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- (54) Silver halide color photographic material.
- A silver halide color photographic material exhibiting excellent color reproduction, processing dependence, sharpness at high speed, and image storage properties having at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler containing naphthol and having a substituent group in the 5-position, at least one green-sensitive silver halide emulsion containing at least one magenta coupler containing-pyrazoloazole and having an alkoxy group or an aryl oxy group in the 6-position, and at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, wherein the cyan and the magenta coupler are of a defined formula.

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### SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

### FIELD OF THE INVENTION

The present invention is directed toward silver halide color photographic materials and, more precisely, it is directed toward silver halide color photographic materials which contain naphthol based cyan couplers which have a substituent group in the 5-position and pyrazoloazole based magenta couplers which have an alkoxy group or an aryloxy group in the 6-position.

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#### BACKGROUND OF THE INVENTION

Good color forming properties, color reproduction and sharpness, good processing dependence, stability and colored image storage properties are desirable in silver halide color photosensitive materials. Naphthol based cyan couplers which satisfy the above mentioned requirements have been suggested in European Patent No. 161,626A, and magenta couplers have been suggested in U.S. Patent 4,540,654 and European Patent No. 226,849A. However, the use of either of these alone, results in only minimal improvement.

The combination of some of these couplers has been suggested in JP-A-62-180365 (the term "JP-A" as used herein signifies "unexamined published Japanese patent application"). The utilization of this combination results in the improvement of color reproduction, processing dependence and image storage properties. However, problems affecting photographic performance have arisen. These problems include instability of the silver halide photosensitive materials during storage.

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## DETAILED DESCRIPTION OF THE INVENTION

The object of the present invention is to provide photosensitive materials which simultaneously satisfy all of the various properties required of a color sensitive material. More precisely, the first objective of the present invention is to provide color sensitive materials which have excellent color reproduction. The second objective is to provide stable color sensitive materials exhibiting little variation in performance due to the passage of time during the storage of the coating liquids, during the manufacture of the sensitive material, during the storage of the photosensitive material, or during the storage of a latent image. The third objective of the present invention is to provide color sensitive materials whose images have excellent storage properties. The fourth objective of the present invention is to provide color sensitive materials in which the fluctuation in density after processing is slight even when deteriorated or low pH bleach or bleach-fix baths are used. The fifth objective of the present invention is to provide color sensitive materials which exhibit excellent sharpness at high speed.

These objectives are realized by means of silver halide color photographic materials having at least one red sensitive silver halide emulsion layer which contains cyan couplers, at least one green sensitive silver halide emulsion layer which contains magenta couplers, and at least one blue sensitive silver halide emulsion layer which contains yellow couplers. These layers are established on a support. At least one of the aforementioned cyan couplers is a coupler which can be represented by the general formula [A], and at least one of the aforementioned magenta couplers is a coupler which can be represented by the general formula [II].

50 General Formula [A]

In general formula [A], R<sub>1</sub> represents a halogen atom, aliphatic group, aromatic group, heterocyclic group, amidino group, guanidino group or a group which can be represented by -COR<sub>4</sub>, -SO<sub>2</sub>R<sub>4</sub>, -SOR<sub>4</sub>,

-NHCOR4, -NHSO<sub>2</sub>R<sub>4</sub>, -HNSOR<sub>4</sub>, or

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O R<sub>4</sub>
-NHP

 $R_2$  represents a halogen atom, hydroxyl group, carboxyl group, sulfo group, amino group, cyano group, nitro group, aliphatic group, aromatic group, aromatic group, aromatic group, aromatic group, aromatic oxy group, aliphatic oxy group, aromatic oxy group, aliphatic sulfinyl group, aromatic sulfinyl group, aliphatic sulfinyl group, aromatic sulfinyl group, aliphatic oxycarbonyl group, aromatic oxycarbonylamino group, aromatic oxycarbonylamino group, sulfamoylamino group, heterocyclic group or an imido group.  $\mathbf{t}'$  is 0 or an integer of value 1 to 3.  $R_3$  represents a hydrogen atom or an  $R_6U$  group. T represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine developing agent. Here  $R_4$  and  $R_5$  each independently represent an aliphatic group, aromatic group, heterocyclic group, amino group, aliphatic oxy group or an aromatic oxy group,  $R_6$  represents a hydrogen atom, aliphatic group, aromatic group, heterocyclic group, -OR $_7$  group, -SR $_7$  group, -COR $_8$  group,

$$R_9$$
-N group,

-PO(R<sub>7</sub>)<sub>2</sub> group, -PO(-OR<sub>7</sub>)<sub>2</sub> group,

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-CO<sub>2</sub>R<sub>7</sub> group, -SO<sub>2</sub>R<sub>7</sub> group, -SO<sub>2</sub>OR<sub>7</sub> group or an imino group, and U represents

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a -CO- group, an -SO<sub>2</sub>- group, an -SO- group or a single bond. R<sub>7</sub> represents an aliphatic group, aromatic group or a heterocyclic group. R<sub>8</sub> represents a hydrogen atom, aliphatic group, aromatic group, aromatic group, heterocyclic group, acyl group, aliphatic sulfonyl group or an aromatic sulfonyl group.

Moreover, when  $\mathfrak{t}'$  has a value of 2 or more, the  $R_2$  groups may be the same or different, or they may be joined together to form a ring. Further,  $R_2$  and  $R_3$ , or  $R_3$  and  $R_4$ , may be joined to each other to form rings respectively. Also, dimers or larger units (oligomers or polymers) can be formed by linking together via divalent groups or groups of higher valence in any of  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$ .

Compounds which can be used in the invention are described below.

Here the term "aliphatic group" signifies a linear chain, branched or cyclic alkyl group, alkenyl group or alkynyl group, and these may be substituted or unsubstituted groups. The term "aromatic group" signifies a substituted or unsubstituted aryl group and these may have condensed rings. The term "heterocyclic group" signifies a substituted or unsubstituted, simple ring or condensed ring, heterocyclic group.

Actual examples of aliphatic groups include 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, methyl sulfonamidoethyl group, 3-(2-ethylhexyloxy)propyl group, 3-n-decyloxypropyl group, 3-n-dodecyloxypropyl group, 3-n-tetradecyloxypropyl group, oleyl group, propargyl group, ethenyl group, 3-(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.

Actual examples of aromatic groups include 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-toctylphenyl 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-methylsulfonylphenyl group, and 2,4-di-t-pentylphenyl group.

Actual examples of heterocyclic groups include 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-benzo-oxazolyl group, 2-benzthiazolyl group, 1-imidazolyl group, 1-pyrazolyl group, 5-tetrazolyl group, 1,3,4-thiadiazol-2-yl group, 2-pyrrolyl 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-pyrazyl group, succinimido group, phthalimido group, morpholino group, pyrrolidino group, piperidino group, imidazolidin-2,4-dione-1-yl group, and oxazolidin-2,4-dione-3-yl group.

The individual substituent groups in the general formula [A] are described in detail below.

R<sub>1</sub> in general formula [A] represents a halogen atom, aliphatic group, aromatic group, heterocyclic group, amidino group, guanidino group or a group which can be represented by -COR<sub>4</sub>, -SO<sub>2</sub>R<sub>4</sub>, -SO<sub>R<sub>4</sub></sub>,

-NHCOR4, -NHSO2R4, -NHSOR4 or

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R4 and R5 each independently represent an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, a heterocyclic group which has from 1 to 30 carbon atoms, an amino group which has from 0 to 30 carbon atoms [for example an amino group, methylamino group, dimethylamino group, n-butylamino group, anilino group, N-(2-n-tetradecyloxyphenyl)amino group, pyrrolidino group, morpholino group, piperidino group, 2-ethylhexylamino group, n-dodecylamino group, Nmethyl-N-dodecylamino group, 3-dodecyloxypropylamino group, 3-(2,4-di-t-pentylphenoxy)propylamino group, 4-(2,4-di-t-pentylphenoxy)butylamino group], an aliphatic oxy group which has from 1 to 30 carbon atoms [for example a methoxy group, ethoxy group, butoxy group, methoxyethoxy group, n-dodecyloxy group, 3-(2,4-di-t-pentylphenoxy)propoxy group] or an aromatic oxy group which has from 6 to 30 carbon atoms [for example a phenoxy group, 4-n-dodecyloxyphenoxy group, 4-methoxycarbonylphenoxy group]. R₄ and R₅ may also be joined together to form a ring. When R₁ is a halogen atom this halogen atom can be a fluorine atom, chlorine atom, bromine atom or iodine atom. When R<sub>1</sub> is an amidino group or guanidino group the group has from 1 to 30 carbon atoms and may be substituted with aliphatic groups, aromatic groups, hydroxyl groups, aliphatic oxy groups, acyl groups, aliphatic sulfonyl groups, aromatic sulfonyl groups, acyloxy groups, aliphatic sulfonyloxy groups or aromatic sulfonyloxy groups. Further, two nitrogen atoms may be joined together to form a heterocycle such as an imidazole or a benzimidazole.

R<sub>2</sub> in general formula [A] represents a halogen atom (fluorine atom, chlorine atom, bromine atom or iodine atom), hydroxyl group, carboxyl group, sulfo group, cyano group, nitro group, an amino group which has from 0 to 30 carbon atoms (for example an amino group, methylamino group, dimethylamino group, pyrrolidino group, anilino group), an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, a carbonamido group which has from 1 to 30 carbon atoms (for example formamido group, acetamido group, trifluoroacetamido group, benzamido group), a sulfonamido group which has from 1 to 30 carbon atoms (for example methylsulfonamido group, trifluoromethylsulfonamido group, n-butylsulfonamido group, p-tolylsulfonamido group), a carbamoyl group which has from 1 to 30 carbon atoms (for example carbamoyl group, N,N-dimethylcarbamoyl group, Nmethylcarbamoyl group, pyrrolidinocarbonyl group, N-n-hexadecylcarbamoyl group), a sulfamoyl group which has from 0 to 30 carbon atoms (for example sulfamoyl group, N-methylsulfamoyl group, N,Ndimethylsulfamoyl group, morpholinosulfonyl group, N-n-dodecylsulfamoyl group), a ureido group which has from 1 to 30 carbon atoms (for example ureido group, 3-methylureido group, 3-phenylureido group, 3,3dimethylureido group), an acyl group which has from 1 to 30 carbon atoms (for example acetyl group, pivaloy! group, benzoy! group, dodecanoy! group), an acyloxy group which has from 1 to 30 carbon atoms (for example acetoxy group, benzoyloxy group), an aliphatic oxy group which has from 1 to 30 carbon atoms, an aromatic oxy group which has from 6 to 30 carbon atoms, an aliphatic thio group which has from 1 to 30 carbon atoms, an aromatic thio group which has from 6 to 30 carbon atoms, an aliphatic sulfonyl group which has from 1 to 30 carbon atoms, an aromatic sulfonyl group which has from 6 to 30 carbon atoms, an aliphatic sulfinyl group which has from 1 to 30 carbon atoms, an aromatic sulfinyl group which has from 6 to 30 carbon atoms, an aliphatic oxycarbonyl group which has from 2 to 30 carbon atoms, an aromatic oxycarbonyl group which has from 7 to 30 carbon atoms, an aliphatic oxycarbonylamino group which has from 2 to 30 carbon atoms, an aromatic oxycarbonylamino group which has from 7 to 30 carbon atoms, a sulfamoylamino group which has from 0 to 30 carbon atoms (for example sulfamoylamino group, 3,3-dimethylsulfamoylamino group, piperidinosulfonylamino group), a heterocyclic group which has from 1 to 30 carbon atoms or an imido group which has from 4 to 30 carbon atoms (for example a succinimido group, maleimido group, phthalimido group, diglycolimido group, 4-nitrophthalimido group).

 $R_3$  in general formula [A] represents a hydrogen atom or  $R_6U$ . Here  $R_6$  represents a hydrogen atom, an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, a heterocyclic group which has from 1 to 30 carbon atoms, an  $-OR_7$  group, an  $SR_7$  group, a  $-COR_8$  group, an

R9 -N

group, a -PO(R<sub>7</sub>)<sub>2</sub> group, a -PO(-OR<sub>7</sub>)<sub>2</sub> group, a

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$$R_9$$
 $-PO[-N]_2$  group, an  $-SO_2N$  group,  $R_{10}$ 

a  $-CO_2R_7$  group, an  $-SO_2R_7$  group, an  $-SO_2OR_7$  group, or an imido group which has from 4 to 30 carbon atoms (for example succinimido group, maleimido group, phthalimido group, diaceylamino group). U represents

-CO-group, -SO<sub>2</sub>- group, -SO- group or a single bond.  $R_7$  represents an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms or a heterocyclic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms or a heterocyclic group which has from 1 to 30 carbon atoms.  $R_9$  and  $R_{10}$  each independently represents a hydrogen atom, an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, a heterocyclic group which has from 1 to 30 carbon atoms, an acyl group which has from 1 to 30 carbon atoms, an acyl group which has from 1 to 30 carbon atoms (for example acetyl group, trifluoroacetyl group, benzoyl group, p-chlorobenzoyl group) or a sulfonyl group which has from 1 to 30 carbon atoms (for example methylsulfonyl group, n-butylsulfonyl group, phenylsulfonyl group, p-nitrophenylsulfonyl group).  $R_9$  and  $R_{10}$  may be joined together to form a ring.

