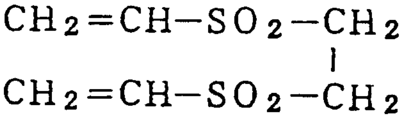
UV−3



Compound Cpd A



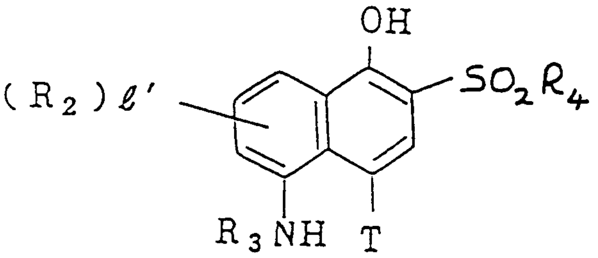
H−1



$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2 \\ \qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2 \end{array}$$

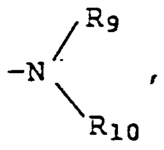
Claims

1. A silver halide color photosensitive material comprising a support having thereon at least one silver halide emulsion layer, at least one of the silver halide emulsion layer(s) containing a substantially monodispersed silver halide grain, and the photosensitive material contains a cyan dye forming coupler characterised in that the cyan dye forming coupler is represented by the general formula (A):



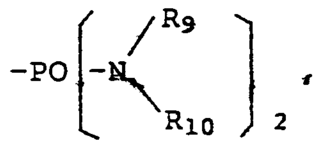
(A)

wherein R_2 represents a halogen atom, hydroxyl group, carboxyl group, sulfo group, amino group, cyano group, nitro group, aliphatic group, aromatic group, carbonamido group, sulfonamido group, carbamoyl group, sulfamoyl group, ureido group, acyl group, acyloxy group, aliphatic oxy group, aromatic oxy group, aliphatic sulfonyl group, aromatic sulfonyl group, aliphatic sulfinyl group, aromatic sulfinyl group, atiphatic carbonyi group, aromatic oxycarbonyl group, aliphatic oxycarbonylamino group, aromatic oxycarbonylamino group, sulfamoylamino group, heterocyclic group or imido group; ℓ' represents an integer of 0 to 3; R_3 represents hydrogen atom or R_6U; T represents a group being releasable upon a coupling reaction with an oxidation product of aromatic primary amine developing agent; R_4 represents an aliphatic group, aromatic group, heterocyclic group, amino group, aliphatic oxy group or aromatic oxy group; R_6 represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-OR_7$, $-SR_7$, $-COR_8$,

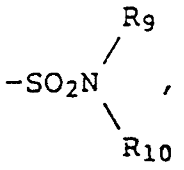


$$-N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix},$$

$-PO(R_7)_2$, $-PO(OR_7)_2$,



$$-PO\left[-N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix}\right]_2,$$



$$-SO_2N\begin{matrix}\diagup R_9\\ \diagdown R_{10}\end{matrix},$$

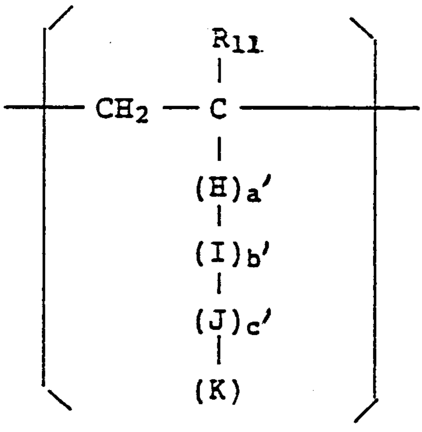
$-CO_2R_7$, $-SO_2R_7$, $-SO_2R_7$ or imido group, U represents $>N-R_9$, -CO-, $-SO_2-$, -SO- or a single bond, wherein R_7 represents an aliphatic group, aromatic group or heterocyclic group; R_8 represents hydrogen atom, an aliphatic group, aromatic group or heterocyclic group; R_9 and R_{10} each independently represent hydrogen atom, an aliphatic group, aromatic group, heterocyclic group, acyl group, aliphatic sulfonyl group or aromatic sulfonyl group; when ℓ' is plural, R_2 may be the same or different or may be bonded to each other to from a ring; R_2 and R_3 or R_3 and T may be bonded to each other to respectively form a ring; and R_4, R_2, R_3 or T may be bonded to each other through a divalent or more valent group to form a dimer or higher polymer.

