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Silver halide color photographic material containing yellow colored cyan coupler.

A silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, wherein said photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:

$$A-(L_1)_v-B-(L_2)_w-DI$$
 (I)

wherein A represents a group which is cleaved from  $(L_1)_v$ -B- $(L_2)_w$ -DI by a reaction of the compound of formula (I) with an oxidation product of a developing agent;  $L_1$  represents a bonding group which is cleaved from B after the cleavage of the bond between  $L_1$  and A; B represents a group which reacts with an oxidation product of a developing agent to release  $(L_2)_w$ -DI;  $L_2$  is a group which is cleaved from DI after the cleavage of the bond between B and  $L_2$ ; DI represents a development inhibitor; v and w each represents an integer of 0 to 2; and when v or w is 2, the two  $L_1$  groups or the two  $L_2$  groups may be the same or different groups.

EP 0 435 334 A2

## SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING YELLOW COLORED CYAN COUPLER

#### FIELD OF THE INVENTION

This invention relates to a silver halide color photographic material. More particularly, it relates to a silver halide color photographic material comprising a novel yellow colored cyan coupler and a development inhibitor-releasing compound which has excellent color reproducibility and sharpness over the whole exposure range and whose color reproducibility and sharpness are scarcely affected by changes in processing.

#### DESCRIPTION OF RELATED ART

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It has been sought in recent years to provide silver halide photographic materials which have excellent color reproducibility, sharpness, and high sensitivity, as typified by ISO 400 photographic materials (e.g., Super HG-400 sold by Fuji Photo Film Co.) having high image quality comparable to ISO 100, particularly in the field of silver halide photographic materials for photographing.

As means for improving color reproducibility and sharpness, the compounds of formula (I) according to the present invention have been proposed in JP-A-60-185950 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-61-233741 (corresponding to U.S. Patent 4,618,571), JP-A-62-151850,JP-A-63-163454 (corresponding to U.S. Patent 4,824,772) and JP-A-63-281160. Interlaminar and edge effects are improved, and color reproducibility and sharpness are also improved to some degree by these compounds. However, there are problems in that when the amount of the development inhibitor released from these compounds is insufficient to inhibit development, sufficient interlaminar and edge effects cannot be obtained; and when the sensitive layers to be inhibited are not properly developed, the desired interlaminar effect cannot be obtained. Further, these compounds do not provide a sufficient effect over the whole exposure range, and the use of these compounds lowers the sensitivity of the photographic material somewhat. Furthermore, when the arrangement of layers in conventional photographic materials for photographing is made, that is, the arrangement is made in the order of a red-sensitive layer containing a cyan coupler, a green-sensitive layer containing a magenta coupler and a blue-sensitive layer containing a yellow coupler with the red-sensitive layer being closest to the support, the red-sensitive layer and the blue-sensitive layer are far away from each other, so that there are problems in that a sufficient interlaminar effect between these layerscannot be obtained by use of these compounds and a lowering in the sensitivity of the green-sensitive layer is caused.

On the other hand, it is disclosed in JP-A-61-221748 and West German Patent Laid-Open No. 3815469A that effects silimar (with respect to photographic performances) to an interlaminar effect of from the red-sensitive emulsion layer to blue-sensitive emulsion layer can be obtained by using a yellow colored cyan coupler in the red-sensitive emulsion layer. However, it is difficult to obtain sufficient effects over the whole exposure range by the methods described in the above patent specifications, that is, by the use of these compounds alone. Conventional yellow colored cyan couplers have problems in that the molecular extinction coefficients of their yellow dyes are low and their coupling activity is also low.

#### 40 SUMMARY OF THE INVENTION

Afirst object of the present invention is to provide a photographic material which has excellent color reproducibility, and particularly red color reproducibility, over the whole exposure range.

A second object of the present invention is to provide a photographic material having excellent sharpness.

A third object of the present invention is to provide a photographic material which is less processing-dependent.

A fourth object of the present invention is to provide a photographic material which is highly sensitive.

These objects of the present invention have been achieved by providing a silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, wherein the photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:

$$A-(L_1)_v-B-(L_2)_w-DI$$
 (I)

wherein A represents a group which is cleaved from  $(L_1)_v$ -B $(L_2)_w$ -DI by a reaction of the compound of formula (I) with an oxidation product of a developing agent;  $L_1$  represents a bonding group which is cleaved from B after the cleavage of the bond between A and  $L_1$ ; B represents a group which reacts with an oxidation product of a developing agent to release  $(L_2)_w$ -DI;  $L_2$  represents a group which is cleaved from DI after the cleavage of the bond between  $L_2$  and B; DI represents a development inhibitor; v and w each represents an integer of 0 to 2; and when v or w is 2, the two  $L_1$  groups or the two  $L_2$  groups may be the same or different groups.

#### DETAILED DESCRIPTION OF THE INVENTION

The compounds represented by general formula (I) will be discussed in more detail below.

The term "aliphatic group" means an aliphatic hydrocarbon group which may be a saturated or unsaturated hydrocarbon group or a straight-chain, branched or cyclic hydrocarbon group such as an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, etc. The term "aryl group means at least a substituted or unsubstituted phenyl and naphthyl groups. An acyl moiety (in acyl group, acylamino group, etc.) means an aliphatic and aromatic acyl moiety. A sulfonyl moiety (in sulfonyl group, sulfonamido group) means an aliphatic and aromatic sulfonyl moieties. A carbamoyl group, sulfamoyl group, amino group and ureido group include unsubstituted and substituted groups thereof. A heterocyclic group is a 3- to 8-membered having at least one of N, O and S atoms as hetero atom.

The compounds represented by general formula (I) are cleaved through the following reaction route during development to release DI:

$$\begin{array}{c} \text{QDI} \\ \text{A-(L_1)_v-B-(L_2)_w-DI} \xrightarrow{} \text{(L_1)_v-B-(L_2)_w-DI} \xrightarrow{} \\ \text{B-(L_2)_w-DI} \xrightarrow{} \text{(L_2)_w-DI} \xrightarrow{} \text{DI} \end{array}$$

wherein A, L<sub>1</sub>, v, B, L<sub>2</sub>, w and DI have the same meaning as in formula (I); and QDI represents an oxidation product of a developing agent.

In more detail, A in formula (I) represents a coupler moiety for color development or a moiety which is cleaved during development, and which is able to reduce the oxidation product of a developing agent, which exists during development.

Conventional groups can be used as the coupler moiety represented by A, including yellow coupler moieties (e.g., open chain ketomethylene couplers moieties), magenta coupler moieties (e.g., 5-pyrazolone, pyrazoloimidazole and pyrazolotriazole coupler moieties), cyan coupler moieties (e.g., phenol and naphthol coupler moieties) and non-color forming coupler moieties (e.g., indanone and acetophenone coupler moieties). Heterocyclic coupler moieties described in U.S. Patent 4,315,070, 4,183,752, 3,961,959 or 4,171,223 can be used.

Preferred examples of A include coupler moieties represented by formulas (Cp-1), (Cp-3), (Cp-4), (Cp-5), (Cp-6), (Cp-7), (Cp-8), (Cp-9), and (Cp-10).

These coupler moieties are preferred, because they have a high coupling rate.

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$$(R_{59})_{d} \xrightarrow{NHCO-R_{58}} (Cp-6)$$

$$(R_{59})_d$$
 NHCONH- $R_{60}$  (Cp-7)

OH CONH-R<sub>61</sub> (Cp-8)
$$(R_{62})_e$$

In the above formulas, the free bonds at the coupling positions represent the bonding positions of the groups which are eliminated by coupling.

When R<sub>51</sub>, R<sub>52</sub>, R<sub>53</sub>, R<sub>54</sub>, R<sub>55</sub>, R<sub>56</sub>, R<sub>57</sub>, R<sub>58</sub>, R<sub>59</sub>, R<sub>60</sub>, R<sub>61</sub>, R<sub>62</sub>, or R<sub>63</sub> in the above formulas contains a nondiffusible group, the total number of carbon atoms in the group is 8 to 40, preferably 10 to 30. In other cases, the total number of carbon atoms is preferably not more than 15. When the couplers are bis type, telomer type or polymer type, any one of the above substituent groups is a bivalent group bonded to a repeating unit. In this case, the total numbers of carbon atoms may be beyond the above range.

 $R_{51}$  to  $R_{63}$ , b, d and e are now illustrated in detail.

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Hereinafter, R<sub>41</sub> represents an aliphatic group, an aromatic group or a heterocyclic group; R<sub>42</sub> represents an aromatic group or a heterocyclic group; and R<sub>43</sub>, R<sub>44</sub>, and R<sub>45</sub>, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group or a heterocyclic group.

 $R_{51}$  has the same meaning as  $R_{41}$ ; b is 0 or 1;  $R_{52}$  and  $R_{53}$  each has the same meaning as  $R_{42}$ ;  $R_{54}$  represents  $R_{41}$ ,

R<sub>41</sub>S-, R<sub>43</sub>O-,

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 $R_{45}NCON-, N \equiv C-;$ | | |  $R_{43} R_{44}$ 

 $R_{55}$  has the same meaning as  $R_{41};\,R_{56}$  and  $R_{57}$  each repersents  $R_{43},\,R_{41}S\text{-},\,R_{43}O\text{-},$ 

R<sub>41</sub>CON-, ! R<sub>43</sub>

R<sub>41</sub>SO<sub>2</sub>N-;

R<sub>58</sub> has the same meaning as R<sub>41</sub>; R<sub>59</sub> represents R<sub>41</sub>,

R<sub>41</sub>CON-, R<sub>41</sub>OCON-, R<sub>41</sub>SO<sub>2</sub>N-;

R<sub>41</sub>O-, R<sub>41</sub>S-, a halogen atom or

include the following groups.

R<sub>41</sub>N-;

d is 0 or an integer of from 1 to 3 and when d is 2 or 3,

plural  $R_{59}$  groups may be the same or different, or each  $R_{59}$  is a divalent group and these divalent groups may be linked to form a ring structure. Typical examples of the divalent groups which form a ring structure

wherein f is O or an integer of 1 to 4 and g is 0, 1 or 2.

 $R_{60}$  has the same meaning as  $R_{41}$ ;  $R_{61}$  has the same meaning as  $R_{41}$ ;  $R_{62}$  represents  $R_{41}$ ,  $R_{41}OCONH$ -,  $R_{41}SO_2NH$ -,

R<sub>43</sub>O-, R<sub>41</sub>S-, a halogen atom or

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R<sub>63</sub> represents R<sub>41</sub>,

R<sub>43</sub>CON-, | | R<sub>44</sub>R<sub>45</sub>

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 $R_{41}SO_2$ -,  $R_{43}OCO$ -,  $R_{43}O$ - $SO_2$ -, a halogen atom, a nitro group, a cyano group or  $R_{43}CO$ -; and e is 0 or an integer of 1 to 4. When two or more  $R_{62}$  or  $R_{63}$  groups are present, they may be the same or different.

In the present invention groups are defined as follows, unless otherwise defined.

The aliphatic group is a saturated or unsaturated linear or cyclic straight-chain or branched chain, substituted or unsubstituted aliphatic hydrocarbon group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms. Typical examples thereof include a methyl group, ethyl group, propyl group, isopropyl group, butyl group, t-butyl group, i-butyl group, t-amyl group, hexyl group, cyclohexyl group, 2-ethylhexyl group, octyl group, 1,1,3,3-tetramethylbutyl group, decyl group, dodecyl group, hexadecyl group and octadecyl group. The aromatic group is a substituted or unsubstituted phenyl or naphthyl group having 6 to 20 carbon atoms. The heterocyclic group is preferably a 3-membered to 8-membered a substituted or unsubstituted heterocyclic group having 1 to 20 carbon atoms, preferably 1 to 7 carbon atoms wherein the hetero-atom is selected from a nitrogen, oxygen and sulfur atom. Typical examples of the heterocyclic group include a 2-pyridyl group, 2-thienyl group, 2-furyl group, 1-imidazolyl group, 1-indolyl group, phthalimido group, 1,3,4-thiadiazole-2-yl group, succinimido group, 1,2,4-triazole-2-yl group and 1-pyrazolyl group.

The above-described aliphatic hydrocarbon group, aromatic group and heterocyclic group may optionally have one or more substituent groups. Typical examples of such substituent groups include a halogen atom,  $R_{47}O$ -,  $R_{46}S$ -,

R46SO2-, R47OCO-,

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R<sub>46</sub>COO-, R<sub>47</sub>OSO<sub>2</sub>-, a cyano group and a nitro group, wherein R<sub>46</sub> represents an aliphatic group, an aromatic group or a heterocyclic group and R<sub>47</sub>, R<sub>48</sub> and R<sub>49</sub> each represents an aliphatic group, an aromatic group, a heterocyclic group or a hydrogen atom. The aliphatic group, the aromatic group and the heterocyclic group have the same meanings as those described above.

Preferred examples of  $R_{51}$  to  $R_{63}$  and d and e are as follows.