T in general formula [A] represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine developing agent. Examples of the latter type of group include halogen atoms (fluorine atom, chlorine atom, bromine atom and iodine atom), sulfo group, thiocyanato group, isothiocyanato group, selenocyanato group, aliphatic oxy groups which have from 1 to 30 carbon atoms, aromatic oxy groups which have from 6 to 30 carbon atoms, aliphatic thio groups which have from 1 to 30 carbon atoms, heterocyclic oxy groups which have from 1 to 30 carbon atoms, aromatic azo groups which have from 6 to 30 carbon atoms, heterocyclic groups which have from 1 to 30 carbon atoms, acyloxy groups which have from 1 to 30 carbon atoms (for example acetoxy group, benzoyloxy group), sulfonyloxy groups which have from 1 to 30 carbon atoms (for example methylsulfonyloxy group, p-tolylsulfonyloxy group), carbamoyloxy groups which have from 1 to 30 carbon atoms (for example methylsulfonyloxy group, pyrrolidinocarbonyloxy group, N-ethylcarbamoyloxy group), thiocarbonyloxy groups which have from 2 to 30 carbon atoms (for example methylthiocarbonyloxy group), and carbonyldioxy groups which have from 2 to 30 carbon atoms (for example methylthiocarbonyloxy group), phenoxycarbonyloxy group, phenoxycarbonyloxy group).

R<sub>2</sub> and R<sub>3</sub>, R<sub>3</sub> and T, or a plurality of R<sub>2</sub> groups in general formula [A] may be joined together to form rings respectively. Examples of cases in which R<sub>2</sub> and R<sub>3</sub> are joined together include the -CH<sub>2</sub>CO- group,

-OCO-group, -NHCO- group, -C(CH<sub>3</sub>)<sub>2</sub>CO- group and the -CH = CHCO-group. Examples of cases in which R<sub>3</sub> and T are joined together include the -CH<sub>2</sub>C- group and the -COO- group. Examples of cases in which a plurality of R<sub>2</sub> groups are joined together include the -(CH<sub>2</sub>)<sub>3</sub>- group, -(CH<sub>2</sub>)<sub>4</sub>-group, -OCO- group, -OCONH- group, -NHCONH- group, -(CH = CH)<sub>2</sub>- group, -OCH<sub>2</sub>O- group, -OCH<sub>2</sub>CH<sub>2</sub>O- group, and the -OC- (CH<sub>3</sub>)<sub>2</sub>O- group.

Examples of the preferred substituent groups for the compounds which can be represented by the general formula [A] are described below.

R<sub>1</sub> in general formula [A] is preferably a halogen atom, a -COR<sub>4</sub> group or an -SO<sub>2</sub>R<sub>4</sub> group, and cases in which R<sub>4</sub> is an amino group are especially desirable. Examples of the -COR<sub>4</sub> group include carbamoyl group, N-ethylcarbamoyl group, N-n-butylcarbamoyl group, N-cyclohexylcarbamoyl group, N-(2-ethylhexyl)-carbamoyl group, N-dodecylcarbamoyl group, N-hexadecylcarbamoyl group, N-(3-decyloxypropyl)-carbamoyl group, N-[3-(2,4-di-t-pentylphenoxy)propyl]carbamoyl group, N-[4-(2,4-di-t-pentylphenoxy)butyl]carbamoyl group, N-nethylcarbamoyl group, N-methyl-N-dodecylcarbamoyl group, N-nethylcarbamoyl group, N-methyl-N-phenylcarbamoyl group, N-(2-tetradecyloxyphenyl)carbamoyl group, N-phenylcarbamoyl group, N-(4 tetradecyloxyphenyl)carbamoyl group, N-(2-chloro-5-dodecyloxyphenyl)carbamoyl group, N-(2-chloro-fodecyloxyphenyl)carbamoyl group, N-(2-chloro-fodecyloxyphenyl)carbamoyl group, N-(3-dodecyloxyphenyl)carbamoyl group, N-N-diethylsulfamoyl group, N-N-diisopropylsulfamoyl group, N-(3-dodecyloxypropyl)sulfamoyl group, N-[3-(2,4-di-t-pentylphenoxy)propyl]sulfamoyl group, N-[4-(2,4-di-t-pentylphenoxy)propyl]sulfamoyl group, N-(2-butoxyphenyl)sulfamoyl group, N-(2-tetradecyloxyphenyl)sulfamoyl group, N-phenylsulfamoyl group, N-(2-butoxyphenyl)sulfamoyl group, N-(2-tetradecyloxyphenyl)sulfamoyl group, R<sub>1</sub> is most desirably a -COR<sub>4</sub> group (R<sub>4</sub> being an amino group).

(R<sub>2</sub>) £ in general formula [A] is preferably such that £ is zero, followed by the case in which £ is equal to 1. When £ = 1; the R<sub>2</sub> group is preferably a halogen atom, aliphatic group, aromatic oxy group, carbonamido group, sulfonamido group, or cyan group. Of these groups the most desirable are the fluorine atom, chlorine atom, trifluoromethyl group, methoxy group and the cyano group. The R<sub>2</sub> group is preferably substituted in the 2-position or the 4-position with respect to the R<sub>3</sub>NH- group.

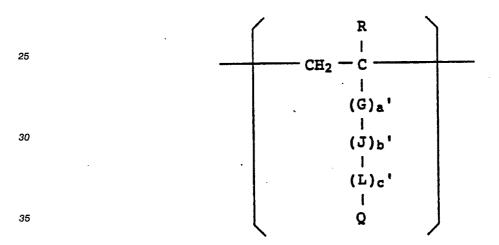
In  $R_3$  in general formula [A],  $R_6$  is preferably an aliphatic group, aromatic group,  $-OR_7$  group or an  $-SR_7$  group, and U is preferably -CO- or  $-SO_2$ -. Examples of aliphatic groups include methyl group, trifluoromethyl group, trichloromethyl group, ethyl group, heptafluoroethyl group, t-butyl group, 1-ethylpentyl group, cyclohexyl group, benzyl group, undecenyl group, tridecenyl group, and 1-(2,4-di-t-pentylphenoxy)-propyl group. Examples of aromatic groups include phenyl group, 1-naphthyl group, 2-naphtyl group, 2-chlorophenyl group, 4-methoxyphenyl group, 4-nitrophenyl group, and pentafluorophenyl group. Examples of  $-OR_7$  groups include methoxy group, isopropoxy group, n-butoxy group, iso-butoxy group, t-butoxy group, n-pentyloxy group, n-hexyloxy group, n-octyloxy group, 2-ethylhexyl group, n-decyloxy group, n-dodecyloxy group, and p-methylphenoxy group, benzyloxy group, trichloroethoxy group, trifluoroethoxy group, phenoxy group, and p-methylphenoxy group, benzylthio group, n-dodecylthio group, phenylthio group, n-butylthio group, benzylthio group, n-dodecylthio group, phenylthio group, p-toctylphenylthio group, p-dodecylphenylthio group, and a p-octyloxyphenylthio group. More desirably,  $R_3$  is an aliphatic oxycarbonyl group ( $R_6$  is  $R_7O$ - and U is  $-SO_2$ ) and, most desirably,  $R_3$  is an aliphatic oxycarbonyl group.

T in general formula [A] is preferably a hydrogen atom, halogen atom, aliphatic oxy group, aromatic oxy group, aliphatic thio group or a heterocyclic thio group. Examples of the aliphatic oxy groups include methoxy group, ethoxy group, 2-hydroxyethoxy group, 2-chloroethoxy group, carboxymethoxy group, 1carboxyethoxy group, methoxyethoxy group, 2-(2-hydroxyethoxy)ethoxy group, 2-methylsulfonylethoxy group, 2-methylsulfonyloxyethoxy group, 2-methylsulfonylamidoethyl group, 2-carboxyethoxy group, 3carboxypropoxy group, 2-(carboxymethylthio)ethoxy group, 2-(1-carboxytridecylthio)ethoxy group, 1-carboxvtridecyl group, N-(2-methoxyethyl)carbamoylmethoxy group, 1-imidazolylmethoxy group, and a 5phenoxycarbonylbenzotriazol-1-ylmethoxy group. Examples of aromatic oxy groups include 4-nitrophenoxy group, 4-acetamidophenoxy group, 2-acetamidophenoxy group, 4-methylsulfonylphenoxy group, and a 4-(3carboxypropanamido)phenoxy group. Examples of the aliphatic thio group include methylthio group, 2hydroxyethylthio group, carboxymethylthio group, 2-carboxyethylthio group, 1-carboxyethylthio group, 3carboxypropylthio group, 2-dimethylaminoethylthio group, benzylthio group, n-dodecylthio group, and a 1carboxytridecylthio group. Examples of heterocyclic thio groups include 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-phenyl1,3,4-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-(ethoxycarbonylmethylthio)-1,3,4-thiadiazol-2-ylthio group, 1,2,4-triazol-3-ylthio group, 4-pyridylthio group, and a 2-pyrimidylthio group. More desirably, T is a hydrogen atom, chlorine atom, aliphatic oxy group or an aliphatic thio group, and most desirably T is a hydrogen atom or an aliphatic oxy group.

Couplers which can be represented by the general formula [A] may take the form of dimers or larger units which are bonded together via divalent groups or groups of higher valency in the substituent groups  $R_1$ ,  $R_2$ ,  $R_3$  or T. In such cases the number of carbon atoms may be outside the specified range for each of the aforementioned types of substituent groups.

Typical examples of cases in which the couplers represented by the general formula [A] are in an oligomeric form include homopolymers or copolymers of addition polymerizable ethylenic unsaturated compounds which have cyan dye forming coupler residual groups (cyan color forming monomers). In this case the oligomer has repeating units of general formula [B], and, one or more types of the cyan color forming repeating units represented by the general formula [B] can be included in the oligomer, or the oligomer may take the form of a copolymer which contains one or more non-color forming ethylenic monomers as a copolymerized component.

#### General Formula [B]



In this formula R represents a hydrogen atom, an alkyl group which has from 1 to 4 carbon atoms or a chlorine atom. G represents a -CONH- group, a -COO-group or a substituted or unsubstituted phenylene group. J represents a substituted or unsubstituted alkylene group, phenylene group or aralkylene group. L represents a -CONH- group, -NHCONH- group, -NHCOO-group, -OCONH- group, -NHCOO-group, -OCONH- group, -NHCOO-group, -OCONH- group, -NHCOO-group, -NHSO2- group or an -SO2NH-group. Moreover, a, b and c each represent 0 or 1. Q represents a cyan coupler residual group in which a hydrogen atom other than that of the hydroxyl group in the 1-position has been removed from a compound which can be represented by 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 preferred as oligomers.

Non-color forming ethylenic monomers which do not couple with the oxidation products of primary aromatic amine developing agents include acrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -alkylacrylic acids (for example methacrylic acid), esters and amides derived from these acrylic acids (for example acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, 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  $\beta$ -hydroxyethylmethacrylate), vinyl esters (for example vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (for example styrene and derivatives thereof, such as vinyltoluene, divinyl benzene, potassium styrenesulfinate,

vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers, (for example vinyl ether), maleic acid esters, N-vinyl-2-pyrrolidone, N-vinylpyridine and 2-and 4-vinylpyridine.

The acrylic acid esters, methacrylic acid esters and maleic acid esters are especially desirable. Two or more types of the non-color forming ethylenic monomers can be used together. For example, it is possible to use methyl acrylate and butyl acrylate, butyl acrylate and styrene, butyl methacrylate and methacrylic acid, methyl acrylate and diacetoneacrylamide, N-(1,1-dimethyl-2-sulfonatoethyl)acrylamide and acrylic acid, or potassium styrenesulfinate and N-vinylpyrrolidone.

The ethylenic unsaturated monomer for copolymerization with a vinyl based monomer corresponding to the aforementioned general formula [B] is selected so as to improve the physical and/or chemical properties of the copolymer which is formed, as is well known in the polymeric coupler field. For example, these properties include solubility, compatibility with binding agents such as gelatin used in photographic colloid compositions, flexibility and heat resistance.