2. A silver halide color photosensitive material as claimed in Claim 1, wherein ℓ' in $(R_2)\ell'$ represents 0.

3. A silver halide color photosensitive material as claimed in Claim 1, wherein R_6 of general formula (A) represents an aliphatic group, an aromatic group, $-OR_7$, or $-SR_7$.

4. A silver halide color photosensitive material as claimed in Claim 1, wherein T in general formula (A) represents a hydrogen atom, a halogen atom, an aliphatic oxy group, an aromatic oxy group, an aliphatic oxy group, or a heterocyclic thio group.

5. A silver halide color photosensitive material as claimed in Claim 1, wherein in the case where the coapler shown by general formula (A) forms a polymer, the polymer contains a repeating unit of the following formula (B):



$$\left[-CH_2-\overset{\displaystyle R_{11}}{\underset{\displaystyle (H)_{a'}-(I)_{b'}-(J)_{c'}-(K)}{C}}- \right]$$

(B)

wherein R_{11} represents hydrogen atom, an alkyl group having 1 to 4 carbon atoms or chlorine atom; H represents -CONH-, -COO- or a substituted or unsubstituted phenylene group; I represents a substituted or unsustituted alkylene group, phenylene group or aralkylene group; J represents -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, $-SO_2-$, $-NHSO_2-$ or $-SO_2NH-$; a', b' and c' each represents 0 or 1; and K represents a cyan coupler residue removing a hydrogen atom other than the hydrogen atom of the hydroxyl group at the 1-position of the compound of the general formula (A).

6. A silver halide color photosensitive material as claimed in Claim 1, wherein the coupler represented by general formula (A) is added to a monodispersed emulsion containing layer.

7. A silver halide color photosensitive material as claimed in Claim 1, wherein in the case where the emulsion layer is divided into two or more layers having same color sensitivities and different photographic sensitivities, a 4-equivalent coupler represented by general formula (A) is added to the lowest sensitivity layer and a 2-equivalent coupler represented by general formula (A) is added to the highest sensitivity layer.

8. A silver halide color photosensitive material as claimed in Claim 1, wherein the substantially monodispersed emulsion means an emulsion which has a grain diameter distribution such that the fluctuation coefficient $S/\bar{r}$ in the grain diameter of silver halide is 0.25 or less, wherein $\bar{r}$ is a mean grain diameter and S is a standard deciation, in which when respective grain diameters are ri and grain number is ni, the mean grain diameter $\bar{r}$ is defined as:

$$\bar{r} = \frac{\Sigma ni \cdot ri}{\Sigma ni}$$

and the standard deviation S is defined as:

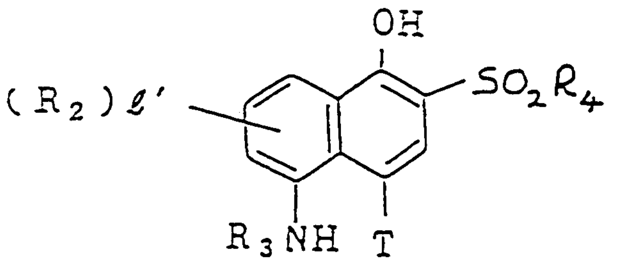
$$S = \sqrt{\frac{\Sigma(\bar{r}-ri)^2 \cdot ni}{\Sigma ni}}$$

9. A silver halide color photosensitive material as claimed in Claim 8, wherein the halogen composition of the silver halide grain is that 60 mol% or more of silver bromide is contained and 10 mol% or less of silver chloride is contained.

10. A silver halide color photosensitive material as claimed in Claim 8, wherein the halogen composition of the monodispersed emulsion is a grain which has substantially a clear layer structure having two layers comprising a core portion of high iodide content layer and a shell portion of low iodide content layer.