Preferably,  $R_{51}$  is an aliphatic group or an aromatic group. Preferably,  $R_{52}$ ,  $R_{53}$  and  $R_{55}$  are each an aromatic group.  $R_{54}$  is preferably  $R_{41}$ CONH- or

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 $R_{56}$  and  $R_{57}$  are each preferably an aliphatic group, an aromatic gorup,  $R_{41}O$ - or  $R_{41}S$ -; and  $R_{58}$  is preferably an aliphatic group or an aromatic group. In formula (Cp-6),  $R_{59}$  is preferably a chlorine atom, an aliphatic group or  $_{41}CONH$ -; d is preferably 1 or 2; and  $R_{60}$  is preferably an aromatic group. In formula (Cp-7),  $R_{59}$  is preferably  $R_{41}CONH$ -; d is preferably 1; and  $R_{61}$  is preferably an aliphatic group or an aromatic group. In formula (Cp-8), e is preferably 0 or 1;  $R_{62}$  is preferably  $R_{41}CONH$ -,  $R_{41}CONH$ - or  $R_{41}SO_2NH$ - and these groups are preferably attached to the 5-position of the naphthol ring. In formula (Cp-9),  $R_{63}$  is preferably  $R_{41}CONH$ -,  $R_{41}SO_2NH$ -,

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a nitro group or a cyano group. In formula (Cp-10), R<sub>63</sub> is preferably

R<sub>43</sub>OCO- or a R<sub>43</sub>CO-.

When A in formula (I) represents a moiety which can conduct reduction, the compounds of formula (I) can be represented byformula (II) according on Kendall-Pelz rule.

$$A_1 - P - (X = Y)_n - Q - A_2 \tag{II}$$

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In formula (II), P and Q represent independently an oxygen atom or a substituted or unsubstituted imino group; at least one of the n X groups and the n Y groups represents a methine group having a group of  $-(L_1)_v$ -B(L<sub>2</sub>)<sub>w</sub>-DI as a substituent group and the other X and Y groups represent independently a substituted or unsubstituted methine group or a nitrogen atom; n represents an integer of 1 to 3 (when n is 2 or greater, the n X groups or n Y groups may be the same or different groups); and A<sub>1</sub> and A<sub>2</sub> each represents a hydrogen atom or a group which can be eliminated by an alkali. Any two substituents of P, X, Y, Q, A<sub>1</sub> and A<sub>2</sub> may be bivalent groups and may be combined together to form a ring structure. All such ring structures

are included within the scope of the present invention. For example, (X = Y)n may form a benzene ring or pyridine ring and other rings such as the following:

$$n=1$$
  $n=2$   $N$   $N$   $N$   $N$   $N$ 

When P and Q are each a substituted or unsubstituted imino group, a sulfonyl or acyl group-substituted imino group is preferred, and P and Q can be represented by the following formulas:

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In formulas (N-1) and (N-2), the mark \* represents a position at which A1 or A2 is bonded; and the mark \*\* represents a position at which one of the free bonds of  $(X=Y)_n$  is bonded.

In formulas (N-1) and (N-2), the group represented by G is preferably a straight-chain or branched, linear or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon group having 1 to 32 carbon atoms (containing carbon atoms of substituent), preferably 1 to 22 carbon atoms (e.g., methyl, ethyl, benzyl, phenoxybutyl, isopropyl), a substituted or unsubstituted aromatic group having 6 to 10 carbon atoms (e.g., phenyl, 4-methylphenyl, 1-naphthyl, 4-dodecyloxyphenyl), a 4-membered to 7-membered substituted or unsubstituted heterocyclic group containing at least one of a nitrogen atom, a sulfur atom and an oxygen atom as hetero atom and the gorup may be condensed with a benzene ring (e.g., 1-phenyl-4imidazolyl, 2-furyl, benzothienyl, 1-benzoxalyl, pyrazolyl, 1-methyl-3-pyrazolyl, and pyridyl), or a group of -O-G' (wherein G' has the same meaning as G). Examples of substituent for G or G' include a halogen atom, a hydroxy group, a carboxy group, a sulfo group, a phospono group, a phosphino group, a cyano group, an alkoxy group, an aryl group, an aryloxy group, an alkoxycarbonyl group, an amino group, an ammoniumyl group, an acyl group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group and a sulfonyl group.

In general formula (II), P and G are preferably independently an oxygen atom or a group represented by formula (N-1).

When A<sub>1</sub> and A<sub>2</sub> are each a group which can be eliminated by an alkali (hereinafter referred to as a precursor group), preferred examples of such a group include a hydrolyzable group such as an acyl, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, imidoyl, oxazolyl and sulfonyl groups (which are preferably have 1 to 6 carbon atoms and which may be substituted with a substituent such as those cited in the definition of G); a precursor group which utilizes reverse Michael reactions as described in U.S. Patent 4,009,029; a precursor group which utilizes, as an intramolecular nucleophilic group, an anion formed after a ring cleavage reaction as described in U.S. Patent 4,310,612; a precursor group which causes a cleavage reaction by the electron transfer of an anion through a conjugated system as described in U.S. Patents 3,674,478, 3,932,480 and 3,993,681; a precursor group which causes a cleavage reaction by the electron transfer of an anion reacted after ring cleavage as described in U.S. Patent 4,335,200; and a precursor group which utilizes an imidomethyl group as described in U.S. Patents 4,363,865 and 4,410,618.

In the formula (II), the cases where P is an oxygen atom and  $A_2$  is a hydrogen atom are preferred.

In formula (II), the X and Y groups which do not represent a methine group having a group of -(L1)<sub>v</sub>-B-(L2)w-DI as a substituent preferably represent substituted or unsubstituted methine groups.

Among the compounds represented by formula (II), those represented by the following general formula (III) or (IV) are particularly preferred:

$$(R_{64})_{q} \xrightarrow{P-A_{1}} * \qquad (III)$$

$$Q-A_{2}$$

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$$(R_{64})_{q} \xrightarrow{A_{1}} A_{2}$$

$$(IV)$$

In formulas (III) and (IV), the mark \* represents a position at which a group of  $-(L_1)_v$ -B- $(L_2)_w$ -DI is attached; P, Q, A<sub>1</sub> and A<sub>2</sub> have the same meaning as in formula (II); R<sub>64</sub> is a substituent group; and q is 0 or an integer of 1 to 3. When q is 2 or greater, the two or more R<sub>64</sub> groups may be the same or different groups. When two R<sub>64</sub> groups are substituent groups attached to adjoining carbon atoms, they each may be a bivalent group and may be combined together to form a ring structure. All such ring structures are included within the scope of the present invention. For example, they may form benzene condensed rings which include such ring structures as naphthanenes, benzonorbornenes, chromans, benzothiophenes, benzofurans, 2,3-dihydrobenzofurans or indenes. These condensed rings may have one or more substituent groups. Preferred examples of the substituent groups for these condensed rings when two R<sub>64</sub> groups form a condensed ring and preferred examples of R<sub>64</sub> when the R<sub>64</sub> groups do not form a condensed ring include an R<sub>41</sub> group, a halogen atom, R<sub>43</sub>O-, R<sub>43</sub>S-, R<sub>43</sub>(R<sub>44</sub>)NCO-, R<sub>43</sub>OOC-, R<sub>43</sub>SO<sub>2</sub>-, R<sub>43</sub>(R<sub>44</sub>)NSO<sub>2</sub>-, R<sub>43</sub>CON(R<sub>43</sub>)-, R<sub>43</sub>CO<sub>2</sub>-, R<sub>43</sub>(R<sub>44</sub>)N-, R<sub>43</sub>(R<sub>44</sub>)N-, R<sub>43</sub>(R<sub>44</sub>)NSO<sub>2</sub>-, R<sub>43</sub>(R<sub>44</sub>)NCON-(R<sub>45</sub>)-, and

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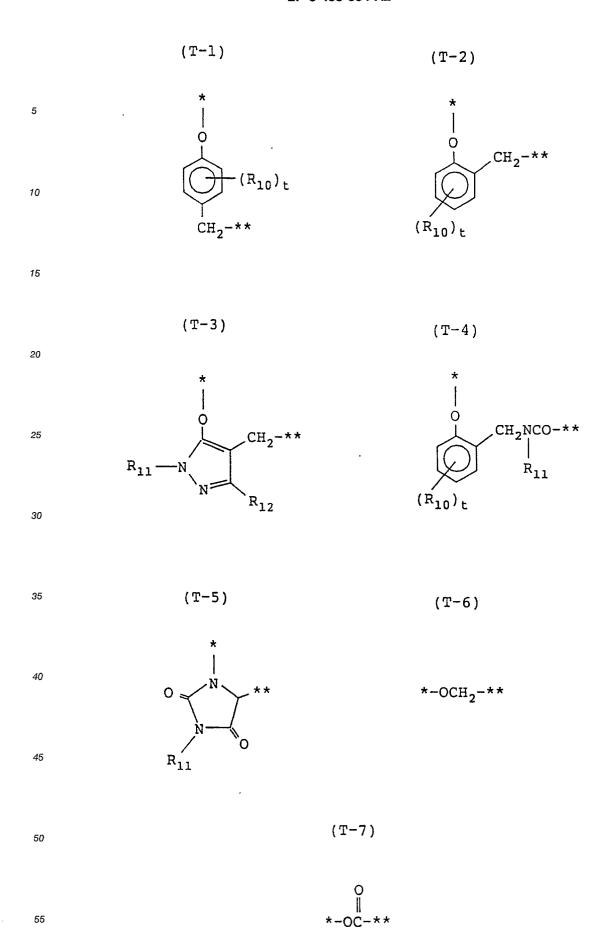
wherein  $R_{41}$ ,  $R_{43}$ ,  $R_{44}$  and  $R_{45}$  are as defined above.

In formulas (III) and (IV), A<sub>1</sub> and A<sub>2</sub> are preferably hydrogen atom.

In formula (I), the cases where A is a coupler moiety for color development are preferred.

The groups represented by  $L_1$  and  $L_2$  in formula (I) may be used or may not be used according to purpose. Examples of the groups represented by  $L_1$  and  $L_2$  when used include the following bonding groups. In the following formulas, either the mark \* represents a position at which A is bonded and the mark \*\* represents a position at which B is bonded, or the mark \* represents a position at which B is bonded and the mark \*\* represents a position at which DI is bonded.

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In the above formulas,  $R_{10}$  is a group which can be substituted to a benzene ring (typical substituents

thereof being those already described above in the definition of  $R_{64}$ );  $R_{11}$  has the same meaning as  $R_{41}$ ;  $R_{12}$  is a hydrogen atom or one of the groups already described above in the definition of  $R_{64}$ ; and t is an integer of 0 to 4.

The group represented by B in formula (I) is preferably a group which can be oxidized and is capable of reducing an oxidation product of a developing agent, or a group which forms a substantially colorless compound by a coupling reaction with an oxidation product of a developing agent. When the group represented by B is a group capable of reducing an oxidation product of a developing agent, B is preferably a group represented by the following general formula (V):

$$*-P'-(X'=Y')n'-Q'-A_2'$$
 (V)

wherein the mark \* represents a position at which the group of formula (V) is bonded to the left side in formula (I);  $A_{2'}$ , P', Q' and n' have the same meaning as  $A_2$ , P, Q and n in formula (II), respectively, with the proviso that at least one of the n' X' groups and the n' Y' groups is a methine group having an  $(L_2)_w$ -DI group as a substituent group and the other X' and Y' groups are a substituted (examples of the substituent include the same group as those in the definition for  $R_{64}$  and a hydroxy gorup) or unsubstituted methine group or a nitrogen atom. When any two of  $A_{2'}$ , P', Q', X' and Y' are a bivalent group, they may be combined together to form a ring structure. All such ring structures are included within the scope of the present invention. Examples of the ring structures include a benzene ring, an imidazole ring and a pyridine ring.

In formula (V), P' is preferably an oxygen atom and Q' is preferably an oxygen atom or a group represented by any one of the following formulas. In the following formulas, the mark \* represents a bond to be bonded to (X' = Y')n' and the mark \*\* represents a bond to be bonded to  $A_{2'}$ :

In the above formulas, G is as defined in formulas (N-1) and (N-2). Particularly preferably, Q' is an oxygen atom or an

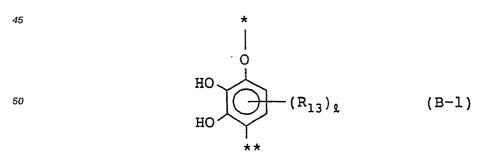
40 group.

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Typical examples of the group represented by B in formula (I) include the following groups wherein the mark \* represents a position where each group is bonded to  $A-(L_1)_n$  in formula (I) and the mark \*\* represents a position where each group is bonded to  $(L_2)_w$ -DI in formula (I).



ΗО 5 (R<sub>13</sub>) 2 (B-2) ОН 10 15 ΗО (B-3) (R<sub>13</sub>) e 20 25 NHSO<sub>2</sub> R<sub>14</sub> (B-4)  $(R_{13})$ 30 35 (B-5) 40 NHSO<sub>2</sub> R<sub>14</sub> 45

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 $(R_{13})_a$ 

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In formulas (B-1) to (B-10),  $R_{13}$  has the same meaning as  $R_{64}$ ,  $R_{14}$  and  $R_{15}$  each have the same meaning as  $R_{41}$ ,  $\ell$  is an integer of 0 to 2, m is an integer of 0 to 3, and a is an integer of 0 or 1.