The selection of a lipophilic non-color forming ethylenic monomer (for example an acrylic acid ester, methacrylic acid ester, maleic acid ester, vinyl benzene) as the principal copolymer component is preferred for obtaining lipophilic polymeric couplers which are soluble in organic solvents.

The lipophilic polymeric couplers obtained by the polymerization of a vinyl monomer provide a coupler unit which can be represented by the aforementioned general formula [B]. [B] can be made by emulsification and dispersion in the form of a latex in aqueous gelatin solution, or by direct emulsion polymerization.

Methods for the emulsification and dispersion of lipophilic polymeric couplers in the form of a latex in aqueous gelatin solution are disclosed in U.S. Patent 3,451,820. Methods for emulsion polymerization are disclosed in U.S. Patents 4,080,211 and 3,370,952.

The use of hydrophilic non-color forming ethylenic monomers such as N-(1,1-diethyl-2-sulfonatoethyl)-acrylamide, 3-sulfonatopropyl acrylate, sodium styrenesulfonate, potassium 2-styrenesulfinate, acrylamide, methacrylamide, acrylic acid, methacrylic acid, N-vinylpyrrolidone, N-vinyl pyridine for the copolymer component is preferred for obtaining hydrophilic polymeric couplers which can be dissolved in neutral or alkaline water.

Hydrophilic polymeric couplers can be added to coating liquids as aqueous solutions, and they can also be added as solutions in solvent mixtures obtained by mixing water with a lower alcohol, tetrahydrofuran, acetone, ethyl acetate, cyclohexane, ethyl lactate, dimethylformamide, or dimethylacetamide. Moreover, they can be added after being dissolved in aqueous alkaline solutions and alkali containing organic solvents. A small quantity of surfactant can also be added.

Actual examples of couplers represented by the general formula [A] which can be used in the invention are indicated below, but the invention is not limited to these examples.

OH CONH (CH<sub>2</sub>)<sub>3</sub>O 
$$-(t)$$
 C<sub>5</sub>H<sub>11</sub>

CF<sub>3</sub>CONH

(A-1)

50

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5

$$CH_3CNH$$
 $CH_3CNH$ 
 $CONH(CH_2)_3O$ 
 $(t)C_5H_{11}$ 
 $(A-2)$ 
 $(t)C_5H_{11}$ 
 $(t)C_5H_{11}$ 
 $(t)C_5H_{11}$ 
 $(t)C_5H_{11}$ 

ОH NHSOzCH: CizHzs C L

$$OH$$

$$NHCONH$$

$$C \ell$$

$$C_{14}H_{33}SO_{2}NH$$

$$(A-5)$$

F F CONH (CH<sub>2</sub>) 
$$_{2}0$$
  $-(t)$   $C \cdot H_{1}$ 

OHCONH

OHCONH

(A-1.0)

(A-11)

(iso) C<sub>4</sub>H<sub>4</sub>O C O N H (A-12)

$$\begin{array}{c}
O H \\
C O N
\end{array} \begin{array}{c}
C H_3 \\
C_{10}H_{37}-n
\end{array}$$

$$(A-14)$$

$$\begin{array}{c}
0 \text{ H} \\
\text{S O 2}
\end{array}$$

$$\begin{array}{c}
0 \text{ H} \\
\text{S O 2}
\end{array}$$

$$\begin{array}{c}
0 \text{ H} \\
\text{S O 2}
\end{array}$$

 $n - C_{12}H_{25}UCUNH$  (A-16)

OH CONH (CH<sub>2</sub>)<sub>3</sub>OC<sub>12</sub>H<sub>25</sub>

(iso) C<sub>4</sub>H<sub>7</sub>O C O N H (A-18)

OH CONH (CH<sub>2</sub>)<sub>3</sub>OC<sub>12</sub>H<sub>25</sub>

. 45

(A-21)

CH<sub>3</sub>SO<sub>2</sub>NH O (CH<sub>2</sub>)<sub>2</sub>SCHCO<sub>2</sub>H

(A-2.5)

C2H3OCONH SCH2CH2COOH

(A - 30)

 $(A-3\ 1)$ 

(A-32)

(A-33)

OH CONH (CH2) 3OC12H25-n

C<sub>2</sub>H<sub>5</sub>
C<sub>4</sub>H<sub>4</sub>CHOCONH
(A-34)

(A-35)

5

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OH CONH (CH<sub>2</sub>)<sub>3</sub>OC<sub>12</sub>H<sub>25</sub>-n

20
CH2SO2NH S-N-N
CH2CH2COOH

(A-36)

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(A-37)

OCH 3

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OH CONH (CH<sub>2</sub>)<sub>3</sub>O-C<sub>5</sub>H<sub>11</sub>(t) C<sub>5</sub>H<sub>11</sub>(t) i-C<sub>4</sub>H<sub>9</sub>OCONH OCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub>

(A-42)

. (A-43)

OH CONH (CH<sub>2</sub>)<sub>3</sub>O - C<sub>5</sub>H<sub>11</sub>(t)

C<sub>5</sub>H<sub>11</sub>(t)

CH2SO2NH OCH2N N

(A-50)

5

$$(A-52)$$

50 ·

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$$CH_{3}SO_{2}NH$$

$$NHSO_{2}$$

$$(A-55)$$

·

CONH (CH<sub>2</sub>):0 C:H<sub>11</sub>(t)
$$C:H_{11}(t)$$

$$C:H_{11}(t)$$

$$(A-59)$$

40 .

(A-64)

(A-65)

$$(CH_2CH_{-})_{x} \qquad (CH_2CH_{-})_{y}$$

$$CONH(CH_2)_{2}SO_{2}NH \qquad COOC_{4}H_{y}$$

$$OH \qquad \qquad X: y = 80: 20$$

$$(weight ratio)$$

$$(A-72)$$

$$(C H_2 C H_3) \times (C H_2 C H_3)$$

$$x : y = 60 : 40$$

$$(weight ratio)$$

$$O H C H_3$$

$$(\Delta - 7)$$

(A - 74)

x : y = 50 : 50

(weight ratio)

(A - 75)

General Formula [I]

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In this formula, R<sub>31</sub> represents an alkyl group, aryl group or a heterocyclic group, and R<sub>32</sub> represents a hydrogen atom or a substituent group. X represents a hydrogen atom or a coupling elimination group.

General Formula [II]

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In this formula, R<sub>31</sub> represents the same groups as mentioned above. R<sub>32</sub> represents an alkyl group, alkylthio group, arylthio group, heterocyclic thio group or an aryl group. X represents a hydrogen atom or a coupling elimination group.

More precisely, R<sub>31</sub> represents an alkyl group such as a methyl group, ethyl group, isopropyl group, t-butyl group, trifluoromethyl group, phenylmethyl group, methoxyethyl group, 2-phenoxyethyl group, 2-methylsulfonylethyl group, 2-hydroxyethyl group, 3,3,3-trifluoropropyl group, 2-fluoroethyl group, 2-chloroethyl group, 2-bromoethyl group, 2-cyanoethyl group, 3-oxobutyl group or an aryl group such as a phenyl group, 4-methylphenyl group, 4-t-butylphenyl group, 4-acylaminophenyl group, 4-halogenophenyl group, 4-alkoxyphenyl group, or a heterocyclic group such as a 2-furyl group, 2-thienyl group, 2-pyrimidyl group, 2-benzothiazolyl group, 2-pyridyl group, 3-pyridyl group, and a 4-pyridyl group. Of these, preferred examples for R<sub>31</sub> include methyl group, ethyl group, isopropyl group, t-butyl group, methoxyethyl group and 2-phenoxyethyl group.

R<sub>32</sub> is a hydrogen atom, a halogen atom (for example a chlorine atom, bromine atom), an alkyl group [for example a substituted alkyl group such as a sulfonamido substituted alkyl group (e.g., sulfonamidomethyl group, 1-sulfonamidoethyl group, 2-sulfonamidoethyl group, 1-methyl-2-sulfonamidoethyl group, 3-sulfonamidopropyl group), acylamino substituted alkyl group (e.g., acylaminomethyl group, 1acylaminoethyl group, 2-acylaminoethyl group, 1-methyl-2-acylaminoethyl group, 3-acylaminopropyl group), sulfonamido substituted phenylalkyl group (e.g., p-sulfonamidophenylmethyl fonamidophenylethyl group, 1-(p-sulfonamidophenyl)ethyl group, p-sulfonamidophenylpropyl group), acylamino substituted phenylalkyl group (e.g., p-acylaminophenylmethyl group, p-acylaminophenylethyl group, 1-(p-acylminophenyl)ethyl group, p-acylaminophenylpropyl group), alkylsulfonyl substituted alkyl group (e.g., 2-dodecylsulfonylethyl group, 1-methyl-2-pentadecylsulfonylethyl group, octadecylsulfonylpropyl group), phenylsulfonyl substituted alkyl group (e.g., 3-(2-butyl-5-t-octylphenylsulfonyl)propyl group, 2-(4dodecyloxyphenylsulfonyl)ethyl group), or an unsubstituted alkyl group such as a methyl group, ethyl group, hexyl group, dodecyl group], an aryl group (for example a substituted aryl group such as a sulfonamidophenyl group, acylaminophenyl group, alkoxyphenyl group, aryloxyphenyl group, substituted alkylphenyl group, sulfonamidonaphthyl group, acylaminonapthyl group or an unsubstituted aryl group such as a phenyl group, naphthyl group), a heterocyclic group (for example a 2-furyl group, 2-thienyl group, 2pyrimidinyl group, 2-benzothiazolyl group), a cyano group, an alkoxy group (for example a methoxy group, ethoxy group, 2-methoxyethoxy group, 2-dodecylethoxy group, 2-methanesulfonylethoxy group), an aryloxy group (for example a phenoxy group, 2-methylphenoxy group, 4-t-butylphenoxy group), an acylamino group (for example an acetamido group, benzamido group, tetradecanamido group, α-(2,4-di-t-amylphenoxy)butylamido group,  $\gamma$ -(3-t-butyl-4-hydroxyphenoxy)butylamido group,  $\alpha$ -[4-(4-hydroxyphenylsulfonylphenoxy)decanamido group), an anilino group (for example a phenylamino group, 2-chloroanilino group, 2-chloro-5tetradecanamidoanilino group, 2-chloro-5-dodecyloxycarbonylanilino group, N-acetylanilino group, 2-chloro- $5-[\alpha-(3-t-butyl-4-hydroxyphenoxy)dodecanamido]anilino group), a ureido group (for example a phenylureido$ group, methylureido group, N,N-dibutylureido group), a sulfamoylamino group (for example an N,Ndipropylsulfamoylamino group, N-methyl-N-decylsulfamoylamino group), an alkylthio group (for example a methylthio group, octylthio group, tetradecylthio group, 2-phenoxyethylthio group, 3-phenoxypropylthio group, 3-(4-t-butylphenoxy)propylthio group), an arylthio group (for example a phenylthio group, 2-butoxy-5-3-pentadecylphenylthio group, 2-carboxyphenylthio t-octvlphenvlthio group. tetradecanamidophenylthio group), an alkoxycarbonylamino group (for example a methoxycarbonylamino group, tetradecyloxycarbonylamino group), a sulfonamido group (for example a methanesulfonamido group, hexadecanesulfonamido group, benzenesulfonamido group, p-toluenesulfonamido group, octadecanesulfonamido group, 2-methyloxy-5-butylbenzenesulfonamido group), a carbamoyl group (for example an Nethylcarbamovi group, N.N-dibutylcarbamovi group, N-(2-dodecyloxyethyl)carbamovi group, N-methyl-Ndodecylcarbamovi group, N-[3-(2,4-di-t-amylphenoxy)propyl]carbamovi group), a sulfamovi group (for example an N-ethylsulfamoyl group, N,N-dipropylsulfamoyl group, N-(2-dodecyloxyethyl)sulfamoyl group, Nethyl-N-dodecylsulfamoyl group, N,N-diethylsulfamoyl group), a sulfonyl group (for example a methanesulfonyl group, octanesulfonyl group, benzenesulfonyl group, toluenesulfonyl group), or an alkoxycarbonyl group (for example a methoxycarbonyl group, butyloxycarbonyl group, dodecyloxycarbonyl group, octadecyloxycarbonyl group). Of these groups the alkyl groups, aryl groups, alkylthio groups and arylthio groups are preferred, and the alkyl groups and aryl groups are the more desirable.