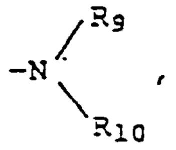
Patentansprüche

1. Farbempfindliches Silberhalogenidmaterial, umfassend einen Träger, der darauf zumindest eine Silberhalogenid-Emulsionsschicht aufweist, wobei zumindest eine der Silberhalogenidemulsionsschichten ein im wesentlichen monodispergiertes Silberhalogenidkorn umfaßt, und wobei das lichtempfindliche Material einen cyanfarbstoffbildenden Kuppler enthält,
dadurch **gekennzeichnet,** daß
der cyanfarbstoffbildende Kuppler durch die allgemeine Formel (A) dargestellt ist:



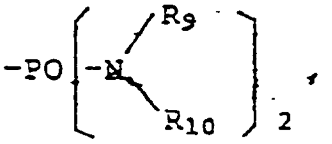
(A)

worin R_2 ein Halogenatom, Hydroxylgruppe, Carboxylgruppe, Sulfogruppe, Aminogruppe, Cyanogruppe, Nitrogruppe, aliphatische Gruppe, aromatische Gruppe, Carbonamidogruppe, Sulfonamidogrupe, Carbamoylgrupe, Sulfamoylgruppe, Ureidogruppe, Acylgruppe, Acyloxygruppe, aliphatische Oxygrupe, aromatische Oxygruppe, aliphatische Sulfonylgruppe, aromatische Sulfonylgruppe, aliphatische Sulfinylgrupe, aromatische Sulfinylgruppe, aliphatische Carbonylgruppe, aromatische Oxycarbonylgruppe, aliphatische Oxycarbonylaminogrupe, aromatische Oxycarbonalyaminogrupe, Sulfamoylaminogruppe, heterocyklische Gurppe oder Imidogruppe ist; worin 1' eine ganze Zahl von 0 bis 3 ist; und worin R_3 Wasserstoffatom oder R_6U ist, T eine Gruppe ist, die aufgrund einer Kupplungsreaktion mit einem Oxidationsprodukt eines aromatischen primären Amins als Entwicklungsmittel freigesetzt werden kann; worin R_4 eine aliphatische Gruppe, aromatische Gruppe, heterocyklische Gruppe, Aminogruppe, aliphatische Oxygruppe oder aromatische Oxygruppe ist, worin R_6 ein Wasserstoffatom, eine aliphatische Gruppe, eine aromatische Gruppe, eine heterocyklische Gruppe, $-OR_7$, $-SR_7$, $-COR_8$,

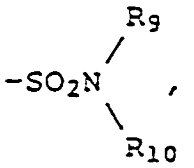


$$-N\begin{matrix} R_9 \\ R_{10} \end{matrix},$$

$-PO(R_7)_2$, $-PO(OR_7)_2$,



$$-PO\left[-N\begin{matrix} R_9 \\ R_{10} \end{matrix}\right]_2,$$



$$-SO_2N\begin{matrix} R_9 \\ R_{10} \end{matrix},$$

-CO_2R_7, -SO_2R_7, -SO_2R_7

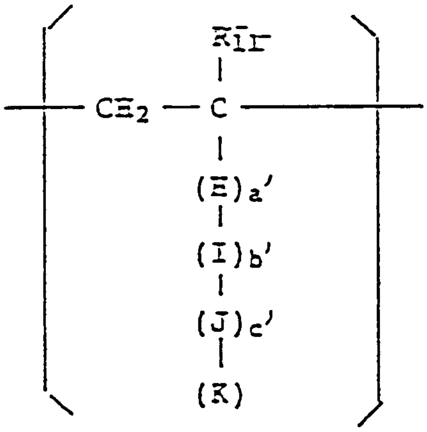
oder Imidogrupppe ist worin U $>$N-R_9, -CO-, -SO_2-, -SO- oder eine Einfachbindung ist, worin R_7 eine aliphatische Gruppe, aromatische Gruppe oder heterocyklische Gruppe ist, worin R_8 Wasserstoffatom, eine aliphatische Gruppe, aromatische Gruppe oder heterocyklische Gruppe ist, worin R_9 und R_{10} jeweils unabhängig Wasserstoffatom, eine aliphatische Gruppe, aromatische Gruppe, heterocyklische Gruppe, Acylgruppe, aliphatische Sulfonylgruppe oder aromatische Sulfonylgruppe sind; worin wenn 1' Plural ist, R_2 gleich oder verschieden oder aneinander zur Bildung eines Ringes gebunden sein können; worin R_2 und R_3 oder R_3 und T aneinander gebunden sein können, um jeweils einen Ring zu bilden, und worin R_4, R_2, R_3 oder T aneinander durch eine divalente oder mehrvalente Gruppe gebunden sein können, zur Bildung eines dimeren oder eines höheren Polymers.