Specific examples of B, which is released and forms a compound exhibiting a reducing action, include

the reducing agents described in U.S. Patents 4,741,994 and 4,477,560, JP-A-61-102646, JP-A-61-107245, JP-A-61-113060, JP-A-64-13547, JP-A-64-13548 and JP-A-64-73346.

When the group represented by B in formula (I) is a group which forms a substantially colorless compound by a coupling reaction with an oxidation product of a developing agent, examples of the group include phenol and naphthol coupler moieties, pyrazolone coupler moieties and indanone coupler moieties. These moieties are bonded to  $A-(L_1)_v$  through an oxygen atom. These coupler moieties become couplers after release from  $A-(L_1)_v$  and are coupled with oxidation products of developing agents. Usually, colored dyes are formed, but when diffusibility is properly increased without any nondiffusing group, the dyes are dissolved into processing solutions during development and hence the dyes are substantially not left behind in the photographic material. Alternatively, when the dyes formed are diffusing dyes, they react with alkaline ingredients (e.g., hydroxyl ion, sulfite ion) in developing solutions during development; the dyes are decomposed and are made colorless; and hence the dyes are substantially not left behind in the photographic material even when colored dyes are formed. Preferred examples of B include the following groups wherein the mark \* represents a position where each group is bonded to  $A-(L_1)_v$  and the mark \* represents a position where each group is bonded to  $(L_2)_w$ -DI

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meaning as R43.

In formulas (B-21), (B-22) and (B-23),  $R_{13}$ ,  $R_{14}$  and m are as defined above and  $R_{16}$  has the same

The group represented by B in formula (I) is preferably a group which reduces an oxidation product of a developing agent after release from  $A-(L_1)_v$ .

The compounds represented by formula (I) according to the present invention may be in the form of a polymer. All such polymers are included within the scope of the present invention. Namely, the polymers are derived from a monomer compound represented by the following general formula (P-1) and composed of a repeating unit represented by the following general formula (P-II), or copolymers of the monomer compound with at least one non-color forming monomer which has at least one ethylene group and is incapable of coupling with oxidation products of aromatic primary amine developing agents. Two or more members of the above monomer compounds may be polymerized simultaneously.

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$$RR$$
|
 $CH_2=C(A_{12})_i (A_{13})_j (A_{11})_k QQ$  (P-I)

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RR

$$(CH_2-C)$$
 $(A_{12})_{i}$ 
 $(A_{13})_{i}$ 
 $(A_{11})_{k}$ 
 $(A_{11})_{k}$ 

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In formulas (P-I) and (P-II), RR represents a hydrogen atom, a lower alkyl group having 1 to 4 carbon atoms or a chlorine atom;  $A_{11}$  represents -CONH-, -NHCONH-, -NHCOO-, -COO- -SO<sub>2</sub>-, -CO-, -NHCO-, -SO<sub>2</sub>NH-, -NHSO<sub>2</sub>-, -OCO-, -OCONH-, -NH- or -O-;  $A_{12}$  represents -CONH- or -COO-;  $A_{13}$  represents a substituted or unsubstituted alkylene or an aralkylene group preferably having 1 to 10 carbon atoms, or an unsubstituted arylene group. The alkylene group or alkylene moiety in the aralkylene group may be straight-chain or branched.

QQ represents a moiety of a compound represented by formula (I) and may be bonded to any site of A,  $L_1$ , B and  $L_2$ .

i, j, and k each represents 0 or 1, but there is no case where i, j and k are 0 simultaneously.

Examples of substituent groups for the alkylene group, the aralkylene group or the arylene group represented by A<sub>13</sub> include aryl (e.g., phenyl, naphthyl), nitro, hydroxyl, cyano, sulfo, alkoxy (e.g., methoxy), aryloxy (e.g., phenoxy), acyloxy (e.g., acetoxy), acylamino (e.g., acetylamino), sulfonamido (e.g., methanesulfonamido), sulfamoyl (e.g., methylsulfamoyl), halogen (e.g., fluorine, chlorine, bromine), carboxy, carbamoyl (e.g., methylsulfamoyl), alkoxycarbonyl (e.g., methoxycarbonyl) and sulfonyl (e.g., methylsulfonyl, phenylsulfonyl). When these groups have two or more substituent groups, the substituent groups may be the same or different.

Examples of the non-color forming ethylenic monomers which do not couple with oxidation products of aromatic primary amine developing agents include acrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -alkylacrylic acids, esters and amides derived from these acrylic acids, methylenebisacrylamide, vinyl esters, acrylonitrile, aromatic vinyl compounds, maleic acid derivatives and vinylpyridines. These non-color forming ethylenic unsaturated monomers may be used either alone or as a mixture of two or more of them.

As the group represented by DI in formula (I), moieties of conventional development inhibitors can be used. For example, a heterocyclic mercapto group, a 1-indazolyl group and a triazolyl group can be preferably used. More specifically, examples thereof include a tetrazolylthio group, a thiadiazolylthio group, an oxadiazolylthio group, a triazolylthio group, a benzomazolylthio group, a benzomazolylthio group, a 1-(or 2-)benztriazolyl group, a 1,2,4-triazole-1-(or 4-)yl group and a 1-indazolyl group. These groups may be substituted. Examples of substituent groups include aliphatic groups, aromatic groups, heterocyclic groups and those groups already described above in the definition of the substituent groups for the aromatic group.

The compounds of formula (I) according to the present invention can be synthesized by the methods described in U.S. Patents 4,618,571 and 4,770,982, JP-A-63-284159, JP-A-60-203943 and JP-A-63-23152.

Specific examples of the compounds of the present invention include, but are not limited to, the

following compounds.

(1) 5 C<sub>z</sub> H<sub>s</sub> NHCOC<sub>3</sub> F<sub>7</sub> оснсоин (t) C<sub>s</sub> H<sub>11</sub> 10 ΗO CONHC<sub>3</sub> H<sub>7</sub> HO 15 SCH2 CH2 CO2 CH3 20 (2) NHCOC<sub>3</sub> F<sub>7</sub> 25 (t) C<sub>5</sub> H<sub>11</sub> OCH2 CONH (t) C<sub>5</sub> H<sub>11</sub> HO. 30 CONHC<sub>3</sub> H<sub>7</sub> HO 35 N=N40

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(t) 
$$C_5 H_{11}$$

OCHCONH

OC

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(4)

$$C_2 H_5$$
 $OH$ 
 $NHCOC_3 F_7$ 

(t)  $C_5 H_{11}$ 
 $OH$ 
 $C_2 H_5$ 
 $OCHCONH$ 
 $OH$ 
 $O$ 

(6)

$$\begin{array}{c|c} C_{z}H_{5} & & & & & & & & \\ C_{z}H_{5} & & & & & & \\ \hline \\ (t)C_{5}H_{11} & & & & & & \\ \hline \\ (t)C_{5}H_{11} & & & & & \\ \hline \\ C & & & & \\ \hline \\ C & & & \\ \hline \\ C & & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ \hline \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ \hline \\ C & & \\ C & & \\ C & & \\ \hline \\ C & & \\$$

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(t) 
$$C_2$$
  $H_5$ 

OH

NHCOC<sub>3</sub>  $F_7$ 

(t)  $C_5$   $H_{11}$ 

OH

N-N

OH

C<sub>2</sub>  $H_5$ 

OCHCONH

OH

C<sub>3</sub>  $F_7$ 

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$$CH_{3}O \longrightarrow CH_{2}-S \longrightarrow N-N$$

$$OH NO_{2}$$

(9)
$$C_{4} H_{9} \longrightarrow NHCO \longrightarrow NHCO \longrightarrow HO \longrightarrow CONHC_{7} H_{15}$$

$$N \longrightarrow N \longrightarrow CO_{2} CH_{3}$$

$$C_{5} H_{11}(t)$$

$$C_{7} H_{11}(t)$$

$$C_{8} H_{11}(t)$$

$$C_{13} H_{11}(t)$$

$$C_{14} H_{11}(t)$$

$$C_{15} H_{11}($$

20 (14)

OH OH

OH OH

$$CH_{2}$$
 $CH_{3}$ 
 $CH_{4}$ 
 $CH_{3}$ 
 $CH_{4}$ 
 $CH_{4}$ 
 $CH_{4}$ 
 $CH_{5}$ 
 $CH_{5}$ 

(15)

(16)

(19)

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$$C_{18}H_{37}O \longrightarrow COCHCONH \longrightarrow OCH_{3}$$
 $OCH_{3}$ 
 $OCH_{3}$ 
 $OCH_{3}$ 
 $OCH_{3}$ 
 $OCH_{3}$ 

NHCOCH3

(23)

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(25)

$$C_{8} H_{17}OOC$$
 $COOC_{8} H_{17}$ 
 $COOC_{8} H_{17}$ 
 $COOC_{8} H_{17}$ 
 $COOC_{8} H_{17}$ 
 $COOC_{8} H_{17}$ 
 $COOC_{8} H_{17}$ 
 $OCH_{3}$ 
 $OCH_{3}$ 

20 (26)

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It is preferred that the compounds of formula (I) according to the present invention be added to sensitive silver halide emulsion layers or adjoining layers in the photographic materials. It is particularly preferred that the compounds be added to the red-sensitive silver halide emulsion layer. The compounds are used in an amount of  $1 \times 10^{-6}$  to  $1 \times 10^{-3}$  mol/m², preferably  $3 \times 10^{-6}$  to  $5 \times 10^{-4}$  mol/m², more preferably  $1 \times 10^{-5}$  to  $2 \times 10^{-6}$  mol/m².

The compounds of formula (I) according to the present invention can be added in the same manner as in the addition of conventional couplers described hereinafter.

The yellow colored cyan couplers of the present invention will be described in more detail below.

The yellow colored cyan couplers of the present invention refer to cyan couplers which have an absorption maximum at 400 nm to 500 nm in the visible absorption region of the couplers and which form cyan dyes having an absorption maximum at 630 nm to 750 nm in the visible absorption region by the coupling thereof with the oxidation product of an aromatic primary amine developing agent.

Among the yellow colored cyan couplers of the present invention, there are preferred cyan couplers which release a moiety of a water-soluble compound. Examples of the moiety include a 6-hydroxy-2-pyridone-5-ylazo group, a pyrazolone-4-ylazo group, a 2-acylaminophenylazo group or a 2-sul-

fonamidophenylazo group, and a 5-aminopyrazol-4-ylazo- gorup by a coupling reaction with the oxidation product of an aromatic primary amine developing agent.

The water soluble compound should be dissolved out from the photographic material during development processing. The compound is preferably soluble in a developing solution of pH 9 to 12 in an amount of at least 1 g/ $\ell$ , more preferably at least 3 g/ $\ell$  at 25° C.

Preferably, the colored cyan couplers of the present invention can be represented by the following general formulas (CI) to (CIV).

C p - (T)<sub>k</sub> - X - Q - N = N 
$$\stackrel{R_1}{\longrightarrow}$$
 R<sub>2</sub>

H O R<sub>3</sub>

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$$C p - (T)_{x} - X - Q - N = N - (R^{5})_{i}$$

$$H N$$

$$|$$

$$R^{4}$$

C p - (T)<sub>i</sub> - X - Q - N = N 
$$\stackrel{R}{\longrightarrow}$$
 (C-III)

H N  $\stackrel{|}{\downarrow}$   $\stackrel{|}{\downarrow}$   $\stackrel{|}{\downarrow}$   $\stackrel{|}{\downarrow}$ 

C p - (T)<sub>k</sub> - X - Q - N = N 
$$\stackrel{R}{\longrightarrow}$$
 (C-IV)

R

R

R

P

R

P

R

P

In formulas (CI) to (CIV), Cp represents a cyan coupler moiety (T is bonded to the coupling site thereof); T represents a timing group; k represents an integer of 0 or 1; X represents an N-, O- or S-containing bivalent group which is bonded to  $(T)_k$  through the N, O or S atom and which also is bonded to Q; and Q represents an arylene group or a bivalent heterocyclic group (preferably containing 6 to 12 carbon atoms, e.g., phenylene, naphthylene).

In formula (CI),  $R_1$  and  $R_2$  are independently a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aryl group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group;  $R_3$  is a hydrogen atom, an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aryl group or a heterocyclic group; and at least one of T, X, Q,  $R_1$ ,  $R_2$  and  $R_3$  has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, amino, ammoniumyl, phosphono, phosphino, hydroxysulfonyloxy).

It will be understood that the group of

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-N=N +N +N +N +N

in formula (CI) can exist in tautomeric forms as follows. All such tautomeric structures are included within the scope of the compounds of formula (I) of the present invention.

(where R<sub>3</sub> is hydrogen)

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(where 
$$R_3$$
 is hydrogen) (where  $R_3$  is hydrogen)

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(where R3 is hydrogen)

In formula (CII),  $R_4$  is an acyl group or a sulfonyl group;  $R_5$  is a group which can be attached to the benzene ring; j is an integer of 0 to 4; when j is 2 or greater, the two or more  $R_5$  groups may be the same or different; and at least one of T, X, Q,  $R_4$  and  $R_5$  has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, phosphono, phosphino, hydroxysulfonyloxy, amino, ammoniumyl).