R<sub>32</sub> represents a substituted alkyl group, such as a sulfonamido substituted alkyl group (for example a sulfonamidomethyl group, 1-sulfonamidoethyl group, 2-sulfonamidoethyl group, 1-methyl-2-sulfonamidoethyl group, 3-sulfonamidopropyl group), an acylamino substituted alkyl group (for example an acylaminomethyl group, 1-acylaminoethyl group, 2-acylaminoethyl group, 1-methyl-2-acylaminoethyl group, 3-acylaminopropyl group), a sulfonamido substituted phenylalkyl group (for example a p-sulfonamidophenylmethyl group, p-sulfonamidophenylethyl group, 1-(p-sulfonamidophenyl)ethyl group, p-sulfonamidophenylpropyl group), an acylamino substituted phenylalkyl group (for example p-acylaminophenylmethyl group, pacylaminophenylethyl group, 1-(p-acylaminophenyl)ethyl group, p-acylaminophenylpropyl group), an alkylsulfonyl substituted alkyl group (for example a 2-dodecylsulfonylethyl group, 1-methyl-2pentadecylsulfonylethyl group, octadecylsulfonylpropyl group), a phenylsulfonyl substituted alkyl group (e.g., 3-(2-butyl-5-t-octylphenylsulfonyl)propyl group, 2-(4-dodecyloxyphenylsulfonyl)ethyl group), or an unsubstituted alkyl group such as a methyl group, ethyl group, hexyl group, dodecyl group, a substituted aryl group such as a sulfonamidophenyl group, acylaminophenyl group, alkoxyphenyl group, aryloxyphenyl group, substituted alkylphenyl group, sulfonamidonaphthyl group, acylaminonaphthyl group, or an unsubstituted aryl group such as a phenyl group, naphthyl group, or an alkylthio group (for examples a methylthio group, octylthio group, tetradecylthio group, 2-phenoxyethylthio group, 3-phenoxypropylthio group, 3-(4-tbutylphenoxy)propylthio group), an arylthio group (for example a phenylthio group, 2-butoxy-5-t-octylphenylthio group, 3-pentadecylphenylthio group, 2-carboxyphenylthio group, 4-tetradecanamidophenylthio group). or a heterocyclic thio group (for example a 2-benzothiazolylthio group, 2,4-diphenoxy-1,3,5-triazol-6-thio group, 2-pyridylthio group).

Of these groups the substituted alkyl groups and substituted aryl groups are preferred, and the substituted alkyl groups are the more desirable.

X represents a hydrogen atom, halogen atom (for example chlorine atom, bromine atom, or iodine atom), carboxyl group or a group which is linked via an oxygen atom (for example acetoxy group, propanoyloxy group, benzoyloxy group, 2,4-dichlorobenzoyloxy group, ethoxyoxaloyloxy group, pyruvinyloxy group, cinnamoyloxy group, phenoxy group, 4-cyanophenoxy group, 4-methanesulfonamidophenoxy group, 4-methanesulfonylphenoxy group,  $\alpha$ -naphthoxy group, 3-pentadecylphenoxy group, benzyloxycarbonyloxy group, ethoxy group, 2-cyanoethoxy group, benzyloxy group, 2-phenethyloxy group, 2-phenoxyethoxy group, 5-phenyltetrazolyloxy group, 2-benzothiazolyloxy group), a group which is linked via a nitrogen atom (for example benzenesulfonamido group, N-ethyltoluenesulfonamido group, heptafluorobutanamido group), 2,3,4,5,6-pentafluorobenzamido group, octanesulfonamido group), pcyanophenylureido group, N,N-diethylsulfamoylamino group, 1-piperidyl group, 5,5-dimethyl-2,4-dioxo-3oxazolidinyl group, 1-benzylethoxy-3-hydantoinyl group, 2N-1,1-dioxo-3(2H)-oxo-1,2-benzoisothiazolyl group, 2-oxo-1,2-dihydroxy-1-pyridinyl group, imidazolyl group, pyrazolyl group, 3,5-diethyl-1,2,4-triazol-1-yl group, 5- or 6-bromobenzotriazol-1-yl group, 5-methyl-1,2,3,4-tetrazol-1-yl group, benzimidazolyl group), or a group which is linked via a sulfur atom (for example phenylthio group, 2-carboxyphenylthio group, 2-methoxy-5-toctylphenylthio group, 4-methanesulfonylphenylthio group, 4-octanesulfonamidophenylthio group, benzylthio group, 2-cyanoethylthio group, 1-ethoxycarbonyltridecylthio group, 5-phenyl-2,3,4,5-tetrazolylthio group, 2benzothiazolyl group). Of these, preferred examples for X include chlorine atom, an aryloxy group (e.g., phenoxy group, 4-cyanophenoxy group, 4-methanesulfonamidophenoxy group, 4-methanesulfonylphenoxy group), and an arylthio group (e.g., phenylthio group, 2-methoxy-5-t-octylphenylthio group, 2-butoxy-5 toctylphenylthio group).

In cases where R<sub>31</sub>, R<sub>32</sub>, R<sub>32</sub> or X is a divalent linking group and dimers are formed, R<sub>31</sub>, R<sub>32</sub> or R<sub>32</sub> represents a substituted or unsubstituted alkylene group (for example methylene group, ethylene group, 1,10- decylene group, -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>- group), a substituted or unsubstituted phenylene group (for example 1,4-phenylene group, 1,3-phenylene group,

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and X represents a divalent group corresponding appropriately with the above mentioned univalent groups.

The linking groups represented by any of R<sub>31</sub>, R<sub>32</sub> or R<sub>32</sub> when the compounds represented by the general formulae [I] and [II] are included in a vinyl monomer are groups established by combining groups selected from among the alkylene groups (substituted or unsubstituted alkylene groups, for example methylene group, ethylene group, 1,10-decylene group, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>- group), phenylene groups (substituted and unsubstituted phenylene groups, for example 1,4-phenylene group, 1,3-phenylene group,

$$CH_3$$
  $C\ell$   $group,$   $CH_3$   $C\ell$ 

-NHCO-group, -CONH- group, -O- group, -OCO- group and the aralkylene groups (for example

group,

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The preferred linking groups are indicated below:

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Moreover, the vinyl group may have substituent groups other than that represented by the general formula [I] and the preferred substituent groups are hydrogen atoms, chlorine atoms and lower alkyl groups which have from 1 to 4 carbon atoms (for example methyl group, ethyl group).

Monomers which contain a part which can be represented by general formula [II] can be formed into copolymers with non-color forming ethylenic monomers which do not couple with the oxidation products of primary aromatic amine developing agents.

Examples of non-color forming ethylenic monomers which do not couple with the oxidation products of primary aromatic amine developing agents include acrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -alkylacrylic acids (for example methacrylic acid), esters and amides derived from these acrylic acids (for example acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and

β-hydroxyethylmethacrylate), methylenebisacrylamide, vinyl esters (for example vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (for example styrene and derivatives thereof, vinyltoluene, divinyl benzene, vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (for example vinyl ethyl ether), maleic acid, maleic anhydride, maleic acid esters, N-vinyl-2-pyrrolidone, N-vinylpyridine and 2-and 4-vinylpyridine. Two or more types of non-color forming ethylenic monomer used here can be used together. For example, it is possible to use n-butyl acrylate and methyl methacrylate, styrene and methacrylic acid, methacrylic acid and acrylamide, or methyl acrylate and diacetoneacrylamide.

The non-color forming ethylenic unsaturated monomer for copolymerization with a solid water insoluble monomeric coupler is selected so as to improve the physical and/or chemical properties of the copolymer which is formed, as is well known in he polymeric field. For example, these properties include solubility, compatibility with binding agents such as gelatin used in photographic colloid compositions, flexibility and heat resistance.

The polymeric couplers used in the present invention may be water soluble or water insoluble. The use of the polymeric coupler latexes from among these materials is preferred.

Actual examples of typical magenta couplers in this invention are indicated below, but the invention is not limited by these examples.

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(CII3)2CHQ (2) 

ξ55 (<del>ξ</del>)

(28)

5 
$$CH_3O$$
 Br  
NHCO  $NHSO_2$   $C_8H_{17}(t)$   $C_8H_{17}(t)$   
15  $CH_3O$   $C\ell$   $C\ell$   $OCH_3$   
20  $CH_3O$   $C\ell$   $OCH_3$   
NHCO  $NHSO_2$   $C_8H_{17}(t)$   
 $OC_8H_{17}(t)$   
 $OC_8H_{17}(t)$   
 $OC_8H_{17}(t)$   
 $OC_8H_{17}(t)$   
 $OC_8H_{17}(t)$ 

$$\begin{array}{c} \text{OC}_4\text{H}_9\\ \text{OC}_4\text{H}_9\\ \text{C}_8\text{H}_{17}(t)\\ \text{N}\\ \text{N}=\\ \text{S}-(\text{CH}_2)_2\text{NHSO}_2 \end{array}$$

$$(3/) OC_4H_9$$

$$CH_3 CHO C_8H_{17}(t)$$

$$NH OC_4H_9$$

$$N-NHSO_2 - NHSO_2$$

$$C_8H_{17}(t)$$

(32)

CH<sub>3</sub>O 5 10

(33) 15

CH<sub>3</sub>O 20 25

(34)

30

CH<sub>3</sub>Q 35 C<sub>5</sub>H<sub>11</sub>(t) OCHCHN (CH<sub>2</sub>)<sub>2</sub> I C<sub>4</sub>H<sub>9</sub> 40

(35) 45

CH<sub>3</sub>Q OC8H17 50 55

(38) (CH<sub>3</sub>)<sub>2</sub>CHO 5 OC 8H17 10 OC 8H17 SO2NH 15 Ć<sub>8</sub>H<sub>17</sub>(t) (37) 20 Cl OC<sub>4</sub>H<sub>9</sub> 25 SO<sub>2</sub>HN (CH<sub>2</sub>)<sub>2</sub>  $\acute{C}_8H_{17}(t)$ 30 (38)35  $(C_2H_5)_2NO_2S$ Br OC8H17 40 (39) Ć<sub>8</sub>H<sub>17</sub>(t) 45  $C_2H_5O$ 50

H<sub>25</sub>C<sub>12</sub>O

5 
$$C_8H_{17}O$$
  $S$   $C_8H_{17}(t)$   $C_8H_{17}(t)$ 

(44)

55

5 
$$C_2H_5O$$
  $C\ell$ 

N
NH
OC 8H17

S-(CH2)2-SO2

C 8H17(t)

(46)

$$\begin{array}{c}
CH_{3} \\
CHC \\
CONH-(CH_{2})_{2} \\
N \\
N \\
X
\end{array}$$

$$\begin{array}{c}
CH_{2}CH \\
CO_{2}C_{4}H_{9-n} \\
CO_{2}C_{4}H_{9-n} \\
COCH_{3}
\end{array}$$

x : y = 50 : 50(weight ratio)

x : y = 45 : 55(weight ratio)

x : y = 45 : 55(weight ratio)

55

5.0

$$(49)$$

$$CH_{3}$$

$$CH_{2}C$$

$$CONH(CH_{2})_{3}$$

$$HN$$

$$N$$

$$(t)C_{8}H_{9}$$

$$OC_{4}H_{9}$$

$$CH_{2}CH$$

$$CO_{2}C_{2}H_{3}$$

$$X$$

x : y = 50 : 50

(weight ratio)

x : y = 45 : 55

40

45

50

(weight ratio)

5
$$\begin{array}{c} CH_{3} \\ CHC \\ \hline CONH (CH_{2})_{2} \\ \hline N \\ NH \\ \hline \end{array}$$

$$\begin{array}{c} CH_{2}CH \\ \hline CO_{2}C_{4}H_{9-n} \\ \hline \end{array}$$

$$(CH_{3})_{2}CHO \qquad CU$$

$$x : y = 50 : 50$$
(weight ratio)

C<sub>4</sub>H<sub>9</sub>

25

(52)  $CF_3CH_2O$   $C_8H_{17}(t)$   $C_5H_{11}(t)$ 35

NHCOCHO  $C_5H_{11}(t)$ 

·

55

 $C_8H_{17}(t)$ 

5 
$$CH_3CH_2O$$
  $C_8H_{17}(t)$ 

10  $C_8H_{17}(t)$ 

15  $C_8H_{17}(t)$ 

20 (57)

(58)

OC<sub>4</sub>H<sub>9</sub>

$$C_{8}H_{17}(t)$$

$$NHSO_{2}$$

$$C_{8}H_{17}(t)$$

(59)

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The cyan couplers which can be represented by the general formula [A] can be prepared easily using the method disclosed in European Patent No. 161,626A. Furthermore, the magenta couplers represented by the general formulae [I] and [II] can be prepared easily using the methods disclosed in European Patent No. 226,849A and U.S. Patent 4,540,654.