2. Farbempfindliches Silberhalogenidmaterial nach Anspurch 1, worin 1' in $(R_2)1'$ 0 ist.

3. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin R_6 der allgemeinen Formel (A) eine aliphatische Gruppe, eine aromatische Gruppe, -OR_7 oder -SR_7 ist.

4. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin T in der allgemeinen Formel (A) ein Wasserstoffatom, ein Halogenatom, eine aliphatische Oxygruppe, eine aromatische Oxygruppe, eine aliphatische Oxygruppe oder eine heterocyklische Thiogruppe ist.

5. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin in dem Fall, wenn der Kuppler, gezeigt durch die allgemeine Formel (A), ein Polymer bildet, das Polymer eine Wiederholungseinheit der folgenden Formel (B) enthält:



$$\left(\begin{array}{c} R_{11} \\ | \\ -CH_2-C- \\ | \\ (H)_{a'} \\ | \\ (I)_{b'} \\ | \\ (J)_{c'} \\ | \\ (K) \end{array} \right) \qquad (B)$$

worin R_{11} Wasserstoffatom, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen oder Chloratom ist, worin H -CONH-, -COO- oder eine substituierte oder unsubstituierte Phenylengruppe ist, worin I eine substituierte oder unsubstituierte Alkylengruppe, Phenylengruppe oder Aralkylengruppe ist, worin J -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-,-CO-, -O-, -SO_2-, -$NHSO_2$- oder -SO_2NH- ist, worin a', b' und c' jeweils 0 oder 1 ist, und worin K ein Cyankupplerrest ist, der ein anderes Wasserstoffatom als das Wasserstoffatom der Hydroxylgruppe an der 1-Position der Verbindung der allgemeinen Formel (A) entfernt.

6. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin der durch die allgemeine Formel (A) gezeigte Kuppler zu einer Schicht gegeben wird, die eine monodispergierte Emulsion enthält.

7. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin in dem Fall, wenn die Emulsionsschicht in 2 oder mehr Schichten mit gleichen Farbempfindlichkeiten und unterschiedlichen fotografischen Empfindlichkeiten unterteilt wird, 4-Äquivalente des Kupplers, dargestellt durch die allgemeine Formel (A), zu der Schicht mit geringster Empfindlichkeit zugegeben wird, und 2-Äquivalente des Kupplers, dargestellt durch die allgemeine Formel (A), zu der Schicht mit höchster Empfindlichkeit gegeben werden.

8. Farbempfindliches Silberhalogenidmaterial nach Anspruch 1, worin die im wesentlichen monodispergierte Emulsion eine Emulsion bedeutet, die eine Kordurchmesserverteilung hat, so daß der Fluktuationskoeffizient S/F in dem Korndurchmesser von Silberhalogenid 0,25 oder weniger ist, worin F ein mittlerer Korndurchmesser und S eine Standardabweichung ist, worin der mittlere Korndurchmesser F wie folgt definiert ist, wenn die jeweiligen Korndurchmesser ri und die Kornzahl ni sind:

$$F = \frac{\Sigma ni \cdot ri}{\Sigma ni}$$

und worin die Standardabweichung S wie folgt definiert ist:

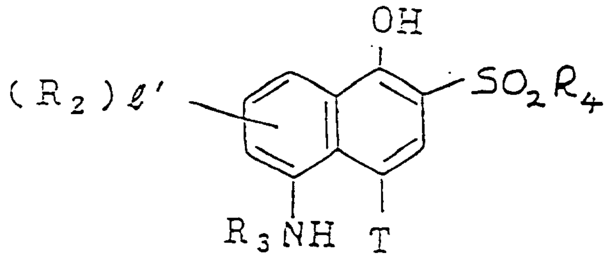
$$S = \sqrt{\frac{\Sigma(\bar{r} - ri)^2 \cdot ni}{\Sigma ni}}$$

9. Farbempfindliches Silberhalogenidmaterial nach Anspruch 8, worin die Halogenzusammensetzung des Silberhalogenidkornes so ist, daß 60 Mol% oder mehr Silberbromid enthalten sind und daß 10 Mol% oder weniger Silberchlorid enthalten sind.