In formulas (CIII) and (CIV), R<sub>3</sub> is a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aryl group, an alkoxy group, a cycloal-kyloxy group, an aryloxy group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, an alkylsulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group or a sulfonyl group; R<sub>10</sub> is a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; and at least one of T, X, Q, R<sub>3</sub> and R<sub>10</sub> has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, phosphono, phosphino, hydroxysulfonyloxy, amino, ammoniumyl).

Further, the compounds having the following group exist in a tautomeric form.

The compounds represented by general formulas (CI) to (CIV) will be discussed in more detail below. Examples of the coupler moiety represented by Cp include conventional cyan coupler moiety (e.g.,

Examples of the coupler molety represented by Cp include conventional cyan coupler molety (e.g. phenol and naphthol couplers).

Preferred examples of Cp are coupler moiety represented by general formulas (Cp-6), (Cp-7) and (Cp-8) among those exemplified in the description of the compounds of formula (I).

The timing group represented by T in formulas (CI) to (CIV) is a group which is cleaved from X after the cleavage of the bond between Cp and T by the coupling reaction of the couplers with an oxidation product of an aromatic primary amine developing agent. The timing group is used for various purposes, e.g., stabilizing the couplers, controlling the release timing of X, etc. Examples of the timing group include conventional timing groups represented by formulas (T-1) to (T-7) exemplified in the description of the compounds of formula (I).

Though k may be an integer of 0 or 1, it is generally preferred the case where k is 0, that is, Cp is directly bonded to X.

X is a bivalent group which is bonded to  $(T)_k$  through an N, O or S atom. Preferably, X is -O-, -S-,

-OSO<sub>2</sub>-, -OSO<sub>2</sub>NH- or a bivalent group which is bonded to (T)<sub>k</sub> through N, such as a heterocyclic group (e.g., a group derived from pyrrolidine, piperidine, morpholine, piperazine, pyrrole, pyrazole, imidazole, 1,2,4-triazole, benztriazole, succinimide, phthalimide, oxazolidine-2,4-dione, imidazolidine-2,4-dione, 1,2,4-triazolidine-3,5-dione or the like) or a composite group derived from these groups and an alkylene group (e.g., methylene, ethylene, propylene), a cycloalkylene group (e.g., 1,4-cyclohexylene), an arylene group (e.g., o-phenylene, p-phenylene), a bivalent heterocyclic group (e.g., a group derived from pyridine, thiophene or the like), -CO-, -SO<sub>2</sub>-, -COO-, -CONH-, -SO<sub>2</sub>NH-, -SO<sub>2</sub>O-, -NHCO-, NHSO<sub>2</sub>-, -NHCONH-, -NHSO<sub>2</sub>NH- or -NHCOO-. More preferably, X is a group represented by the following general formula (II):

$$*-X_1-(L-X_2)_m**$$
 (II)

In formula (II), the mark \* represents the position where the group is bonded to  $(T)_k$ ; the mark \*\* represents the position where the group is bonded to Q;  $X_1$  represents -O- or -S-; L represents an alkylene group;  $X_2$  represents a single bond, -O-, -S-, -CO-, -SO<sub>2</sub>-,

-\$O<sub>2</sub>NH-, -NHSO<sub>2</sub>-, -\$O<sub>2</sub>O-, -OSO<sub>2</sub>-,

-NHSO2NH-,

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 $-OSO_2NH$ - or  $NHSO_2O$ -; and m represents an integer of 0 to 3. The sum total of carbon atoms (hereinafter referred to as the carbon number) in X is preferably 0 to 12, more preferably 0 to 8. Most preferably, X is  $-OCH_2CH_2O$ -.

Q is an arylene group or a bivalent heterocyclic group. When Q is an arylene group, the arylene group may be a condensed ring and may have one or more substituent groups (examples of the substituent groups include halogen atom, hydroxyl, carboxyl, sulfo, nitro, cyano, amino, ammonium, phosphono, phosphino, alkyl, cycloalkyl, aryl, carbonamido, sulfonamido, alkoxy, aryloxy, acyl, sulfonyl, carboxyl, cabamoyl and sulfamoyl). The arylene group has preferably 6 to 15 carbon atoms, more preferably 6 to 10 carbon atoms. When Q is a bivalent heterocyclic group, the heterocyclic group is a 3-membered to 8-membered, preferably 5-membered to 7-membered, monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, O, S, P, Se and Te as a member of the heterocyclic ring (e.g., a group derived from pyridine, thiophene, furan, pyrrole, pyrazole, imidazole, thiazole, oxazole, benzthiazole, benzoxazole, benzofuran, benzothiophene, 1,3,4-th-

iodiazole,indole, and quinoline) and may have one or more substituent groups (examples of the substituent groups being the same as those for the arylene group of Q). The carbon number is preferably 2 to 15, more preferably 2 to 10. Preferably, Q is

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Accordingly, the most preferred -(T)<sub>k</sub>-X-Q- is

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The aliphatic hydrocarbon group represented by R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> may be any of a straight-chain and branched (e.g., alkyl), and may contain unsaturated bonds and may have one or more substituent groups (examples of the substituent groups include halogen atom, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxycarbonyl, amino, ammoniumyl, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, and sulfonyl).

When  $R_1$ ,  $R_2$  or  $R_3$  is an alicyclic hydrocarbon group, the group is a 3-membered to 8-membered group which may have crosslinking groups, unsaturated bonds or substituent groups (examples of the substituent groups being the same as those described above in the definition of the substituent groups for the aliphatic hydrocarbon group of  $R_1$ ,  $R_2$  or  $R_3$ ).

When  $R_1$ ,  $R_2$  or  $R_3$  is an aryl group, the aryl group may be a condensed ring and may have one or more substituent groups (examples of the substituent groups being an alkyl group, a cycloalkyl group and those described above in the definition of the substituent groups for the aliphatic hydrocarbon group of  $R_1$ ,  $R_2$  or  $R_3$ ).

When  $R_1$ ,  $R_2$  or  $R_3$  is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered, preferably 5-membered to 7-membered, monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring (e.g., imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl, quinolynyl) and may have one or more substituent groups (examples of the substituent groups being the same as those described above in the definition of the substituent groups for the aryl group of  $R_1$ ,  $R_2$  or  $R_3$ ).

In this description, carboxyl group may include carboxylato group, sulfo group may include sulfonato group, phosphino group may include phosphinato group and phosphono group may include phosphonato group. Counter ions are Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, ammonium, etc.

Preferably, R<sub>1</sub> is a hydrogen atom, a carboxyl group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, t-butyl, sulfomethyl, 2-sulfomethyl, carboxymethyl,2-carboxymethyl, 2-hydroxymethyl, benzyl, ethyl, isopropyl) or an aryl group having 6 to 12 carbon atoms (e.g., phenyl, 4-methoxyphenyl, 4-sulfophenyl) with a hydrogen atom, a methyl group or a carboxyl group being particularly preferred.

Preferably,  $R_2$  is a cyano group, a carboxyl group, a carbamoyl group having 1 to 10 carbon atoms, a sulfamoyl group having 0 to 10 carbon atoms, a sulfo group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, sulfomethyl), a sulfonyl group having 1 to 10 carbon atoms (e.g., methylsulfonyl, phenylsulfonyl), a carbonamido group having 1 to 10 carbon atoms (e.g., acetamido, benzamido) or a sulfonamido group having 1 to 10 carbon atoms (e.g., methanesulfonamido, toluenesulfonamido) with a cyano group, a carbamoyl group or a carboxyl group being particularly preferred.

Preferably,  $R_3$  is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms (e.g., methyl, sulfomethyl, carboxymethyl, ethyl, n-butyl, benzyl, 4-sulfobenzyl) or an aryl group having 6 to 15 carbon atoms (e.g., phenyl, 4-carboxyphenyl, 3-carboxyphenyl, 4-methoxyphenyl, 2,4-dicarboxyphenyl, 2-sulfophenyl, 3-sulfophenyl, 4-sulfophenyl, 2,5-disulfophenyl) among which an alkyl group having 1 to 7 carbon atoms or an aryl group having 6 to 10 carbon atoms is more preferred.

R<sub>4</sub> preferably is an acyl group represented by the following general formula (III) or a sulfonyl group represented by the following general formula (IV):

$$R_{11}^{C-}$$
 (III)

 $R_{11}^{SO_2-}$  (IV)

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When R<sub>11</sub> is an aliphatic hydrocarbon group, the group includes both straight-chain and branched groups (preferably having1 to 6 carbon atoms), and may contain unsaturated bonds and may have one or more substituent groups (examples of the substituent groups include halogen atom, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxycarbonyl, amino, ammoniumyl, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, and sulfonyl).

When  $R_{11}$  is an alicyclic hydrocarbon group, the group is a 3-membered to 8-membered group which may contain crosslinking groups and unsaturated bonds and may have one or more substituent groups (examples of the substituent groups being those described above in the definition of the substituent groups for the aliphatic hydrocarbon group of  $R_{11}$ ).

When  $R_{11}$  is an aryl group, the aryl group may be a condensed ring and may have one or more substituent groups (examples of the substituent groups include an alkyl group, a cycloalkyl group and those described above in the definition of the substituent groups for the aliphatic hydrocarbon group of  $R_{11}$ ).

When R<sub>11</sub> is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring (e.g., imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl, quinolyl) and may have one or more substituent groups (examples of the substituent groups being those described above in the definition of the substituent groups for the aryl group of R<sub>11</sub>).

In this description, carboxyl group may include carboxylato group, sulfo group may include sulfonato group, phosphino group may include phosphinato group and phosphono group may include phosphonato group. Counter ions are Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, ammonium, etc.

Preferably,  $R_{11}$ , is an alkyl group having 1 to 10 carbon atoms (e.g., methyl, carboxymethyl, sulfoethyl, cyanoethyl), a cycloalkyl group having 5 to 8 carbon atoms (e.g., cyclohexyl, 2-carboxycyclohexyl) or an aryl group having 6 to 10 carbon atoms (e.g., phenyl, 1-naphthyl, 4-sulfophenyl) among which an alkyl group having 1 to 3 carbon atoms and an aryl group having 6 carbon atoms are particularly preferred.

 $R_5$  is a group which can be attached to the benzene ring and is preferably an electron donative group. Particularly preferably,  $R_5$  is a group of  $-NR_{12}R_{13}$  or  $-OR_{14}$  which is preferably attached to the 4-position of the ring.  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are each a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group and each has the same meaning as  $R_{11}$ .  $R_{12}$  and  $R_{13}$  may be combined together to form a ring. As the ring to be formed, a nitrogen-containing heterocyclic ring wherein atoms other than the nitrogen all are carbon atoms is preferred.

j is an integer of 0 to 4, preferably 1 to 2, particularly preferably 1.

When  $R_9$  or  $R_{10}$  is an aliphatic hydrocarbon group, the group may be any of a straight chain group and a branched group, may contain unsaturated bonds and may have one or more substituent groups (e.g., halogen atom, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxycarbonyl, amino, ammonium, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, sulfonyl).

When  $R_9$  or  $R_{10}$  is an alicyclic hydrocarbon group, the group is a 3-membered to 8-membered group which may have crosslinking groups, unsaturated bonds or substituent groups (examples of the substituent groups being those described above in the definition of the substituent groups for the aliphatic hydrocarbon group of  $R_9$  or  $R_{10}$ ).

When  $R_9$  or  $R_{10}$  is an aryl group, the aryl group may be a condensed ring and may have one or more substituent groups (examples of the substituent groups being an alkyl group, a cycloalkyl group and those described above in the definition of the substituent groups for the alipahtic hydrocarbon group of  $R_9$  or  $R_{10}$ ).

When  $R_9$  or  $R_{10}$  is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring (e.g., imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl, quinolynyl) and may have one or

more substituent groups (examples of the substituent groups being those described above in the definition of the substituent groups for the aryl group of  $R_9$  or  $R_{10}$ ).

In this description, carboxyl group may include carboxylato group, sulfo group may include sulfonato group, phosphino group may include phosphinato group and phosphono group may include phosphonato group. Counter ions are Li<sup>†</sup>, Na<sup>†</sup>, K<sup>†</sup>, ammonium, etc.

Preferably, R<sub>9</sub> is a cyano group, a carboxyl group, a carbamoyl group having 1 to 10 carbon atoms, an alkoxycarbonyl group having 2 to 10 carbon atoms, an aryloxycarbonyl group having 7 to 11 carbon atoms, a sulfamoyl group having 0 to 10 carbon atoms, a sulfo group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, carboxymethyl, sulfomethyl), a sulfonyl group having 1 to 10 carbon atoms (e.g., methylsulfonyl), a carbonamido group having 1 to 10 carbon atoms (e.g., acetamido, benzamido), a sulfonamido group having 1 to 10 carbon atoms (e.g., methanesulfonamido, toluenesulfonamido), an alkyloxy group (e.g., methoxy, ethoxy) or an aryloxy group (e.g., phenoxy) among which a cyano group, a carbamoyl group, an alkoxycarbonyl group and a carboxyl group are particularly preferred.