The cyan couplers represented by the general formula [A] of the present invention are added to a red sensitive emulsion layer and/or adjacent layers, and the total amount added is from 0.01 to 1.5 grams per square meter, preferably from 1.0 to 1.2 grams per square meter, and more desirably from 0.2 to 1.0 gram per square meter. The red sensitive emulsion layer preferably consists of two or more layers which have different speeds. And, of the cyan couplers, the use of four equivalent cyan couplers in which T is a hydrogen atom is preferred in the low speed layer and the use of two equivalent couplers in which T is a group other than a hydrogen atom is preferred in the high speed layer. The method used to add the cyan couplers of the present invention to the photosensitive material is based on the method used for the other couplers described hereinafter. However, the amount of high boiling point organic solvent which is used as a dispersing medium with respect to the couplers is preferably from 0 to 1.0, more desirably from 0 to 0.5,

and most desirably from 0 to 0.3, in terms of the ratio by weight.

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The magenta couplers represented by general formula [I] or [II] of the present invention are added to the green sensitive emulsion layer and/or adjacent layers, and the total amount added is from 0.01 to 1.0 gram per square meter, preferably from 0.05 to 0.8 grams per square meter, and more desirably from 0.1 to 0.5 gram per square meter. The method used to add the magenta couplers of this invention to the photosensitive material is based on the method used for the other couplers described hereinafter. However, the amount of high boiling point organic solvent which is used as a dispersing medium with respect to the couplers is from 0 to 4.0, preferably from 0.1 to 2.0, and more desirably from 0.3 to 1.0, in terms of the ratio by weight.

In the photographic material of this invention, at least one silver halide emulsion layer (e.g., blue-sensitive layer, green-sensitive layer, red-sensitive layer) is coated on a support. There are no restrictions with respect to the order and the number of the silver halide emulsion layer and the non light-sensitive layer. As a typical example, there is a silver halide photographic material comprising a light- sensitive layer consisting of a plural silver halide emulsion layer which has a substantially same color sensitivity but has a different light sensitivity, wherein a unit light-sensitive layer has a sensitivity with respect to any one of blue light, green light, or red light. Furthermore, in a multilayer silver halide color photographic material, the order of a unit light-sensitive layer is generally a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer from a support. According to a purpose, this coating order may be in reverse order, or a layer having a different light sensitivity may be inserted into a layer having the same color sensitivity.

Various types of a non light-sensitive layer such as an intermediate layer may be coated between the silver halide light-sensitive layers, and it may be used as an uppermost layer, a lowermost layer, etc.

The intermediate layer may contain the coupler described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-20038, DIR coupler and so on or a color-mixing preventing agent as in a conventional photographic material.

The plural silver halide layers which constitutes unit light-sensitive layer is preferably comprised of two layers having a high sensitive emulsion layer and a low sensitive emulsion layer as disclosed in West German Patent 1,121,470 and British Patent 923,045 Usually, the preferred order is such that the light sensitivity of the silver halide layers decreases orderly toward a support, and a non light-sensitive may be coated between each silver halide emulsion layers. Moreover, as disclosed in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, a low-sensitive layer may be coated on the farther side from a support and a high-sensitive emulsion layer may be coated in the nearer side from a support.

As an illustrative example, there are, from the farthest side from a support, a low-sensitive blue-sensitive layer (BL)/a high-sensitive green-sensitive layer (GH)/a low-sensitive green-sensitive layer (GL)/a high-sensitive red-sensitive layer (RH)/a low-sensitive layer (

As disclosed in JP-B-55-34932 (the term "JP-B" as used herein means an "examined Japanese patent publication"), the order of a blue-sensitive layer/GH/RH/GL/RL from the farthest side from a support may be used. Moreover, as disclosed in JP-A-56-25738 and JP-A-62-63936, the order of a blue-sensitive layer/GL/RL/GH/RH from the farthest side from a support may be used.

As disclosed in JP-B-49-15495, the arrangement having the constitution of three layers differing in light sensitivity in which a silver halide emulsion layer having the highest light sensitivity is used as an upper layer, a silver halide emulsion layer having a lower light sensitivity than that of the upper layer is used as a middle layer, and a silver halide emulsion layer having a lower light sensitivity than that of the middle layer is used as a lower layer and the light sensitivity of the silver halide emulsion layers decreases orderly toward a support may be used. Even when such a structure having three layers differing in light-sensitivity is used, the order of a middle-sensitive emulsion layer/a high-sensitive emulsion layer/a low-sensitive emulsion layer from the farthest side from a support may be used in a same color sensitivity layer as described in JP-A-59-202464.

As described above, various types of a layer structure and a layer order can be selected according to the purpose of a photographic materials.

The silver halide contained in the photographic emulsions of the photographic materials of the present invention, is preferably a silver iodobromide, silver iodochloride or silver iodochlorobromide which contains not more than about 30 mol% of silver iodide. The most desirable silver halides are silver iodobromides which contain from about 2 mol% to about 25 mol% of silver iodide.

The silver halide grains in the photographic emulsion may have a regular crystalline form, such as a cubic form, octahedral form or tetradecahedral form, an irregular crystalline form such as a spherical form or tabular from, a form in which there are crystal defects such as twinned crystal planes, or forms in which these various forms are combined.

The grain size of the silver halide may be fine with a grain diameter of less than about 0.2 microns or large with a projected area diameter up to about 10 microns. Further, the grains may take the form of a poly-disperse emulsion or a mono-disperse emulsion.

The silver halide photographic emulsion used in the present invention can be prepared utilizing known methods including those disclosed on pages 22 to 23 of Research Disclosure (RD) No. 17643 (February 1978), "I, Emulsion Preparation and Types", in RD No. 18716 (November 1979), page 648; in Chemie et Physique Photographique, by P. Glafkides, published by Paul Montel, 1967; in Photographic Emulsion Chemistry, by G.F. Duffin, published by Focal Press, 1966; and in Making and Coating Photographic Emulsions, by V.L. Zelikman et al., published by Focal Press, 1964.

The mono-disperse emulsions disclosed in U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748 are preferred.

Furthermore tabular grains which have an aspect ratio of at least about 5 can be used in the present invention. Tabular grains can be prepared easily utilizing known methods including those disclosed by Gutoff in Photographic Science and Engineering, Volume 14, pp. 248 - 257 (1970), in U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and in British Patent 2,112,157.

The crystal structure of the grains may be uniform, the interior and exterior parts may have a heterogeneous halogen composition or the grains may have a layered structure. Further, silver halides of different compositions may be joined with an epitaxial junction or they may be joined to compounds other than silver halides such as silver thiocyanate or lead oxide.

Mixtures of grains of various crystalline forms may also be used.

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The silver halide emulsions used are normally subjected to physical ripening, chemical ripening and spectral sensitization. Additives which can be used in these processes have been disclosed in Research Disclosure Nos. 17643 and 18716 and the locations of these items are summarized in the table below.

Known photographically useful additives which can be used in the present invention are also disclosed in the two Research Disclosures mentioned above and the locations of these disclosures are also shown in the table below.

Kind of Additives	RD 17643	RD 18716
Chemical sensitizers     Speed increasing     agents	Page 23	Page 648, right column as above
Spectral sensitizers     and supersensitizers     4. Whiteners	Pages 23 to 24 Page 24	Page 648, right column to page 649, right column
5. Anti-foggants and stabilizers	Pages 24 to 25	Page 649, right column
6. Light absobers, filter dyes and UV absorbers     7. Anti-staining agents	Pages 25 to 26 Page 25, right column	Page 649, right column to page 650, left column Page 650, left column to right column
8. Dye image stabilizers     9. Film hardening     agents	Page 25 Page 26	Page 651, left column
10. Binders 11. Plasticizers and lubricants	Page 26 Page 27	as above Page 650, right column
12. Coating promoters, surfactants	Pages 26 to 27	as above
13. Anti-static agents	Page 27	as above

Various color couplers can be used in this invention, and examples of these are disclosed in the patents discussed in Research Disclosure (RD) No. 17643, VII-C to G.

The use of the yellow color couplers of U.S. Patents 3,933,501, 4,022,620, 4,326,024 and 4,401,752, JP-B-58-10739, and in British Patents 1,425,020 and 1,476,760 is preferred.

The 5-pyrazolone based and pyrazoloazole based compounds are preferred as magenta couplers. The magenta couplers disclosed in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure

No. 24230 (June 1984), JP-A-60-43659, and in U.S. Patents 4,500,630 and 4,540,654 are most desirable.

Phenol based and naphthol based couplers are used as cyan couplers, and those disclosed 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, and in U.S. Patents 3,446,622, 4,333,999, 4,451,559 and 4,427,767 are preferred.

The colored couplers for correcting the unwanted absorptions of the colored dyes disclosed in Research Disclosure No. 17643, section VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and in British Patent 1,146,368 are preferred.

Couplers whose colored dyes have a suitable degree of diffusibility such as those disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and in West German Patent Application (OLS) No. 3,234,533 are preferred.

Typical examples of polymerized dye forming couplers have been disclosed in U.S. Patents 3,451,820, 4,080,211 and 4,367,282, and in British Patent 2,102,173.

Couplers that release residual groups and are useful photographically in coupling, are also desirable for use in the present invention. The use of the DIR couplers which release development inhibitors disclosed in the patents indicated in the aforementioned Research Disclosure No. 17643, section VII-F, in JP-A-57-151944, JP-A-57-254234 and JP-A-60-184248, and in U.S. Patent 4,248,962 is desirable.

The use of couplers, which release nucleating agents or development accelerators in the form of the image during development, disclosed in British Patents 2,097,140 and 2,131,188, and in JP-A-59-157638 and JP-A-59-170840 is desirable.

Other couplers which can be used in the photosensitive materials of the present invention include the competitive couplers disclosed in U.S. Patent 4,130,427, the multi-equivalent couplers disclosed in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, the DIR redox compound releasing couplers disclosed in JP-A-60-185950, the couplers which release a dye which restores coloration after elimination disclosed in European Patent 173,302A, the bleach accelerator releasing couplers disclosed in Research Disclosure No. 11449 and 24241, and in JP-A-61-201247, and the ligand releasing couplers disclosed in U.S. Patent 4.553.477.

The couplers which are used in the present invention can be introduced into the light sensitive materials by various known methods of dispersion.

Examples of high boiling point solvents which can be used in the oil in water dispersion methods have been disclosed in U.S. Patent 2,322,027.

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Examples of the latex dispersion method and of latexes for impregnation purposes have been disclosed in U.S. Patent 4,199,363 and in West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Suitable supports which can be used in the present invention have been disclosed on page 28 of the aforementioned Research Disclosure No. 17643, and in the section from the right hand column of page 647 to the left hand column of page 648 of Research Disclosure No. 18716.

In the photographic material of the present invention, it is preferrred that a total film thickness of the hydrophilic colloid layer is 28 µm or less in the side of the emulsion layers and a film sevelling speed (T<sub>1/2</sub>) is 30 sec. or less. The film thickness means a film thickness which is determined under moisture conditioning at 25 °C for 55% RH (2 days). The film swelling speed (T<sub>1/2</sub>) is determined according to a known method in the art, for example, using a swelling meter whose type is described in A. Green et al, Photoraphic Science and Engineering, vol. 19, No. 2, pages 124 to 129. The film swelling speed (T<sub>1/2</sub>) is defined as a time that the film thickness reaches a saturated film thickness which is 90% of the maximum swell thickness when treated with a color developer at 30 °C for 3 min. 15 sec.

The film swelling speed  $(T_{1/2})$  can be adjusted be adding a hardner to gelatin as a binder or changing conditions with time after coating. Furthermore, the swell (%) is preferably 150 to 400%. The swell (%) is calculated from the following equation using a maximum swell film thickness in the above condition:

The color development bath used, is preferably an aqueous alkaline solution which contains a primary aromatic amine based color developing agent as the principal component. Aminophenol based compounds are useful as color developing agents. The use of p-phenylenediamine based compounds is preferred. Typical examples of these compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methy

amino-N-ethyl-N- $\beta$ -methoxyethylaniline, and the sulfate, hydrochloride and p-toluenesulfonate salts of these compounds. Two or more of these compounds can be used conjointly, depending on the intended purpose.

The color development baths generally contain pH buffers such as the carbonates, borates or phosphates of alkali metals, and development inhibitors or anti-fogging agents such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds. They may also contain, as required, various preservatives, such as hydroxylamine, diethylhydroxylamine, sulfite, hydrazines, phenylsemicarbazides, triethanolamine, catechol sulfonic acids, triethylenediamine(1,4-diazabicyclo[2,2,2]octane), organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, poly-(ethylene glycol), quaternary ammonium salts and amines, color forming couplers, competitive couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity imparting agents, various chelating agents as typified by the aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, typical examples of which include ethylenediamine tetraacetic acid, nitrilotriacetic acid, diethylenetriamine pentaacetic acid, cylohexanediamine tetraacetic acid, hydroxyethylimino diacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N, reteramethylenephosphonic acid, ethylenediamine di(o-hydroxyphenylacetic acid), and salts of these compounds.