10. Farbempfindliches Silberhalogenidmaterial nach Anspruch 8, worin die Halogenzusammensetzung der monodispergierten Emulsion ein Korn ist, das im wesentlichen eine klare Schichtstruktur mit 2 Schicht hat, umfassnd einen Kernbereich aus einer Schicht mit hohem Jodidgehalt und einen Hüllenbereich aus einer Schicht mit geringem Jodidgehalt.

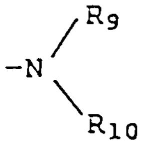
Revendications

1. Matériau photosensible couleur à l'halogénure d'argent, comportant un support portant au moins une couche d'émulsion d'halogénure d'argent, au moins une des couches d'émulsion d'halogénure d'argent contenant un grain d'halogénure d'argent essentiellement mono-dispersé, et le matériau photosensible contenant un copulant formant un pigment cyan,
caractérisé en ce que le copulant formant un pigment cyan est représenté par la formule générale (A):

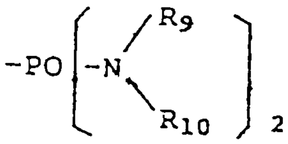


(A)

dans laquelle R_2 représente un atome d'halogène, un radical hydroxyle, un radical carboxyle, un radical sulfo, un radical amino, un radical cyano, un radical nitro, un radical aliphatique, un radical aromatique, un radical carbonamido, un radical sulfonamido, un radical carbamoyle, un radical sulfamoyle, un radical uréido, un radical acyle, un radical acyloxy, un radical aliphatique-oxy, un radical aromatique-oxy, un radical aliphatique sulfonyle, un radical aromatique sulfonyle, un radical aliphatique sulfinyle, un radical aromatique sulfinyle, un radical aliphatique carbonyle, un radical aromatique oxycarbonyle, un radical aliphatique oxycarbonylamino, un radical aromatique oxycarbonylamino, un radical sulfamoylamino, un radical hétérocyclique ou un radical imido; l' représente un entier valant entre 0 et 3; R_3 représente un atome d'hydrogène ou R_6U; T représente un radical pouvant être libéré dans une réaction de couplage avec un produit d'oxydation d'un agent de développement à amine aromatique primaire; R$_4$ représente un radical aliphatique, un radical aromatique, un radical hétérocyclique, un radical amino, un radical aliphatique-oxy ou un radical aromatique-oxy; R$_6$ représente un atome d'hydrogène, un radical aliphatique, un radical aromatique, un radical hétérocyclique, -OR$_7$, -SR$_7$, -COR$_8$,


,

-PO(R$_7$)$_2$, -PO(OR$_7$)$_2$,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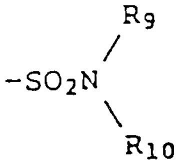

,

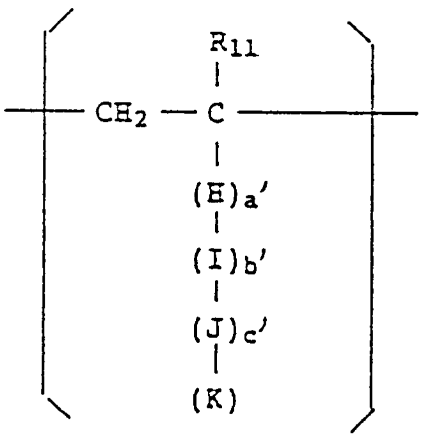
-CO$_2$R$_7$, -SO$_2$R$_7$, -SO$_2$R$_7$ ou un radical imido, U représente $>$N-R$_9$, -CO-, -SO$_2$-, -SO- ou une liaison simple, où R$_7$ représente un radical aliphatique, un radical aromatique ou un radical hétérocyclique; R$_8$ représente un atome d'hydrogène, un radical aliphatique, un radical aromatique ou un radical hétérocyclique; R$_9$ et R$_{10}$ représentent chacun indépendamment un atome d'hydrogène, un radical aliphatique, un radical aromatique, un radical hétérocyclique, un radical acyle, un radical aliphatique sulfonyle ou un radical aromatique sulfonyle; lorsque l' est un multiple, les R$_2$ peuvent être identiques ou différents, ou peuvent être liés entre eux pour former un radical cyclique; R$_2$ et R$_3$ ou R$_3$ et T peuvent être liés entre eux pour former respectivement un radical cyclique; et R$_4$, R$_2$, R$_3$ ou T peuvent être liés entre eux par l'intermédiaire d'un radical de valence deux ou plus, pour former un dimère ou un polymère d'ordre plus élevé.

2. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel l' dans (R$_2$)l' représente 0.

3. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel R$_6$ dans la formule générale (A), représente un radical aliphatique, un radical aromatique, -OR$_7$, ou -SR$_7$.

4. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel T dans la formule générale (A), représente un atome d'hydrogène, un atome d'halogène, un radical aliphatique-oxy, un radical aromatique-oxy, un radical aliphatique-oxy, ou un radical hétérocyclique-thio.

5. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1 dans lequel, dans le cas où le copulant représenté par la formule générale (A) forme un polymère, le polymère contient un motif de la formule (B):



$$\left[\begin{array}{c} R_{11} \\ | \\ -CH_2-C- \\ | \\ (H)_{a'} \\ | \\ (I)_{b'} \\ | \\ (J)_{c'} \\ | \\ (K) \end{array}\right]$$

(B)

dans laquelle R_{11} représente un atome d'hydrogène, un radical alkyle possédant 1 à 4 atomes de carbone ou un atome de chlore; H représente -CONH-, -COO- ou un groupe phénylène substitué ou non substitué; I représente un radical alkylène substitué ou non substitué, un radical phénylène ou un radical aralkylène; J représente -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, $-SO_2-$, $-NHSO_2-$ ou $-SO_2NH-$; a', b', et c' représentent chacun 0 ou 1; et K représente un résidu du copulant cyan enlevant un atome d'hydrogène autre que l'atome d'hydrogène du radical hydroxyle situé en position 1 du composé de la formule générale (A).

6. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel le copulant représenté par la formule générale (A) est ajouté à une couche contenant une émulsion mono-dispersée.

7. Matériau photosensible couleur a l'halogénure d'argent selon la revendication 1 dans lequel, dans le cas cas où la couche d'émulsion est divisée en deux ou plusieurs couches présentant les mêmes sensibilités aux couleurs et des sensibilités photographiques différentes, 4 équivalents d'un copulant représenté par la formule générale (A) sont ajoutés à la couche de sensibilité la plus basse, et 2 équivalents d'un copulant représenté par la formule générale (A) sont ajoutés à la couche de sensibilité la plus élevée.

8. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel l'émulsion essentiellement mono-dispersée signifie une émulsion qui présente une distribution du diamètre des grains telle que le coefficient de fluctuation $S/\bar{r}$ du diamètre des grains d'halogénure d'argent vaut 0,25 ou moins, où $\bar{r}$ est un diamètre moyen du grain et S est un écart standard, avec, lorsque les diamètres respectifs des grains sont ri et le nombre de grains est ni, le diamètre moyen de grain $\bar{r}$ est défini par:

$$\bar{r} = \frac{\Sigma ni \cdot ri}{\Sigma ni}$$

et l'écart standard S est défini par:

$$S = \sqrt{\frac{\Sigma(\bar{r} - ri)^2 \cdot ni}{\Sigma ni}}$$

9. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 8, dans lequel la composition en halogène du grain d'halogénure d'argent est telle qu'il contient 60% molaires ou davantage de bromure d'argent et 10% molaires ou moins de chlorure d'argent.

10. Matériau photosensible couleur à l'halogénure d'argent selon la revendication 8, dans lequel la composition d'halogène de l'émulsion mono-dispersée est un grain qui présente essentiellement une nette structure en couches, à deux couches, comportant une partie de coeur d'une couche à haute teneur en iodure et une partie d'enveloppe d'une couche à faible teneur en iodure.