Preferably, R<sub>10</sub> is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms (e.g., methyl, sulfomethyl, carboxymethyl, ethyl, 2-sulfoethyl, 2-carboxyethyl, 3-sulfopropyl, 3-carboxypropyl, 5-sulfopentyl, 5-carboxypentyl, 4-sulfobenzyl) or an aryl group having 6 to 15 carbon atoms (e.g., phenyl, 4-carboxyphenyl, 3-carboxyphenyl, 2,4-dicarboxyphenyl, 4-sulfophenyl, 3-sulfophenyl, 2,5-disulfophenyl, 2,4-disulfophenyl) among which an alkyl group having 1 to 7 carbon atoms or an aryl group having 6 to 10 carbon atoms is more preferred.

Specific examples of Cp, X, Q,

35 HN | R<sup>5</sup> | 1

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o in formulas (CI) to (CIV) include the following groups.

(Examples of Cp)

45

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50

20

25

OH 
$$CONH(CH_2)_3OC_{12}H_{25}(n)$$

OH  $CONH(CH_2)_3OC_{12}H_{25}(n)$ 

OH  $CONH(CH_2)_4OC_{12}H_{25}(n)$ 

45 CONH CONH

50

$$\begin{array}{c|c} OH & C_5H_{11}(t) \\ \hline \\ CONH(CH_2)_3O & -C_5H_{11}(t) \\ \hline \\ C_5H_{11}(t) \\ \hline \\ C$$

50

55

- 40

0H 
$$CONH(CH_2)_4SO_2 - C_{12}H_{25}(soft)$$

(Examples of X)

(Examples of Q)

40 CH<sub>2</sub>CH<sub>2</sub>SU<sub>3</sub>N a

$$CH,CONH$$

$$= O$$

$$CH,COOH$$

$$CH,COOH$$

$$CH,COOH$$

C H 2 S O 3 N a

C N

$$= O$$

H O C H 2 C H 2 S O 3 N a

ΗÓ CH2CH2SO3K 35

45

COOH COOH CONH 2. 40 ΗÓ Н  $CH_2COOH$ ΗO

50

CH3, CH2SO3Na CH3,CONHCH3 5 C 2 H 5 HO H O  $SO_3Na$ CH<sub>3</sub>,CN 10 ΗÓ COOH 15 COOH 20 CH3, CONH2 25 ΗÓ C H 2 C H 2 N (C H 3) 2 ΗCℓ 30 CH3,SO2CH3 = 0 ΗO -SO<sub>3</sub>Na 35  $SO_3N$ a

*4*5

40

50

CH2CO2H
CONH2
$$= O$$
HO CH2CH2SO3N a

$$\begin{array}{c} C H_2 C O_2 H \\ C N \\ = O \\ H O C H_2 C H_2 S O_3 N a \end{array}$$

$$\begin{array}{c} C H_2 S O_3 N a \\ C O N H_2 \end{array}$$

$$= O$$

$$H O C O_2 H$$

C H 2 C O 2 H

C N

$$= O$$
H O

S O 3 N a

SO3Na

$$CH_3CN$$

$$= O SO_3Na$$

$$HO$$

$$SO_3Na$$

$$\begin{array}{c}
C H_3 C O N H_2 \\
\longrightarrow = O \\
H O \\
N a O_3 S \\
\end{array}$$

$$\begin{array}{c}
S O_3 N a
\end{array}$$

$$\begin{array}{c} CH_3CN \\ \longrightarrow \\ HO \end{array}$$

$$\begin{array}{c|c}
C H_3 C N \\
\longrightarrow & = O \\
H O & C O O H
\end{array}$$

 $\begin{array}{c}
C H_{3} C N \\
\longrightarrow N \\
+ O \\
\end{array}$ 

$$CH_3$$
  $CN$ 

$$CH-COOH$$

$$CH_3$$

$$\begin{array}{c}
 & C & O & O & H \\
 & C & O & O & H \\
 & C & O & O & H
\end{array}$$

Examples of 
$$HN$$

$$R$$

10 
$$\begin{array}{c|c} & C_2H_5 \\ \hline & C_2H_4SO_3N_2 \end{array}$$

$$-N = C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$\begin{array}{c|c}
& C H \cdot C O \cdot H \\
& C H \cdot C O \cdot H \\
& H \cdot N \cdot C \cdot O \cdot C \cdot H \\
\end{array}$$

$$\begin{array}{c|c}
& C_2H_3 \\
& C_2H_3O_3N_2
\end{array}$$

Examples of 
$$CH_1$$
 $CH_1$ 
 $CH_1$ 
 $CH_2$ 
 $CH_3$ 
 $CH_3$ 

C O 2 H

 $C H_2 C H_2 S O_3 N a$ CH2CO2H CH2CH2SO3Na O C 2 H 5 CH2CH2SO;Na 

NHCOCH, 5 CH2CH2SO1Na 10 NHCOCH<sub>3</sub> N | CH2CO2H 15 NHCOCH; 20 25 SO:Na 30 NHCOC2H: 35 S O i N a

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N H C O C H,

l C O ₂ H

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NHCOC(CH<sub>3</sub>)<sub>3</sub>

20 H O 2 C O 2 H

25 O N N C H 2 C O 2 H

CONHC<sub>2</sub>H<sub>5</sub>

N

CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>N a

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C O 2 C 2 H 5 5 CH2CO2H 10 C O 2 C 2 H 5 HN 15 20  $SO_3Na$ CONH2 25 CH2CH2SO3Na 30 CONH<sub>2</sub> 35 40

45

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5 HNNN CONH 2

SO3N a

HNNNN OCH 3

HN N N CH2CH2SO3Na

HO2CCCO2H

CH;

HN

N

CH2CH2SO3Na

Examples of Colored Couplers of the Invention

(YC - 1)

$$0 CH_2 CH_2 O \longrightarrow -N = N \longrightarrow 0$$

$$0 CH_2 CH_2 SO_3 Na$$

15 (YC-2)

$$\begin{array}{c}
0H \\
CONHC_{12}H_{25}-n
\end{array}$$

$$\begin{array}{c}
CH_{3} & CONH_{2} \\
CH_{3} & CONH_{2}
\end{array}$$

$$\begin{array}{c}
0CH_{2}CH_{2}0 - N = N - N = N
\end{array}$$

$$(YC - 3)$$

30

OH

$$CONH$$
 $C_6H_{13}-n$ 
 $CH_3CN$ 
 $CH_3CN$ 
 $CH_3CN$ 
 $CH_3CN$ 
 $CH_3CN$ 
 $CH_3CN$ 
 $CH_3CN$ 

· SO₃Na

(YC - 10)

$$\begin{array}{c|c}
OH & & & & & & & & & & & & & & & \\
\hline
CONH(CH_2)_3 & & & & & & & & & & \\
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CONH(CH_2)_3 & & & & & & & & & \\
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CH_3 & & & & & & & & \\
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$$(YC - 11)$$

CONH(CH<sub>2</sub>)<sub>3</sub>0  $\leftarrow$  C<sub>5</sub>H<sub>11</sub>-t

C<sub>5</sub>H<sub>11</sub>-t

CH<sub>3</sub> CN

NaO<sub>3</sub>S

(YC - 12)

$$i - C_4 H_8 O CNH$$

$$0$$

$$CH_3 CN$$

$$N = N$$

$$CONH(CH_2)_40 \longrightarrow C_5H_{11}-t$$

$$C_5H_{11}-t$$

CH2CH2SO3Na

$$N = N - CH_2 SO_3 Na$$

$$N = N - O$$

$$HO CH_2 COOH$$

(YC - 14)

5
$$0H$$

$$CONHC_{12}H_{25}-n$$

$$0CH_{2}CONH$$

$$N = N$$

$$HO$$

$$CH_{2}CH_{2}SO_{3}Na$$

20

(YC - 15)

15

35

OH
$$CONHC_{1} \in H_{3} = n$$

$$CH_{2} SO_{3} Na$$

$$CONH_{2}$$

$$CONH_{2}$$

$$OCH_{2} CH_{2} CONH$$

$$S$$

$$OCH_{2} CH_{2} CONH$$

$$CH_{2} CH_{2} COOH$$

40

**45** 

(YC - 16)

$$C_{5}H_{11}-t \longrightarrow NHCONH \longrightarrow -CN$$

$$C_{4}H_{5}-n \longrightarrow 0$$

$$C_{5}H_{11}-t \longrightarrow 0$$

$$C_{4}H_{5}-n \longrightarrow 0$$

$$C_{7}H_{2}CH_{2}SO_{2}Na$$

(YC - 17)

$$C \mathcal{L}$$

$$C_{\mathfrak{s}} H_{1 \, 1} - OCHCONH$$

$$C_{\mathfrak{s}} H_{1 \, 1} - OCHCONH$$

(YC - 18)

5 
$$t-C_5H_{11}$$
 OH
$$C_5H_{11}-t$$

$$-0CHCONH$$

$$C_4H_9-n$$

$$0CH_2COOCH_2CH_2O$$

$$-N=N$$

$$CH_2CH_2SO_3Na$$

(YC - 19)

25

$$C \, \ell \qquad \qquad NHCOC_{15} \, H_{31} - n$$

$$C_{2} \, H_{5} \qquad \qquad O$$

$$CH_{3} \quad CONH_{2}$$

$$N = N \qquad \qquad = 0$$

$$N = N \qquad \qquad O$$

40

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$$(YC - 20)$$

$$0H$$

$$0CH_{2}CH_{2}O$$

$$CO_{2}H$$

$$0CH_{3}$$

$$CONHC_{1} * H_{3} * (n)$$

$$CH_{3}$$

$$CONH_{2}$$

$$H_{0}$$

$$N$$

$$N$$

$$0$$

CH2CH2SO3Na

$$(YC-21)$$

25
$$CONH(CH_2)_3OC_{12}H_{25}N$$

$$CH_3$$

$$CH_3$$

$$CONH_2CHO \longrightarrow N = N$$

$$CONH_2$$

$$CONH_2$$

CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na

(YC - 21)

5

OH

$$C_5H_{11}$$
 $C_5H_{11}$ 
 $C_5H_{11}$ 

$$(YC - 23)$$

CONHC<sub>1</sub> 
$$_{2}$$
  $_{2}$   $_{5}$ 

CH<sub>3</sub>

CONH<sub>2</sub>  $_{2}$   $_{6}$   $_{7}$   $_{1}$   $_{2}$   $_{5}$ 

CH<sub>3</sub>

CONH<sub>2</sub>

CONH<sub>2</sub>
 $_{1}$   $_{2}$   $_{1}$   $_{2}$   $_{3}$   $_{4}$   $_{1}$   $_{1}$   $_{5}$   $_{6}$   $_{1}$   $_{1}$   $_{1}$   $_{1}$   $_{2}$   $_{3}$   $_{4}$   $_{1}$   $_{5}$   $_{1}$   $_{1}$   $_{2}$   $_{3}$   $_{4}$   $_{1}$   $_{4}$   $_{5}$   $_{5}$   $_{1}$   $_{2}$   $_{3}$   $_{4}$   $_{4}$   $_{5}$   $_{5}$   $_{2}$   $_{5}$   $_{4}$   $_{5}$   $_{5}$   $_{5}$   $_{5}$   $_{6}$   $_{7}$ 

(YC - 24)

$$\begin{array}{c}
OH & C_6H_{13}-n \\
\hline
CONHCH_2CC_8H_{17}-n \\
\hline
OCH_2CH_2O \longrightarrow -N=N \longrightarrow = 0 \\
HO
\end{array}$$

(YC - 25)

OH 
$$C_6H_{13}-n$$

$$CONHCH_2CHC_8H_{17}-n$$

$$CH_3 CN$$

$$CH_3 CN$$

$$N=N$$

$$HO$$

$$C00H$$

(YC - 26)

5

OH

$$C_6H_{13}-n$$
 $CONHCH_2CHC_8H_{17}-n$ 
 $CH_3$ 
 $CONH_2$ 
 $OCH_2CH_2O$ 
 $N=N$ 
 $N=N$ 
 $N=0$ 
 $N=0$ 

(YC - 27)

$$\begin{array}{c}
OH & C_2H_5 \\
\hline
CONH(CH_2)_3OCH_2CHC_4H_9-n \\
\hline
CH_3 & CN \\
OCH_2CH_2O \longrightarrow -N=N \longrightarrow = 0 \\
HO
\end{array}$$

COOH

соон 

(YC - 28)

$$0 CH_2 CH_2 O \longrightarrow -N = N \longrightarrow 0$$

$$0 CH_3 CN$$

$$0 CH_2 CH_2 O \longrightarrow -N = N \longrightarrow 0$$

$$0 COOH$$

(YC - 29)

30 НО N СООН

(YC - 30)