Color development is carried out after a normal black and white development in the case of reversal processing. The known black and white developing agents, for example the dihydroxybenzenes such as hydro quinone, the 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and the amino phenols such as N-methyl-p-aminophenol, can be used individually or in combinations in the black and white development bath.

The pH of the color and black and white developing baths is generally within the range of from 9 to 12. Furthermore, the replenishment rate of the development bath depends on the color photographic material which is being processed, but it is generally less than 3 liters per square meter of photosensitive material and it is possible, by reducing the bromide ion concentration in the replenisher, to use a replenishment rate of less than 500 ml per square meter of photosensitive material. The prevention of evaporation, and aerial oxidation, by minimizing the contact area with the air in the processing tank is desirable in cases where the replenishment rate is low. Furthermore, the replenishment rate can be reduced by suppressing the accumulation of bromide ion in the developer.

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The photographic emulsion layers are subjected to a normal bleaching process after color development. The bleaching process may be carried out at the same time as the fixing process (in a bleach-fix process) or it may be carried out as a separate process. Moreover, a bleach-fix process can be carried out after a bleach process in order to speed-up processing. Also, processing can be carried out in two connected bleach-fix baths, a fixing process can be carried out before carrying out a bleach-fix process, or a bleaching process can be carried out after a bleach-fix process, according to the intended purpose of the processing. Compounds of a multivalent metal such as iron(III), cobalt(III), chromium(VI), copper(II), peracids, quinones, nitro compounds can be used as bleaching agents. Typical bleaching agents include ferricyanides; dichromates; organic complex salts of iron(III) or cobalt(III). Examples of complex salts with aminopolycarboxylic acids include ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid, cyclohexanediamine tertraacetic acid, methylimino diacetic acid, 1,3-diaminopropane tetraacetic acid, glycol ether diamine tetraacetic acid or citric acid, tartaric acid, malic acid etc.; persulfates; bromates; permanganates and nitrobenzenes. Of these materials the use of the aminopolycarboxylic acid iron(III) complex salts, principally ethylenediamine tetraacetic acid iron(III) complex salts, and persulfates, is preferred from the points of view of both rapid processing and the prevention of environmental pollution. Moreover, the amino polycarboxylic acid iron(III) complex salts are especially useful in both bleach baths and bleach-fix baths. The pH of the bleach or bleach-fix baths in which aminopolycarboxylic acid iron(III) complex salts are being used is normally from 5.5 to 8, but processing can be carried out at lower pH values to speed-up processing.

Bleach accelerators can be used, as required, in the bleach baths, bleach-fix baths, or bleach or bleach-fix pre-baths. Actual examples of useful bleach accelerators have been disclosed in the following specifications: compounds having a mercapto group or a disulfide gorup are disclosed 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 and JP-A-53-28426, and in Research Disclosure No. 17129 (July 1978); the thiazolidine derivatives disclosed in JP-A-50-140129; the thiourea derivatives disclosed in JP-B-45-8506, JP-A-50-20832 and JP-A-53-32735, and U.S. Patent 3,706,561; the iodides disclosed in West German Patent 1,127,715 and in JP-A-58-16235; the polyoxyethylene compounds disclosed in West German Patents 966,410 and 2,748,430; the polyamine compounds disclosed in JP-B-55-8836; the other compounds disclosed 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; and bromide ions. Among these compounds, those which have a mercapto group or a disulfide group are preferred in view of their large acceleration effect, and the use of the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 is especially desirable. Moreover, the use of the compounds disclosed in U.S. Patent 4,552,834 is also desirable. These bleach accelerators may be added to the sensitive material. These bleach accelerators are especially effective when bleach-fixing color photosensitive materials for photographic purposes.

Thiosulfates, thiocyanates, thioether based compounds, thioureas and large quantities of iodides can be used as fixing agents, but thiosulfates are generally used for this purpose, and ammonium thiosulfate in particular can be used in the widest range of applications. Sulfites or bisulfites, or carbonyl-bisulfite addition compounds, are the preferred preservatives for bleach-fix baths.

The silver halide color photographic materials of this invention are generally subjected to a water washing and/or stabilizing process after the desilvering process. The amount of water used in the water washing process can be fixed within a wide range according to the nature of the photosensitive material (for example the materials, such as the couplers, which are being used), the porpose for use, the wash water temperature, the number of washing tanks (the number of washing stages), the replenishment system, i.e., whether a counter-flow or a sequential-flow system is used, and various other conditions. The relationship between the amount of water used and the number of water washing tanks in a multi-stage counter-flow system can be obtained using the method outlined on pages 248 to 253 of Journal of the Society of Motion Picture and Television Engineers, Volume 64 (May 1955).

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The amount of wash water can be greatly reduced by using the multi-stage counter-flow system noted in the aforementioned literature, but bacteria proliferate due to the increased residence time of the water in the tanks, thus causing sediments to form on the photosensitive material. A method to reduce calcium ion and manganese ion concentrations is disclosed in JP-A-62-288838. This method can be used very effectively to overcome problems of sedimentation in the processing of color photosensitive materials of the present invention. Furthermore, the isothiazolone compounds and thiabendazoles disclosed in JP-A-57-8542, and the chlorine based disinfectants such as chlorinated sodium isocyanurate, and benzotriazoles, and the disinfectants disclosed in Chemistry of Biocides and Fungicides by Horiguchi, Reduction of Microorganisms, Biocidal and Fungicidal Techniques, published by the Health and Hygiene Technical Society and in A Dictionary of Biocides and Fungicides, published by the Japanese Biocide and Fungicide Society, can be used for this purpose.

The pH of the wash water used in the processing of the photosensitive materials of invention is within the range of from 4 to 9, and preferably within the range of from 5 to 8. The wash water temperature and washing time can be set variously according to the nature of the photosensitive material and the application. In general, washing conditions of from 20 seconds to 10 minutes at a temperature of from 15 to 45 °C, and preferably of from 30 seconds to 5 minutes at a temperature of from 25 to 40 °C, are selected. Moreover, the photosensitive materials of the present invention can be processed directly in a stabilizing bath instead of being subjected to a water wash as described above. The known methods disclosed in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can all be used for this purpose.

Furthermore, a stabilization process may be carried out following the aforementioned water washing process. The stabilizing baths contain formalin and surfactant and are used as a final bath for color photosensitive materials. Various chelating agents and fungicides can be added to these stabilizing baths.

The overflow which accompanies replenishment of the above mentioned wash water and/or stabilizer can be re-used in other processes such as a desilvering process.

A color developing agent may also be incorporated into the silver halide color photosensitive materials of the present invention in order to simplify and speed-up processing. The use of various color developing agent precursors is preferred for incorporation. For example, the indoaniline based compounds disclosed in U.S. Patent 3,342,597, the Schiff's base type compounds disclosed in U.S. Patent 3,342,599 and in Research Disclosure Nos. 14850 and 15159, the aldol compounds disclosed in Research Disclosure No. 13924, the metal salt complexes disclosed in U.S. Patent 3,719,492, and the urethane based compounds disclosed in JP-A-53-135628 can be used for this purpose.

Various 1-phenyl-3-pyrazolidones can be incorporated, as required, into the silver halide color photosensitive materials of this invention with a view to accelerating color development. Typical compounds of this type have been disclosed in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

The various processing baths are used at a temperature of from 10 to 50 °C in the present invention. The standard temperature is normally from 33 to 38 °C, but processing is accelerated and the processing time is shortened at higher temperatures and, conversely, higher picture quality and improved stability of the processing baths can be achieved at lower temperatures. Furthermore, processes using hydrogen

peroxide intensification or cobalt intensification as disclosed in West German Patent 2,226,770 or U.S. Patent 3,674,499 can be carried out in order to economize on silver in the photosensitive material.

Furthermore, the silver halide photosensitive materials of this invention can also be used as heat developable photosensitive materials as disclosed in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443 and JP-A-61-238056, and in European Patent 210,660A2, etc.

### **EXAMPLES**

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The following examples further illustrate the present invention in detail, but not to be construed to limit the scope thereof.

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### **EXAMPLE 1**

Sample 101, a multi-layer color photosensitive material, was prepared by the lamination coating of each of the layers on an undercoated cellulose triacetate film support. The composition of the layers is indicated

### (Photosensitive Layer Compositions)

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The numbers corresponding to each component indicate the amount coated onto the support, in units of grams per square meter, the amount after calculation as silver being shown in the case of the silver halides and colloidal silver. In the case of the sensitizing dyes, the amount coated is indicated in units of mols per mol of silver halide in the same layer.

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#### Sample 101

#### (Anti-halation Layer) First Layer

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Black colloidal	silver	as	silver	0.18
Gelatin				0.40

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#### (Intermediate Layer) Second Layer

2,5-Di-t-pentadecylhydroquinone

0.18

EX-1

0.07

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	EX-3	0.02
	EX-12	0.002
5	U-1	0.06
	U-2	0.08
10	U-3	0.10
70	HBS-1	0.10
	HBS-2	0.02
15	Gelatin	1.04
	Third Layer (First Red Sensitive Emulsion Layer	)
20	Mono-disperse silver iodobromide as silver emulsion (6 mol% AgI, Average grain size 0.6 µ, Variation coefficient of grain size 0.15)	0.55
25	Sensitizing dye I	6.9×10 <sup>-5</sup>
	Sensitizing dye II	1.8×10 <sup>-5</sup>
	Sensitizing dye III	3.1×10 <sup>-4</sup>
30	Sensitizing dye IV	4.0×10 <sup>-5</sup>
	EX-2	0.350
35	HBS-1	0.005
	EX-10	0.020
	Gelatin	1.30
40	Fourth Layer (Second Red Sensitive Emulsion Lay	er)
45	Tabular silver iodobromide as silver emulsion (10 mol% AgI, average grain size 0.7 $\mu$ , Average aspect ratio 5.5, Average thickness 0.02 $\mu$ )	1.0
	Sensitizing dye I	5.1×10 <sup>-5</sup>

	Sensitizing dye II	1.4×10 <sup>-5</sup>
	Sensitizing dye III	2.3×10 <sup>-4</sup>
5	Sensitizing dye IV	3.0×10 <sup>-5</sup>
	EX-2	0.400
10	EX-3	0.050
.0	EX-10	0.015
	Gelatin	1.30
15	Fifth Layer (Third Red Sensitive Emulsion Laye	r)
20	Silver iodobromide emulsion as silver (16 mol% AgI, Average grain size l.l µ)	1.60
	Sensitizing dye IX	5.4×10 <sup>-5</sup>
•	Sensitizing dye II	1.4×10 <sup>-5</sup>
25	Sensitizing dye III	2.4×10 <sup>-4</sup>
	Sensitizing dye IV	3.1×10 <sup>-5</sup>
30	EX-13	0.005
	EX-3	0.240
	EX-4	0.120
35	HBS-1	0.22
	HBS-2	0.10
40	Gelatin	1.63
	Sixth Layer (Intermediate Layer)	
	EX-5	0.040
<i>4</i> 5	HBS-1	0.020
	Gelatin	0.80

### Seventh Layer (First Green Sensitive Emulsion Layer) Tabular silver iodobromide as silver 0.40 emulsion (8 molt AgI, average 5 grain size 0.6 µ, Average aspect ratio 6.0, Average thickness $0.15 \mu$ $3.0 \times 10^{-5}$ Sensitizing dye V 10 Sensitizing dye VI 1.0×10<sup>-4</sup> $3.8 \times 10^{-4}$ Sensitizing dye VII 15 EX-6 0.260 EX-1 0.021 EX-7 0.030 20 0.025 EX-8 0.260 HBS-1 25 HBS-4 0.010 Gelatin 1.50 (Second Green Sensitive Emulsion Layer) Eighth Layer 30 as silver 0.80 Mono-disperse silver iodobromide emulsion (9 mol% AgI, Average grain size $0.7 \mu$ , Variation coefficient of grain size 0.18) 35 2.1×10<sup>-5</sup> Sensitizing dye V 7.0×10<sup>-5</sup> Sensitizing dye VI 40 2.6×10<sup>-4</sup> Sensitizing dye VII **EX-6** 0.180 0.010 **EX-8** 45 0.008 EX-1 0.012 EX-7

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	HBS-1		0.160
	HBS-4		0.008
5	Gelatin		1.20
	Ninth Layer (Third Green Sensitive Em	ulsion Lay	er)
10	Silver iodobromide emulsion (12 mol% AgI, Average grain size 1.0 µ)	as silver	1.2
	Sensitizing dye V		3.5×10 <sup>-5</sup>
15	Sensitizing dye VI		8.0×10 <sup>-5</sup>
	Sensitizing dye VII		3.0×10 <sup>-4</sup>
20	EX-6		0.005
	EX-13		0.007
	EX-11		0.118
25	EX-1		0.025
	HBS-1		0.25
30	HBS-2		0.10
	Gelatin		1.74
	<u>Tenth Layer</u> (Yellow Filter Layer)		
35	Yellow colloidal silver	as silver	0.05
	EX-5		80.0
40	HBS-3		0.03
	Gelatin		0.95
	Eleventh Layer (First Blue Sensitive	Emulsion L	ayer)
45 50	Tabular silver iodobromide emulsion (6 mol% AgI, average grain size 0.6 μ, Average aspect ratio 5.7, Average thickness 0.15 μ)	as silver	0.24
	- · - + F /		