OH 
$$C_6H_13-n$$

$$CONH(CH_2)_3OCH_2CHC_8H_17-n$$

$$CH_3CN$$

$$OCH_2CH_2O \longrightarrow -N=N \longrightarrow 0$$

$$HO COOH$$

$$0CH_{2}CH_{2}O \longrightarrow -N = N \longrightarrow 0$$

$$HO \qquad COOH$$

$$(YC - 32)$$

5
$$0H$$

$$CONHC_{12}H_{25}$$

$$0CH_{2}CH_{2}O$$

$$NHCOCH_{3}$$

$$C_{2}H_{4}SO_{3}Na$$

$$(YC - 33)$$

20 
$$CONHC_{12}H_{25}(n)$$

$$OCH_{2}CH_{2}O \longrightarrow -N = N \longrightarrow -N \xrightarrow{C_{2}H_{5}} C_{2}H_{4}SO_{3}Na$$

$$NHSO_{2}CH_{3}$$

$$(YC - 34)$$

$$\begin{array}{c|c}
OH & C_8H_17 \\
\hline
CONHCH_2CHC_6H_15 \\
\hline
OCH_2CH_2O & \longrightarrow -N = N \longrightarrow -N \\
\hline
CH_2CO_2H_5 \\
\hline
CH_2CO_2H_5
\end{array}$$

$$(Y C - 3 5)$$

$$0H$$

$$CONH(CH_2)_3OC_{12}H_{25}$$

$$(1)C_1H_3OCN OCH_2CH_2O O O N = N O NHCOCH_3$$

$$C_2H_4SO_3N$$

$$0H CONH(CH_2)_3O O O C_5H_{11}(t)$$

$$0CH_2CH_2O O O N = N O NHCOCH_3$$

$$(Y C - 3 6)$$

$$0CH_2CH_2O O O N = N O NHCOC_2H_3$$

$$(Y C - 3 7)$$

$$0H CONH(CH_2)_4O O O C_5H_{11}(t)$$

$$0CH_2CH_2O O O N = N O NHCOC_2H_3$$

$$0CH_2CH_2O O O N = N O NHCOC_2H_3$$

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45

(YC - 38)

OH
$$CONHC._{1} \cdot H_{3} \cdot (n)$$

$$OCH_{2}CH_{2}O \longrightarrow -N = N \longrightarrow -N(CH_{3})$$

$$CO_{2}H \qquad NHCOCH_{3}$$

$$(Y C - 3 9)$$

$$0H$$

$$CONHC_{12}H_{25}(n)$$

$$0CH_{2}CHCH_{2}O$$

$$CO_{2}H$$

$$NHSO_{2}CH_{3}$$

(YC - 40)

$$\begin{array}{c|c}
0H & \text{NHCONH} & -\text{CN} \\
\downarrow 0 & \text{OCHCN} \\
C_5H_{11} & \text{C}_{11} & \text{C}_{11} \\
N = N & -N & \text{C}_2H_5 \\
C_7H_2CO_2H_3 & \text{C}_{12}CO_2H_3
\end{array}$$

(YC - 41).

$$\begin{array}{c|c} C_{5}H_{13}(n) & \text{NHCO} \\ \hline \\ C \ell & 0 & 0 \\ \hline \\ N = N & -N \\ \hline \\ C_{2}H_{4}SO_{3}Na \\ \hline \\ NHCOCH_{3} \end{array}$$

(YC - 42)

$$(YC - 43)$$

$$C = N + SO_3 = Na_1$$

$$N = N - N(C_2 + SO_3 + SO_3 + A)_2$$

(YC - 44)

5
$$0H \longrightarrow 0C_{14}H_{29}(n)$$

$$0CH_{2}CH_{2}O \longrightarrow -N = N \longrightarrow -N \longrightarrow C_{2}H_{5}$$

$$CH_{2}CO_{2}H_{3}$$

$$(YC - 45)$$

OH 
$$CONH$$
 $OCH_2CHC_6H_{13}$ 
 $C_8H_{17}$ 
 $OCH_2CH_2O$ 
 $OCH_2N$ 
 $OCH_2CH_3O$ 
 $OCH_2CH_3O$ 
 $OCH_3CH_3O$ 
 $OCH_3CH_3O$ 
 $OCH_3CH_3O$ 
 $OCH_3CH_3O$ 
 $OCH_3CH_3O$ 
 $OCH_3CH_3CH_3O$ 
 $OCH_3CH_3CH_3CH_3O$ 

$$(YC - 46)$$

OH CONHC 1 2 H 2 5

 $N = N \longrightarrow -N$   $C_2 H_4 SO_3 Na$   $NHCOCH_3$ 

$$(YC - 47)$$

$$\begin{array}{c} OH \\ \hline \\ OCH_2CH_2O \end{array} \begin{array}{c} ONHC_{12}H_{25}(n) \\ \hline \\ OCH_2CH_2O \end{array} \begin{array}{c} CO_2 \\ \hline \\ ONHC_{12}H_{25}(n) \\ \hline \\ ONHC_{12$$

$$(YC-48)$$

$$CONHC_{12}H_{25}(n)$$

$$OCH_{2}CH_{2}O$$

$$OCH_{2}N=N$$

CH<sub>2</sub>CH<sub>3</sub>

$$(Y C - 4 9)$$

$$0H$$

$$CONHC_{12}H_{25}(n)$$

$$0CH_{2}CH_{2}O \longrightarrow N = N$$

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

$$CH_{2}CH_{2}SO_{3}Na$$

$$(YC-50)$$
0H
$$CONH(CH_2)_3OC_{12}H_{25}(n)$$
25
$$OCH_2CH_2O \longrightarrow N=N$$

$$CN$$

$$CN$$

$$CH_2CH_2SO_3Na$$

(YC - 51)

OH 
$$C_8H_{17}(n)$$

$$CONHCH_2CHC_6H_{13}(n)$$

$$OCH_2CH_2O \longrightarrow -N=N$$

(YC - 52)

25

OH

$$C_8H_{17}(n)$$

CONHCH<sub>2</sub>CHC<sub>6</sub>H<sub>13</sub>(n)

OCH<sub>2</sub>CH<sub>2</sub>O

 $N$ 

N

 $N$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 

(YC-53)  $OH \qquad C_5H_{11}(t)$   $OCH_2CH_2O \qquad -N=N \qquad NHCOCH_3$   $C_5H_{11}(t)$   $OCH_2CH_2O \qquad -N=N \qquad NHCOCH_3$   $CH_2CH_2SO_3Na$ 

CH<sub>2</sub>CO<sub>2</sub>H

(YC - 55)

$$(YC - 56)$$

OH 
$$C_{10}H_{21}$$

$$CONHCH_{2}CHC_{6}H_{13}$$

$$OCH_{2}CH_{2}O$$

$$OCH_{2}N=N$$

$$CONH_{2}$$

CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na

# (YC - 57)

5

$$OH$$
 $CONH(CH_2)_3OC_{12}H_{25}(n)$ 

10

 $(i)C_4H_9OCN$ 
 $OCH_2CH_2O$ 
 $OCH_2CH_2$ 

(YC - 58)

$$\begin{array}{c} OH \\ CONH(CH_2)_3OC_{12}H_{25}(n) \\ OCH_2CH_2O \\ OONH_2 \\ O$$

(YC - 59)

(YC - 60)

$$\begin{array}{c} OH \\ CONH(CH_2)_3OC_{12}H_{25} \\ (i)C_4H_9OCN \\ OCH_2CH_2O \\ O \\ \\ O \\$$

.

$$(Y C - 6 1)$$

$$(t) C_{5} H_{11}$$

$$(t) C_{5} H_{12}$$

$$(t) C_{5} H_{11}$$

$$(t) C_{5} H_{12}$$

$$(t) C_{5} H_{12}$$

$$(t) C_{5} H_{13}$$

(YC - 63)

$$(t)C_{5}H_{11} \longrightarrow 0CHCN \longrightarrow CN$$

$$(t)C_{5}H_{11} \longrightarrow 0CHCN \longrightarrow CN$$

$$C_{5}H_{11} \longrightarrow 0CH_{2}CH_{2}O \longrightarrow N=N$$

$$C_{5}H_{11} \longrightarrow N$$

$$C_{7}H_{11} \longrightarrow N$$

$$C_{$$

(YC - 64)

COzH

(YC - 65)

$$\begin{array}{c} OH \\ OC_{14}H_{29}(n) \\ OCH_{2}CH_{2}O \end{array} \\ \begin{array}{c} OC_{14}H_{29}(n) \\ OCH_{2N}H_{2N} \end{array}$$

$$\begin{array}{c|c}
0H \\
0C_{1} & H_{2} & (n) \\
0CH_{2}CH_{2}O & \longrightarrow N = N \\
\hline
0 & N \\
CH_{2}CH_{2}SO_{3}Na
\end{array}$$

(YC - 67)

$$0 CH_2 CH_2 O \qquad \longrightarrow -N = N \qquad N$$

$$(YC - 68)$$

$$0 CH_2 CH_2 O$$

$$N = N$$

$$CO_2 H$$

CH2CH2SO3Na

SO<sub>3</sub>Na

(YC-69) OH  $CONHC_{12}H_{25}(n)$   $OCH_{2}CH_{2}O$   $C \ell$   $OCNH_{2}$ 

5

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$$(YC - 70)$$

35 O N

40 -

50

C.8 H 1.7

# (YC - 71)

OH 5 - CONHCH2CHC6H13

$$0 \text{ CH}_2 \text{ CH}_2 \text{ O} \qquad \qquad N = N \qquad N$$

15

$$(YC-72)$$

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$$0CH_{2}CH_{2}O \longrightarrow -N = N \longrightarrow N$$

50

20 (YC-74)

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25

OH  $CONHC_{12}H_{25}(n)$   $OCH_{2}CH_{2}O$   $OCH_{2}CH_{2}O$ 

CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na

45

50

(YC - 75)

OH 
$$C_8H_{17}(n)$$

CONHCH<sub>2</sub>CHC<sub>6</sub>H<sub>13</sub>(n)

CONH<sub>2</sub>

CONH<sub>2</sub>

HN

CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na

(YC - 76)

20
$$0H \qquad C_8H_{17}(n)$$

$$CONHCH_2CHC_6H_{13}(n)$$

$$0CH_2CH_2O \qquad N=N \qquad N$$

$$HN \qquad N$$

$$N$$

(YC - 77)

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

OCH<sub>2</sub>CH<sub>2</sub>O 
$$\longrightarrow$$
 N = N  $\longrightarrow$  N  $\longrightarrow$  N  $\longrightarrow$  N  $\longrightarrow$  N  $\longrightarrow$  CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na

(YC-78)

$$\begin{array}{c}
OH \\
C_5H_{11}(t) \\
-C_5H_{11}(t)
\end{array}$$

$$OCH_2CH_2O \longrightarrow -N = N \longrightarrow N$$

$$HN N N$$

35 SO<sub>3</sub> Na

(YC - 79)

5

OH

$$CONH(CH_2)_3OC_{12}H_{25}$$

10

(i)  $C_4H_3OCN$ 
 $OCH_2CH_2O$ 
 $HN$ 
 $N$ 
 $N$ 
 $CH_2CH_2SO_3N_3$ 

(YC - 80)

25

OH

$$CONH(CH_2)_3OC_{12}H_{25}$$

30

(i)C<sub>4</sub>H<sub>2</sub>OCN

OCH<sub>2</sub>CH<sub>2</sub>O

OCH<sub>2</sub>CH<sub>2</sub>O

HN

N

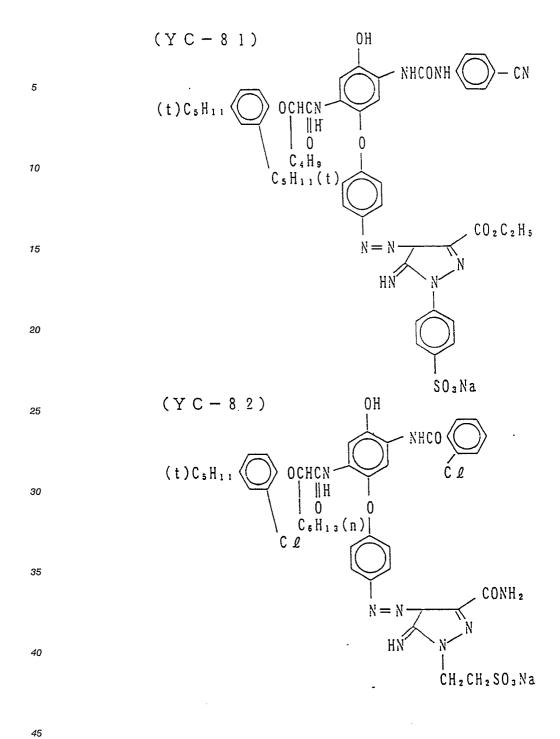
CO<sub>2</sub>H

CO<sub>2</sub>H

CO<sub>2</sub>H

OCH

CO<sub>2</sub>H



$$OCH_{2}CH_{2}O$$

$$N=N$$

$$HN$$

$$N$$

$$N$$

 $SO_3Na$ 

(YC - 85).

(YC-86)

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50

(YC - 87).

(YC-8.8)

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$$(YC - 89)$$

$$(YC - 90)$$

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The colored couplers represented by formula (CI) of the present invention can be generally synthesized by the diazo coupling reaction of a 6-hydroxy-2-pyridone compound with an aromatic diazonium salt or heterocyclic diazonium salt having a coupler structure.

The former 6-hydroxy-2-pyridone compounds can be synthesized by methods described in Klinsberg, Heterocyclic Compound - Pyridine and Its Derivatives, Part 3 (Interscience 1962); J. Am. Chem. Soc., Vol. 65, page 449 (1943); J. Chem. Tech. Biotechnol., Vol. 36, page 410 (1986); Tetrahedron, Vol. 22, page 445 (1966); JP-B-61-52827 (the term "JP-B" as used herein means an "examined Japanese patent publication"); West German Patents 2,162,612, 2,349,709 and 2,902,486; and U.S. Patent 3,763,170.

The latter diazonium salts can be synthesized according to the methods described in U.S. Patents 4,004,929 and 4,138,258, JP-A-61-72244 and JP-A-61-273543. The diazo coupling reaction of the 6-hydroxy-2-pyridone compounds with the diazonium salts can be carried out in a solvent such as methanol, ethanol, methyl cellosolve, acetic acid, N,N-dimethylformamide, N,N-dimethylacetamide, tetrahydrofuran, dioxane, water or the like or a mixture thereof. In this reaction, sodium acetate, potassium acetate, sodium

carbonate, potassium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, pyridine, triethylamine, tetramethylurea, or tetramethyl guanidine can be used as a base. The reaction temperature is generally from -78 to  $+60^{\circ}$  C, preferably from -20 to  $+30^{\circ}$  C.

Synthesis examples of the colored couplers of the present invention are described below.

### Synthesis Example 1

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Synthesis of Coupler (YC-1)

$$\text{NCCH}_2\text{COOCH}_3\text{+H}_2\text{NCH}_2\text{CH}_2\text{SO}_3\text{H} \longrightarrow \text{NCCH}_2\text{CONHCH}_2\text{CH}_2\text{SO}_3\text{K}$$

а

$$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 \\ \\ & \end{array} \end{array} \\ \begin{array}{c} \text{NC} \\ \\ \text{O} \\ \end{array} \\ \begin{array}{c} \text{NC} \\ \\ \text{OH} \\ \\ \text{CH}_2\text{CH}_2\text{SO}_3\text{H} \end{array}$$

b

OH 
$$CONHC_{12}H_{25-n}$$
  $NaNO_2$   $b$   $Coupler (YC-1)$ 

OCH<sub>2</sub>CH<sub>2</sub>O  $NH_2$ 

### Synthesis of Compound a

125.2 g of taurine and 66 g of potassium hydroxide were added to 500 ml of methanol. The mixture was stirred with heat-refluxing. 110 g of methyl cyanoacetate was added dropwise thereto over a period of about one hour. The mixture was heated to reflux for 5 hours and then left to stand overnight. The precipitated crystal was recovered by filtration, washed with ethanol and dried to give 202.6 g of the compound a as a crystal.

#### Synthesis of Compound b

11.5 g of the compound a and 3.5 g of potassium carbonate were added to 11.5 ml of water. While heating the mixture on a steam bath with stirring, 7.8 g of ethyl acetoacetate was added dropwise thereto. The mixture was stirred for 7 hours and then allowed to cool. 9.2 ml of concentrated hydrochloric acid was added thereto, whereby a crystal was precipitated. The crystal was recovered by filtration, washed with methanol and dried to give 10.4 g of the compound b as a crystal.

### Synthesis of Coupler (YC-1)

10.1 g of compound  $\underline{c}$  synthesized by the method described in U.S. Patent 4,138,258 was dissolved in

60 ml of N,N-dimethylformamide and 60 ml of methyl cellosolve. While cooling the resulting solution with ice, 4.3 ml of concentrated hydrochloric acid was added thereto and a solution of 1.84 g of sodium nitrite in 5 ml of water was added dropwise thereto to prepare a diazonium solution. 60 ml of methyl cellosolve and 20 ml of water were added to 7.8 g of the compound b and 8.2 g of sodium acetate. While stirring the resulting solution under ice cooling, the above diazonium solution was added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for 2 hours. The precipitated crystal was recovered by filtration, washed with water, dried and dispersed in 500 ml of methanol. The dispersion was heated to reflux for one hour and then allowed to stand to cool it. The crystal was recovered by filtration, washed with methanol and dried to give 13.6 g of the desired coupler (YC-1) as a red crystal with a melting point of 269 to 272° C (decomposition). The structure of the compound was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 457.7 nm and had an molecular extinction coefficient of 41300. The compound was found to have good spectral ¤¤sorption characteristics as a yellow colored coupler.

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#### Synthesis Example 2

Synthesis of Coupler (YC-3)

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75 ml of N,N-dimethylformamide and 75 ml of methyl cellosolve were added to 19.2 g of compound d synthesized by the method described in JP-A-62-85242 (U.S. Patent 4,837,136) to dissolve it. While stirring the resulting solution under ice cooling, 5.6 ml of concentrated hydrochloric acid was added thereto and a solution of 2.5 g of sodium nitrite in 5 ml of water was then added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for one hour to prepare a diazonium solution.

75 ml of methyl cellosolve and 26 ml of water were added to 10.1 g of the compound <u>b</u> and 10.7 g of sodium acetate. While stirring the resulting solution under ice cooling, the above diazonium solution was added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for 2 hours. The precipitated crystal was recovered by filtration and dispersed in 200 ml of methanol. A solution of 2.2 g of sodium hydroxide in 10 ml of water was added dropwise thereto. The mixture was stirred for 3 hours and neutralized with concentrated hydrochloric acid. The precipitated crystal was washed with water and then methanol and dried. The resulting crude crystal was purified from hot methanol in the same manner as in Synthesis Example 1 to give 14.8 g of the desired coupler (YC-3) with a melting point of 246 to 251 °C (decomposition). The structure of the compound was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 457.6 nm and had a molecular extinction coefficient of 42700. The compound was found to have good spectral absorption characteristics as a yellow colored coupler.

Synthesis Example 3

Synthesis of Coupler (YC-30)

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$$\begin{array}{c} \text{OH} & \text{C}_{6}^{\text{H}_{13}(n)} \\ \text{CONH(CH}_{2})_{3} \text{OCH}_{2} \text{CHC}_{8}^{\text{H}_{17}(n)} \\ \\ \text{OCH}_{2} \text{CH}_{2} \text{O} & \text{NH}_{2} \end{array}$$

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$$\frac{\text{NaNO}_2}{\text{Doupler (YC-30)}}$$

g

Synthesis of Compound e

137.1 g of anthranilic acid was added to 600 ml of acetonitrile. The mixture was heat-refluxed with stirring. 92.5 g of diketene was added dropwise thereto over a period of about one hour. The mixture was heated to reflux for one hour and cooled to room temperature. The precipitated crystal was recovered by filtration, washed with acetonitrile and dried to obtain 200.5 g of the compound e as a crystal.

### Synthesis of Compound f

199.1 g of the compound e, 89.2 g of ethyl cyanoacetate and 344 g of 28% sodium methoxide were added to 0.9 l of methanol. The mixture was reacted at 120°C in an autoclave for 8 hours. After the reaction mixture was left to stand overnight, the reaction mixture was concentrated under reduced pressure. 700 ml of water was added thereto and the mixture was acidified with 230 ml of concentrated hydrochloric

acid. The precipitated crystal was recovered by filtration. The resulting crude crystal was washed with a mixed solvent of ethyl acetate and acetonitrile with heating to give 152 g of the compound f.

### Synthesis of Coupler (YC-30)

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13.0 g of compound g synthesized according to the method described in U.S. Patent 4,138,258 was dissolved in 40 ml of N,N-dimethylformamide. While cooling the resulting solution with ice, 4.5 ml of concentrated hydrochloric acid was added thereto and a solution of 1.48 g of sodium nitrite in 5 ml of water was added dropwise thereto to prepare a diazonium solution. 20 ml of N,N-dimethylformamide and 15 ml of water were added to 6.0 g of compound f and 8 g of sodium acetate. While stirring the mixture under ice cooling, the above diazonium solution was added dropwise thereto. After the addition, the mixture was stirred at room temperature for 30 minutes and acidified with hydrochloric acid. The product was extracted with ethyl acetate, washed with water and concentrated under reduced pressure. The concentrate was crystallized from a mixed solvent of ethyl acetate and methanol to give 13 g of the coupler (YC-30) as a yellow crystal.

The coupler (YC-30) had a melting point of 154-6 °C. The structure thereof was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 458.2 nm and had a molecular extinction coefficient of 42800. The compound was found to have good spectral absorption characteristics as a yellow colored coupler.

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### Synthesis Example 4

Synthesis Coupler (YC-86)

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$$\begin{array}{c}
0 \\
0 \\
0
\end{array}$$

$$\begin{array}{c}
0 \\
0
\end{array}$$

$$\begin{array}{c}
0 \\
0
\end{array}$$

$$\begin{array}{c}
1 \\
0
\end{array}$$

O OH OC-CH CoH13

Pd-C/H2

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# Coupler (YC-86)

### (1) Synthesis of Compound 3

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445.5 g of phenyl ether compound 1 and 90.1 g of isopropanol amine 2 were addded to 600 ml of acetonitrile and the mixture was heated to reflux for 2 hours. After allowing to cool with water, crystals precipitated were recovered by filtration. The crystals were dried to give 342 g of compound 3 having a melting point of 162-5° C.

### (2) Synthesis of Compound 5

341 g of hydroxyl compound  $\underline{3}$  and 231 g of 2-hexyldecanoyl chloride were added to 880 m $\ell$  of acetnitrile. The mixture was heated to reflux for 2 hours. After allowing to cool with ice, crystals precipitated were recovered by filtration. The crystals were dried to give 437 g of compound  $\underline{5}$  having a melting point of 97-100  $^{\circ}$  C.

### (3) Synthesis of Compound 6

370 g of nitro compound 5, 6 g of a 10% Pb-C catalyst and 1 l of ethylacetate were placed in an autoclave and hydrogenation was conducted at 50°C for 3 hours. After completion of reduction reaction, the catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue obtained was crystallized with n-hexane. The precipitated crystals were recovered by filtration and were dried to give 327 g of amine compound 7 having a melting point of 95-7°C.

#### (4) Synthesis of coupler (YC-86)

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20 g of amine compoune 7 was dissolved in 60 l of dimethylformamide. While cooling the solution obtained with ice 7.6 ml of concentrated hydrochloric acid was added thereto. Furthermore, a solution of 2.7 g of sodium nitrite in 10 ml of water was added dropwise thereto over a period of 20 minutes and the solution was further stirred for 30 minutes to give a diazo solution.

9.7 g of pyridone 7 and 13 g of sodium acetate were added to a mixture of 30 ml of water and 30 ml of dimethylformamide and dissolved. After cooling the solution obtained with water, the diazo solution was added thereto gradually with stirring at a temperature of not higher than 10°C. After further stirring for 15 minutes, the product was extracted with ethylacetate, washed with water 3 times and the organic layer was concentrated under reduced pressure. The residue was crystallized with a methanol-ethylacetate mixture, precipitated crystals were recovered by filtration and dried to give 21.2 g of coupler (YC-86) having a melting point of 117 to 119°C.

The yellow colored cyan couplers represented by formulas (CII) to (CIV) can be synthesized by methods described in JP-B-58-6939 (the term "JP-B" as used herein means an "examined published Japanese patent publication") and JP-A-1-197563. The couplers represented by general formula (CI) can be synthesized by the methods described in patent specifications cited above.

Among the yellow colored cyan couplers of the present invention, the couplers represented by formulas (CI) and (CII) are more preferred, and the couplers of formula (CI) are particularly preferred.

It is preferred that the yellow colored cyan couplers of the present invention be added to sensitive silver halide emulsion layers or adjoining layers in the photographic materials. It is particularly preferred that the yellow colored cyan couplers be added to the red-sensitive emulsion layer. The total amount of the couplers to be added to the photographic material is 0.005 to 0.30 g/m², preferably 0.02 to 0.20 g/m², more preferably 0.03 to 0.15 g/m².

The yellow colored couplers of the present invention can be added in the same manner as in the addition of conventional couplers described hereinafter.

It is preferred from the viewpoints of enhancing the interlaminar effect between the red-sensitive layer and the blue-sensitive layer and improving sharpness that a polymer coupler obtained from a monomer represented by the following general formula (P) be used in the green-sensitive layer of the silver halide color photographic material (especially, the order of layers from the support is red-, green- and blue-sensitive layers, and the yellow colored coupler of the present invention and the compound represented by formula (I) are incorporated to the red-sensitive layer) of the present invention:

 $CH_{2}=C$  (P)  $(D)_{p}(E)_{q}(F)_{r}T$ 

In formula (P), R<sub>121</sub> represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms or a chlorine atom; -D- represents -COO-, -CONR<sub>122</sub>- or a substituted or unsubstituted phenylene group; -E-represents a substituted or unsubstituted alkylene, phenylene or aralkylene group; -F- represents -CONR<sub>122</sub>-, -NR<sub>122</sub>CONR<sub>122</sub>-, -NR<sub>122</sub>COO-, -NR<sub>122</sub>CO-, -OCONR<sub>122</sub>-, -NR<sub>122</sub>-, -COO-, -CO-, -CO-, -CO-, -S-, -SO<sub>2</sub>-, -NR<sub>122</sub>SO<sub>2</sub>-, or -SO<sub>2</sub>NR<sub>122</sub>-; R<sub>122</sub> represents a hydrogen atom or a substituted or unsubstituted, saturated or unsaturated aliphatic group or a substituted or unsubstituted aryl group and when two or more R<sub>122</sub> groups per molecule exist, they may be the same or different groups; and p, q and r each represents 0 or 1 with the proviso that there is no case where p, q and r are 0 simultaneously. Examples of substituents for groups represented by D, E, R<sub>122</sub> include a halogen atom, a hydroxy group, a carboxy group, a sulfo group, a phospono group, a phosphino group, a cyano group, an alkoxy group, an aryl group, an aryloxy group, an alkoxycarbonyl group, an amino group, an ammoniumyl group, an acyl group, a

carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group and a sulfonyl group.