	Sensitizing dye VIII	3.5×10 <sup>-4</sup>
	EX-9	0.85
5	EX-8	0.12
	EX-10	0.01
10	HBS-1	0.28
70	Gelatin	1.28
	Twelfth Layer (Second Blue Sensitive Emulsion L	ayer)
15	Mono-disperse silver iodobromide as silver emulsion (14 mol% AgI, Average grain size 0.8 µ, Variation coefficient of grain size 0.16)	0.45
_ 20	Sensitizing dye VIII	2.1×10 <sup>-4</sup>
	EX-9	0.20
25	EX-10	0.015
	HBS-1	0.03
	Gelatin	0.46
30	Thirteenth Layer (Third Blue Sensitive Emulsion	Layer)
35	Silver iodobromide emulsion as silver (14 mol% AgI, Average grain size 1.3 µ)	0.77
	Sensitizing dye VIII	2.2×10 <sup>-4</sup>
	EX-9	0.20
40	HBS-1	0.07
	Gelatin	0.69
45	Fourteenth Layer (First Protective Layer)	
	Silver iodobromide emulsion as silver (1 mol% AgI, Average grain size 0.07 µ)	0.5
50	U-4	0.11

	U-5	0.17
	HBS-1	0.90
5	Gelatin	1.00
	Fifteenth Layer (Second Protective Layer)	
10	Poly(methyl acrylate) grains (Average diameter about 1.5 µm)	0.54
	S-1	0.15
	S-2	0.05
15	Gelatin	0.72

The gelatin hardening agent H-1 and surfactant were added to each layer as well as the components indicated above.  $^{20}$ 

## Samples 102 to 117

Samples 102 to 117 were prepared by replacing the couplers in the fifth and ninth layers of Sample 101 with other couplers as shown in Table 1. Here EX-11 was replaced with 0.5 times molar of the other coupler.

These samples were exposed imagewise in such a way as to provide a maximum exposure of 10 CMS using light source A of which the color temperature had been adjusted to 4800° K with filters, after which they were color developed as indicated below.

The color development process was carried out in accordance with the scheme indicated below at a temperature of 38°C.

Color Development	3 minutes 15 seconds
Bleach-A	6 minutes 30 seconds
Water Wash	2 minutes 10 seconds
Fix	4 minutes 20 seconds
Water Wash	3 minutes 15 seconds
Stabilization	1 minute 05 seconds

The composition of the processing bath used in each process was as indicated below.

## Color Development Bath

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	Diethylenetriamine pentaacetic acid	1.0 g
-	1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
	Sodium sulfite	4.0 g
5	Potassium carbonate	30.0 g
J	Sodium bromide	1.4 g
	Potassium iodide	1.3 mg
	Hydroxylamine sulfate	2.4 g
10 ·	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
	Water	to make up to 1.0 t
	pH 10.0	
		· · · · · · · · · · · · · · · · · · ·

### Bleach A Bath

Ethylenediamine tetraacetic acid, ferric ammonium salt

Ethylenediamine tetraacetic acid, disodium salt

10.0 g

Ammonium bromide

Ammonium nitrate

Water

pH 6.0

Fixer Bath

25

30		
	Ethylenediamine tetraacetic acid, disodium salt	1.0 g
	Sodium sulfite	4.0 g
	Aqueous ammonium sulfate solution (70%)	175.0 ml
	Sodium bisulfite	4.6 g
35	Water	to make up to 1.0 £
	pH 6.6	

## 40 Stabilizer Bath

	Formalin (40%)	2.0 ml
15	Polyoxyethylene p-monononylphenyl ether (average degree of polymerization 10)	0.3 g
70	Water	to make up to 1.0 £

Next, development processing was carried out as described above except that the bleach-A bath was replaced by the processing bath indicated below. The bleach-B bath was prepared so as to simultate forcedly deteriorated bath, i.e., as if the bath had been used to process a large amount of photosensitive material.

The bleach-B bath was prepared by mixing 900 ml of solution (B-1) with 100 ml of solution (B-2).

## Bleach Bath Composition

	(B-1)	(B-2 <sup>'</sup> )
Ethylenediamine tetraacetic acid, ferric ammonium salt	90 g	100 g
Ethylenediamine tetraacetic acid, disodium salt	10 g	
Ammonium bromide	<sup>.</sup> 150 g	
Ammonium nitrate	. 10 g	
Aqueous ammonia (27%)	6.5 mi	
Water	to make up to 900 ml	1

The (B-2) bath was prepared by introducing steel wool into (B-2), closing the container and leaving the mixture to stand so as to provide a solution in which the Fe(III)-EDTA had been turned into Fe(II)-EDTA.

The decrease in density, when processing photosensitive material in bleach-B bath at an exposure which gave a cyan density of 0.50 on processing in fresh bleach-A bath, is shown in Table 1.

The increase in magenta fog density and the latent image storage properties (reduction in speed at fog + 0.2) on leaving samples which had been exposed imagewise in the same way as before and then left to stand for 14 days at a temperature of 40 °C, with 80% relative humidity, before being processed using bleach-A bath, is shown in Table 1.

It is clear from Table 1 that the samples of the present invention exhibit, a smaller increase in fogging under forced conditions, excellent latent image storage properties and little loss of density on processing in a forcedly fatigued bleach bath, and no loss of speed, when compared to the comparative samples.

More specifically, it can be said that Samples 107 to 117 of the present invention exhibit little loss of density on processing in the tired bleach-B bath as compared with Samples 101 and 102 for comparison, high sensitivity in a green-sensitive layer as compared with Sample 103, and little loss of relative sensitivity in a green-sensitive layer on processing in a forced condition.

5		Decrease in Density in Tired Bath-B	<b>.</b>	28	12	12	12	12	12	10	12	12	10
15		Properties of the Green Sensitive Layer under Forced Conditions	-0.03	-0.03	-0.02	-0.10	-0.12	-0.13	-0.02	-0.03	-0.02	-0.03	-0.03
20		Properti Green S Layer und Condi	0.01	0.01	0.01	0.04	0.05	0.05	0.01	0.01	0.01	0.02	0.01
25 30	Table 1	Speed <sup>2)</sup> Green Sensitive Layer	<b>o</b> ·	0.04	0	0.02	0.03	0.03	0.04	0.02	0.01	0.02	0.03
35		Relative Speed <sup>2)</sup> Red Green Sensitive Sensiti	•	-0.01	0	-0.01	-0.02	-0.01	0	0	0	0	0.01
40		Ninth Layer Coupler	EX-11	15	EX-11	EX-14	EX-15	EX-15	15	12	13	où	15
45		Fifth Layer Coupler	EX-4	EX-4	A-28	A-28	A-28	A-25	A-28	A-28	A-28	A-28	A-25
50		- 1	Comparative Example 101	102	103	1041)	1051)	1061)	This Invention 107	108	109	110	111
55	-		C X						Thi				

	•	I									and
5		Decrease in Density in Tired Bath-B	12	10	12	12	10	10		a	to give a cyan and
10								-			
15		of the sitive Forced ons	-0.02	-0.03	-0.02	-0.02	-0.03	-0.03			exposure required
		perties of een Sensitir under Fo									nsodx
20		Properties of the Green Sensitive Layer under Forced Conditions	0.01	0.02	0.01	0.01	0.02	0.02		;	of the e
25	(cont'd)			-	_	_	_	_			reciprocal
30	e 1 (co	Speed <sup>2)</sup> Green Sensitive	0.03	0.03	0.03	0.03	0.03	0.03		;	the rec
35	Table 1	Relative Speed <sup>2)</sup> Red Greer Sensitive Sensiti	0.01	0.01	0	-0.02	-0.02	-0.02			in terms of
40		Winth Layer Coupler	15	15	15	15	15	15		d in JP-A-(	speed expressed
<b>4</b> 5		Fifth Layer Coupler	A-26	A-27	A-30	A-35	A-23	A-33		Samples incl	Relative sp
50			This Invention	113	114	115	116	117	·	1):	2):
55			This								

### **EXAMPLE 2**

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Samples 201 to 214 were prepared by replacing the various couplers in the third, fourth, fifth, seventh, eighth and ninth layers of sample 101 as shown in Table 2. Equimolar amounts of the couplers 5, 6, 18 and 19 of the present invention were used to replace EX-6 in the seventh and eighth layers, and the amounts of 10 HBS-1 and gelatin in the seventh layer were changed to 0.10 and 1.00 respectively while the amount of HBS-1 and gelatin in the eighth layer were changed to 0.08 and 0.80 respectively. Furthermore, coupler 18 of the present invention was used at a rate of 1/2 molar to replace EX-11 in the ninth layer.

In samples 215 to 218, the HBS-1 in the third and fourth layers of sample 214 was added at a rate of 0.2, 0.4, 0.8 and 1.1 times by weight respectively with respect to A-18, and the amount of gelatin was changed to 1.40, 1.50, 1.65 and 1.80.

These samples were exposed to green light and white light in the same way as in Example 1, after which they were processed using an automatic developing machine and the method indicated below. (Cumulative replenishment of the bath was carried out to 3 times the Tank volume.)

20	Operation	Processing Time	Processing Temperature	Replenishment Rate	Tank Volume
25	Color Development Bleach Bleach-fix Rinse (1) Rinse (2) Stabilization Drying	3 min. 15 sec. 1 min. 00 sec. 3 min. 15 sec. 40 sec. 1 min. 00 sec. 40 sec. 1 min. 15 sec.	38 ° C 38 ° C 35 ° C 35 ° C 38 ° C 55 ° C	45 ml 20 ml 30 ml Counter-flow pipework from (2) to (1) 30 ml 20 ml	10

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Replenishment rates per 1 meter length×35 mm wide.

The compositions of the processing baths were as follows:

## Color Development Bath

		Tank (g)	Replenisher (g)
40	Diethylenetriamine pentaacetic acid	1.0	1.1
	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
	Sodium sulfite	4.0	4.4
	Potassium carbonate	30.0	37.0
45	Potassium bromide	1.4	0.7
45	Potassium iodide	1.5 mg	
	Hydroxylamine sulfate	2.4	2.8
	4-[N-ethyl-N-β-hydroxyethylamino]-2-methylaniline sulfate	4.5	5.5
	Water	to make up to 1.0 £	1.0 t
50	На	10.05	10.10

Bleach Bath Tank = Replenisher

	•	(Units: g)
5	Ethylenediamine tetraacetic acid, ferric ammonium dihydrate salt	120.0
Ů	Ethylenediamine tetraacetic acid, disodium salt	10.0
10	Ammonium bromide	100.0
10	Ammonium nitrate	10.0
	Bleach accelerator:	.′
15	$\left( \begin{pmatrix} H_3C \\ H_3C \end{pmatrix} N - CH_2 - CH_2 - S \end{pmatrix}_2 \cdot 2HC1$	0.005 mol
20		
	Aqueous ammonia (27%)	15.0 ml

Bleach-Fix Bath Tank = Replenisher

Water

pН

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	(Units: g)
Ethylenediamine tetraacetic acid, ferric ammonium dihydrate salt	50.0
Ethylenediamine tetraacetic acid, disodium salt	5.0
Sodium sulfite	12.0
Aqueous ammonium thiosulfate solution (70%)	240.0 ml
Aqueous ammonia (27%)	6.0 ml
Water	to make up to 1.0 £
pH	7.2

to make up to 1.0 ℓ

16.3

### Rinse bath Tank = Replenisher

Town water was treated by passing through a mixed bed type column which had been packed with an H-type strongly acidic cation exchange resin ("Amberlite IR-120B", made by the Rhom and Haas Co.) and an OH-type anion exchange resin ("Amberlite IR-400", made by the same company) so as to reduce the calcium and magnesium ion concentrations to less than 3 mg/liter, after which 20 mg/liter of sodium dichlroisocyanurate and 1.5 g/liter of sodium sulfate were added.

The pH of this bath was within the range of from 6.5 to 7.5.

Stabilization Bath Tank = Replenisher

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		(Units: g)
	Formalin (37%)	2.0 ml
	Polyoxyethylene p-monononylphenylether (average degree of polymerization 10)	0.3
5	Ethylenediamine tetraacetic acid, disodium salt	0.05
	Water	to make up to 1.0 £
	рН	5.0 <b>-</b> 8.0

The relative speeds of the red sensitive layers and green sensitive layers were obtained from processed strips in the same way as in Example 1. Furthermore, the value obtained by subtracting the yellow fog density from the yellow density at the point at which the magenta density was equal to fog + 1.0 with processed samples which had been exposed to green light are shown as the color turbidity in Table 2.

The samples were exposed to white light with a pattern intended for MTF value measurement purposes, and the MTF value for 25 cycles/mm was obtained with the cyan image.

Moreover, the decreases in density resulting from the utilization of a forcedly fatigued bleach bath were obtained using the same method as in Example 1.

It is clear from Table 2 that the samples of the present invention exhibited little loss of cyan density on processing in tired baths, gave little color turbidity, and had excellent sharpness as represented by the MTF value.

More specifically, it can be said that Samples 205 to 214 of the present invention exhibit excellent sharpness as represented by MTF value and excellent color reproducibility represented by color turbidity as compared with Samples 101, 201, and 202 for comparison, and little loss of density on processing in the tired bleach-B bath as compared with Samples 101, 203, and 204. From the results of Samples 214 to 218, it can be said that the smaller amount of a high boiling point organic solvent for dispersing the cyan coupler of the present invention is preferred in view of sharpness.

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50 55	45	<b>40</b>	35	30	25	20	15	10	
				Table	2	·			
· .	Coupler in the Third and Fourth Layers	Coupler in the Fifth Layer	Coupler in the Seventh and Eighth Layers	Coupler in the Winth	Relative Red Sensitive Layer	Relative Speed Red Green sitive Sensitive	Decrease in Density in Tired Bath-B	Color Turbidity	MTF value Cyan Density
Comparative Example 101	EX-2	4-XI	EX-6	EX-11	0	, <b>o</b>	<b>64</b>	0.15	0.41
201	1 A-17	EX-4	EX-6	EX-11	0.01	0	17	0.14	0.42
202	2 A-18	EX-4	2X-6	EX-11	0.01	0	11	0.15	0.41
203	3 EX-2	EX-4	រស	EX-11	•	0.01	65	0.08	0.44
204	1 EX-2	EX-4	18	EX-11	0	0.03	49	90.0	0.44
This Invention 205	ion 5 A-3	EX-4	រហ	EX-11	0.01	0.01	17	0.08	0.44
206	6 A-11	EX-4	ĸ	EX-11	0.02	0.01	16	0.09	0.44
207	7 A-17	EX-4	ĸ	EX-11	0.01	0.01	7.1	0.08	0.44
208	8 A-18	EX-4	ĸ	EX-11	0.01	0.01	16	0.08	0.44
209	9 A-18	EX-4	y	EX-11	0.01	0.01	16	0.08	0.44
210	0 A-18	EX-4	19	EX-11	0.01	0.03	17	0.08	0.44

5	MTF value Cyan Density	0.44	0.44	0.44	0.44	0.43	0.42	0.41	0.40
10	Color Turbidity	0.08	0.08	0.08	90.0	0.05	0.05	0.05	0.05
15	Decrease in Density in	16	r	0	0	7	0	0	0
20	Relative Speed Red Green sitive Sensitive	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04
25	Cont'd) Relative Red Sensitive Layer	0.01	0.02	0.01	0.01	0.01	00.0	-0.01	-0.01
30	Table 2 (cont'd)  Rela Coupler in Red the Winth Sensiti	EX-11	EX-11	EX-11	18	18	18	18	18
35	Coupler in the Seventh and Eighth	18	18	18	. 18	18	18	<b>80</b> FI	18
40	Coupler in the Fifth	EX-4	A-27	A-28	A-28	A-28	A-28	A-28	A-28
45	Coupler in the Third and Fourth	A-18	A-18	A-18	A-18	A-18	A-18	A-18	A-18
50	U = # }	is Invention 211	212	213	214	215	216	217	218
		<b>10</b>							

U-1

C & H,(t)

C & H,(t)

15 U - 2

25

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20 O H

N

t C 4 H • (t)

.

U-3

OH C. H. (sec)

N
C. H. (t)

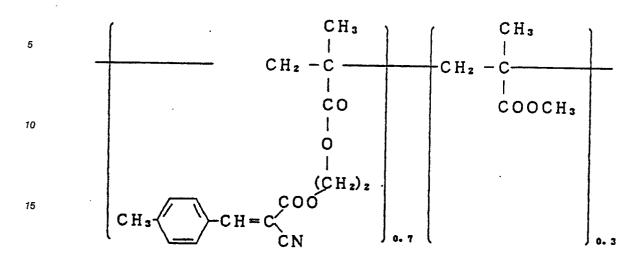
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**55** ...

U-4



U-5

$$C_2 H_5$$
 N-CH=CH-CH=C COOC<sub>8</sub> H<sub>17</sub>(n)

5 
$$tC_5H_{11}$$
 OCH<sub>2</sub> CONH

CONH

N=N-OCH<sub>3</sub>

CONH

COL

COL

COL

EX-2

EX-3

OH CONHC<sub>12</sub>H<sub>25</sub>(n)

OCH<sub>2</sub> CH<sub>2</sub> O 
$$N=N$$

OH NHCOCH<sub>3</sub>

SO<sub>3</sub> Na SO<sub>3</sub> Na

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30 E X - 6

5
$$C_{2} H_{5}$$

$$O C H C O N H$$

$$C_{2} H_{5}$$

$$C \ell$$

$$C \ell$$

$$C \ell$$

$$C \ell$$

$$C \ell$$

EX-8

$$CH_{3} O \longrightarrow COCHCONH$$

$$C \varrho$$

EX-10

EX-12

EX-13

NHCO (CH<sub>2</sub>)<sub>3</sub> O—

(t) C<sub>5</sub> H<sub>11</sub>

(cH<sub>3</sub>)<sub>2</sub> CCOCHCONH

$$(CH_{2})_{3} C C \ell$$

$$NH C - CHO - SO_{2} - OH$$

$$C + CHO - CHO - CHO - OH$$

# EX-15 (M-5 of JP-A-62-180365)

HBS-1 Tricresyl phosphate

HBS-2 Dibutyl phthalate

HBS-3 Bis(2-ethylhexyl)phthalate

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45

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HBS-4

C<sub>2</sub> H<sub>5</sub>

$$(t) C_5 H_{11} \longrightarrow OCHCONH$$

$$(t) C_5 H_{11} \longrightarrow COOH$$

H-1

$$CH_2 = CH - SO_2 - CH_2 CONH - CH_2$$

$$CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$$

## Sensitizing Dye

I

 $\begin{array}{c} C_2 H_5 \\ S \\ CH = C - CH = \\ N \\ C R \\ CH_2)_4 SO_3^6 \\ (CH_2)_3 SO_3 N_2 \end{array}$ 

I

$$C_{2} H_{5}$$

$$C_{2} H_{5}$$

$$C_{2} H_{5}$$

$$C_{3} H_{5}$$

$$C_{4} H_{5}$$

$$C_{5} H_{5}$$

$$C_{7} H_{7}$$

$$C_{8} H_{7}$$

IV

30
$$C_{2} H_{5}$$

$$C P \longrightarrow N \longrightarrow CH - CH = N \longrightarrow C_{2} H_{5}$$

$$C_{2} H_{5}$$

V

15 VI

$$CH = CH - CH = O$$

$$C_2 H_5 \qquad (CH_2)_4 SO_3^{\Theta}$$

•

VI

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W

IX

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

### Claims

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1. A silver halide color photographic material comprising at least one red sensitive silver halide emulsion layer containing at least one cyan coupler: at least one green sensitive silver halide emulsion layer containing at least one magenta coupler; and at least one blue sensitive silver halide emulsion layer containing at least one yellow coupler, wherein said layers are established on a support and at least one of the cyan couplers is represented by the general formula (A), and at least one of the magenta couplers is represented by the general formula (II)

$$(R_2)\ell$$
 $R_3NH$ 
 $T$ 
 $R_1$ 
 $R_1$ 

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wherein  $R_1$  represents a halogen atom, aliphatic group, aromatic group, heterocyclic group, amidino group, guanidino group or a group which can be represented by  $-COR_4$ ,  $-SO_2R_4$ ,  $-SOR_4$ ,

-NHCOR4, -NHSO<sub>2</sub>R<sub>4</sub>, -HNSOR<sub>4</sub>, or

O R4
or -NHP ,

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R<sub>2</sub> 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, aryl group, acyloxy group, aliphatic oxy group, aromatic oxy group, aliphatic sulfonyl group, aromatic sulfonyl group, aliphatic sulfinyl group, aromatic oxycarbonyl group, aliphatic oxycarbonylamino group, aromatic oxycarbonylamino group, sulfamoylamino group, heterocyclic group or an imido group,

t is 0 or an integer up to 3,

R₃ represents a halogen atom or an R₅U group,

T represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine developing agent,

R<sub>4</sub> and R<sub>5</sub> each independently represent an aliphatic group, aromatic group, heterocyclic group, amino group, aliphatic oxy group or an aromatic oxy group,

R<sub>6</sub> represents a hydrogen atom, aliphatic group, aromatic group, heterocyclic group, -OR<sub>7</sub> group, -SR<sub>7</sub> group, -COR<sub>8</sub> group,

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-PO(R<sub>7</sub>)<sub>2</sub> group, -PO(-OR<sub>7</sub>)<sub>2</sub> group,

$$R_9$$
  $R_9$   $R_9$   $R_9$   $R_{10}$   $R_{10}$   $R_{10}$ 

45

-CO<sub>2</sub>R<sub>7</sub> group, -SO<sub>2</sub>R<sub>7</sub> group, -SO<sub>2</sub>OR<sub>7</sub> group or an imino group, and U represents

50

a -CO- group, an -SO<sub>2</sub>- group, an -SO- group or a single bond,

R7 represents an aliphatic group, aromatic group or a heterocyclic group,

55 R<sub>8</sub> represents a hydrogen atom, aliphatic group, aromatic group or a heterocyclic group, and

 $R_9$  and  $R_{10}$  each independently represent a hydrogen atom, aliphatic group, aromatic group, heterocyclic group, acyl group, aliphatic sulfonyl group or an aromatic sulfonyl group,

when 1 has a value of 2 or more, the R2 groups may be the same or different, or they may be joined

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together to form a ring, or  $R_2$  and  $R_3$ , or  $R_3$  and T, may be joined to each other to form rings, respectively, or dimers or larger units (oligomers or polymers) can be formed by linking together via divalent groups or groups of higher valence in any of  $R_1$ ,  $R_2$ ,  $R_3$  or T,

wherein R<sub>31</sub> represents an alkyl group, aryl group or a heterocyclic group, and

- R<sub>32</sub> represents a hydrogen atom or a substituent group, R<sub>32</sub> represents an alkyl group, aryl group, alkylthio group, arylthio group or a heterocyclic thio group, and X represents a hydrogen atom or a coupling elimination group.
  - 2. A color photographic material according to claim 1, wherein
- R<sub>1</sub> is selected from the group consisting of a halogen atom, a -COR<sub>4</sub> group and a -SO<sub>2</sub>R<sub>4</sub> group, whereby R<sub>4</sub> comprises an amino group, and
  - L<sub>1</sub> is 1, and
  - $R_2$  is selected from the group consisting of a halogen atom, an aliphatic group, an aromatic oxy group, a carbonamido group, sulfonamido group and a cyan group, and
  - $R_3$  comprises an  $R_6U$  group, whereby  $R_6$  is selected from the group consisting of an aliphatic group, an aromatic group, a  $-OR_7$  group and an  $-SR_7$  group, and
  - T is selected from the group consisting of a halogen atom, an aliphatic oxy group and an aliphatic thio group, and
  - R<sub>32</sub> is selected from the group consisting of an alkyl group, an aryl group, an alkylthio group and an arylthio group, and
- X is selected from the group consisting of a halogen atom, a carboxyl group, a group which is linked via an oxygen atom, a group which is linked via a nitrogen atom, and a group which is linked via a sulfur atom.
  - 3. A color photographic material according to claim 2, wherein
  - R<sub>1</sub> comprises a -COR<sub>4</sub> group, wherein R<sub>4</sub> comprises an amino group, and
  - ℓ<sub>1</sub> is 1, and
- R<sub>2</sub> is selected from the consisting of a fluorine atom, a chlorine atom, a trifluoromethyl group, a methoxy group and a cyano group, and
  - R<sub>3</sub> is selected from the group consisting of an aliphatic oxy carbonyl group, an aliphatic sulfonyl group and an aromatic sulfonyl group.
- 4. A color photographic material according to claim 1, wherein R<sub>31</sub> represents an alkyl group or an aryl group.
  - 5. A color photographic material according to claim 1, wherein X represents an arylthic group.

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