T in formula (P) represents a magenta coupler moiety (which is bonded to  $\{F\}_{r}$ - at any one site of Ar, Z and R<sub>133</sub>) represented by the following general formula (Q)

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$$\begin{array}{c|c}
R_{133} & Z \\
N & > \\
N & \\
Ar
\end{array}$$

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In formula (Q), Ar represents known substituent groups at the 1-position of 2-pyrazoline-5-one couplers, such as an alkyl group, a substituted alkyl group (e.g., haloalkyl such as fluoroalkyl, cyanoalkyl, benzylalkyl), a substituted or unsubstituted heterocyclic group (e.g., 4-pyridyl group, 2-thiazolyl group), a substituted or unsubstituted aryl group (an example of a substituent group for the heterocyclic group and the aryl group includes an alkyl group, e.g., methyl and ethyl), an alkoxy group (e.g., methoxy, ethoxy), an aryloxy group (e.g., phenyloxy), an alkoxycarbonyl group (e.g., methoxycarbonyl), an acylamino group (e.g., acetylamino), a carbamoyl group, an alkylcarbamoyl group (e.g., methylcarbamoyl), a dialkylcarbamoyl group (e.g., dimethylcarbamoyl), an arylsulfonyl group (e.g., phenylsulfonyl), an alkylsulfonamido group (e.g., methylsulfonamido), an arylsulfonamido group (e.g., phenylsulfonamido), a sulfamoyl group, an alkylsulfamoyl group (e.g., ethylsulfamoyl), a dialkylsulfamoyl group (e.g., dimethylsulfamoyl), an alkylthio group (e.g., methylthio), an arylthio group (e.g., phenylthio), a cyano group, a nitro group and a halogen atom (e.g., fluorine, chlorine, bromine). When two or more of these substituent groups exist, they may be the same or different groups.

Particularly preferred substituent groups are a halogen atom, an alkyl group, an alkoxy group, an alkoxycarbonyl group and a cyano group.

R<sub>133</sub> represents a substituted or unsubstituted anilino group, an acylamino group (e.g., alkylcarbonamido, phenylcarbonamido, alkoxycarbonamido, phenyloxycarbonamido), a ureido group (e.g., alkylureido, phenylureido) or a sulfonamido group. These groups may be substituted. Examples of substituent groups include a halogen atom (e.g., fluorine, chlorine, bromine), a straight-chain or branched alkyl group (e.g., methyl, t-butyl, octyl, tetradecyl), an alkoxy group (e.g., methoxy, ethoxy, 2-ethylhexyloxy, tetradecyloxy), an acylamino group (e.g., acetamido, benzamido, butaneamido, octaneamido, tetradecaneamido,  $\alpha$ -(2,4-di-tert-amylphenoxy)acetamido, $\alpha$ -(2,4-di-tert-amylphenoxy)butylamido,  $\alpha$ -(3-pentadecylphenoxy)hexaneamido, α-(4-hydroxy-3-tert-butylphenoxy)tetradecaneamido, 2-oxo-pyrrolidine-1-yl, 2oxo-5-tetradecylpyrrolidine-1-yl, N-methyltetradecaneamido), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, ethylsulfonamido, p-toluenesulfonamido, octanesulfonamido, p-dodecylbenzenesulfonamido, N-methyl-N-tetradecanesulfonamido), a sulfamoyl group (e.g., sulfamoyl, N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dimethylsulfamoyl, N,N-dihexylsulfamoyl, N-hexadecylsulfamoyl, N-[3-N-methyl-N-tetradecylsul-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-tert-amylphenoxy)butyl]sulfamoyl, famoyl), a carbamoyl group (e.g., N-methylcarbamoyl, N-butylcarbamoyl, N-octadecylcaramoyl, N-[4-(2,4-ditert-amylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl), a diacylamino group (e.g., N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2, 5-dioxo-1-hydantoinyl, 3-(N-acetyl-Ndodecylamino)succinimido), an alkoxycarbonyl group (e.g., methoxycarbonyl, tetradecyloxycarbonyl, benzyloxycarbonyl), an alkoxysulfonyl group (e.g., methoxysulfonyl, butoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl), an aryloxysulfonyl group (e.g., phenoxysulfonyl, p-methylphenoxysulfonyl, 2,4-di-tertamylphenoxysulfonyl), an alkanesulfonylgroup (e.g., methanesulfonyl, ethanesulfonyl, octanesulfonyl, 2ethylhexylsulfonyl, hexadecanesulfonyl), an arylsulfonyl group (e.g., benzenesulfonyl, 4-nonylbenzenesulfonyl), an alkylthio group (e.g., methylthio, ethylthio, hexylthio, benzylthio, tetradecylthio, 2-(2,4-di-tertamylphenoxy)-ethylthio), an arylthio group (e.g., phenylthio, p-tolylthio), an alkyloxycarbonylamino group methoxycarbonylamino, ethyloxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino), an alkylureido group (e.g., N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, Nhexadecylureido, N,N-dioctadecylureido), an acyl group (e.g., acetyl, benzoyl, octadecanoyl, pdodecaneamidobenzoyl), a nitro group, a carboxyl group, a sulfo group, a hydroxyl group and a trichloromethyl group.

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In the above-described substituent groups, the alkyl group and alkyl moiety has 1 to 36 carbon atoms and the aryl group has 6 to 38 carbon atoms.

Z represents a halogen atom (e.g., chlorine atom, bromine atom), a group which is bonded through an oxygen atom and eliminated by a coupling reaction (e.g., acetoxy, propanoyloxy, benzoyloxy, ethoxyoxaloyloxy, pyruvvinyloxy, cinnamoyloxy, phenoxy, 4-cyanophenoxy, 4-titanium sulfonamidophenoxy,  $\alpha$ -naph-3-pentadecylph- $\beta$ -naphthoxy, 4-methanesulfonamidophenoxy, thoxy, 4-cvanoxy. enoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenethyloxy, 2-phenoxyethoxy, 5phenyltetrazolyloxy, and 2-benzothiazolyloxy), a coupling eliminating group which is bonded through a 10 nitrogen atom (as disclosed in, e.g., JP-A-59-99437, such as benzenesulfonamido, N-ethyltoluenesul-2,3,4,5,6-pentafluorobenzamido, octanesulfonamido, heptafluorobutanamido, fonamido, cyanophenylureido, N,N-diethylsulfamoylamino, 1-piperidyl, 5,5-dimethyl-2,4-dioxo-3-oxazolidinyl, 1-benzyl-5-ethoxy-3-hydantoinyl, 2-oxo-1,2-dihydro-1-pyridinyl, imidazolyl, pyrazolyl, 3,5-diethyl-1,2,4-triazole-1-yl, 5or 6-bromobenzotriazole-1-yl, 5-methyl-1,2,4-triazole-1-yl, and benzimidazolyl), a coupling eliminating group which is bonded through a sulfur atom (e.g., phenylthio, 2-carboxyphenylthio, 2-methoxy-5-octylphenylthio, 4-methanesulfonylthio, 4-octanesulfonamidophenylthio, benzylthio, 2-cyanoethylthio, 5-phenyl-2,3,4,5tetrazolylthio and 2-benzothiazolyl).

Preferred coupling eliminating groups are those which are bonded through a nitrogen atom, and an especially preferred coupling eliminating group is a pyrazolyl gorup.

E represents a substituted or unsubstituted alkylene, aralkylene, or phenylene group having 1 to 10 carbon atoms. The alkylene group may be a straight-chain or branched-chain. Examples of the alkylene group include a methylene group, a methylene group, a dimethylene group, a dimethylene group, a dimethylene group, a decylmethylene group, a hexamethylene group, and a decylmethylene group. An example of the aralkylene group include a benzylidene group. An example of the phenylene group include a p-phenylene group, a m-phenylene group and a methylphenylene group.

Examples of substituents for the alkylene group, the aralkylene group or the phenylene group represented by E include an aryl group (e.g., phenyl), a nitro group, a hydroxyl group, a cyano group, a sulfo group, an alkoxy group (e.g., methoxy), an aryloxy group (e.g., phenoxy), an acyloxy gorup (e.g., acetoxy), an acyloxy group (e.g., methanesulfonamido), a sulfamoyl group (e.g., methylsulfamoyl), a halogen atom (e.g., fluorine, chlorine, and bormine), a carboxy group, a carbamoyl group (e.g., methylsulfamoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), a sulfonyl group (e.g., methylsulfonyl). When E has two or more substituents they may be the same or different.

Examples of the non-color forming ethylene monomer which are capable of copolymerizing with a coupler monomer represented by formula (P) and are incapable of coupling with an oxidized product of an aromatic primary amine developing agent include an acrylic acid ester, a methacrylic acid ester, a crotonic acid ester, a vinyl ester, a maleic acid diester, a fumaric acid diester, an itaconic acid diester, an acrylamide, a methacrylamide, a vinyl ether and a styrene.

Specific examples of these monomers are shown below.

Examples of an acrylic acid ester include methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, terbutylacrylate, hexylacrylate, 2-ethylhexyl acrylate, acetoxyethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate and 2-(2-methoxyethoxy)ethyl acrylate. Examples of methacrylic esters include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate and 2-ethoxyethyl methacrylate. Examples of crotonic esters include butyl crotonate and hexyl crotonate. Examples of vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinylmethoxy acetate and vinyl benzoate. Examples of maleic diesters include diethyl maleate, dimethyl maleate and dibutyl maleate. Examples of fumaric diesters include diethyl fumarate, dimethyl fumarate and dibutyl fumarate. Examples of itaconic diesters include diethyl itaconate, dimethyl itaconate and dibutyl itaconate. Examples of acrylamides include acrylamide, methyl acrylamide, ethyl acrylamide, propyl acrylamide, nbutyl acrylamide, tert-butyl acrylamide, cyclohexyl acrylamide, 2-methoxyethyl acrylamide, dimethyl acrylamide, diethyl acrylamide and phenyl acrylamide. Examples of methacrylamides include methyl methacrylamide, ethyl methacrylamide, n-butyl methacrylamide, tert-butyl methacrylamide, 2-methoxy methacrylamide, dimethyl methacrylamide and diethyl methacrylamide. Examples of vinyl ethers include methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether and dimethylaminoethyl vinyl ether. Examples of styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, butylstyrene, chloromethylstyrene, methoxystyrene, butoxystyrene, acetoxvstyrene, chlorostyrene, dichlorostyrene, bromostyrene, methyl vinylbenzoate and 2-methylstyrene.

Examples of other monomers include allyl compounds (e.g., allyl acetate), vinyl ketones (e.g., methyl vinyl ketone), vinyl heterocyclic compounds (e.g., vinylpyridine), glycidyl esters (e.g., glycidyl acrylate), unsaturated nitriles (e.g., acrylonitrile), acrylic acid, methacrylic acid, itaconic acid, maleic acid, monoalkyl itaconates (e.g., monomethyl itaconate), monoalkyl maleates (e.g., monomethyl maleate), citraconic acid, vinylsulfonic acid, acryloyloxyalkylsulfonic acids (e.g., cryloyloxymethylsulfonic acid) and acrylamidoalkylsulfonic acids (e.g., 2-acrylamido-2-methylethanesulfonic acid). These acids may be in the form of a salt such as an alkali metal salt (e.g., Na, K) or a salt of ammonium ion.

Among these monomers, preferred comonomers are acrylic esters, methacrylic esters, styrenes, maleic esters, acrylamides and methacrylamides.

These monomers may be used either alone or in a combination of two or more of them. For example, a combination of n-butyl acrylate and styrene, a combination of n-butyl acrylate and butylstyrene and a combination of t-butyl methacrylamide and n-butyl acrylamide can be used.

Generally, it is preferred that the color forming moiety corresponding to formula (P) account for 5 to 80% by weight of the above magenta coupler. However, it is preferred from the viewpoints of color reproducibility, color formation and stabilization that the ratio of the color forming moiety in the coupler be 30 to 70% by weight. In this case, the equimolecular weight (grams of polymer containing one mol of monomer coupler) is about 250 to 4,000, but is not limited thereto.

The above polymer couplers are added to silver halide emulsion layers or adjoining light-insensitive layers thereto.

The magenta polymer couplers when used in the emulsion layers are used in an amount of 0.005 to 0.5 mol, preferably 0.03 to 0.25 mol (in terms of coupler monomer) per mol of silver used in the same layer.

When the magenta polymer couplers are used in the light-insensitive layers, the polymer couplers are used in a coating weight of 0.01 to 1.0 g/m<sup>2</sup>, preferably 0.1 to 0.5 g/m<sup>2</sup>.

The polymer couplers may be prepared by emulsifying and dispersing a solution of a lipophilic polymer coupler in the form of latex in an organic solvent in an aqueous gelatin solution, said polymer coupler being obtained by polymerizing a monomer coupler in the manner mentioned above. Alternatively, the polymer coupler may be prepared directly by an emulsion polymerization method.

A method for emulsifying and dispersing the lipophilic polymer coupler in the form of a latex in an aqueous gelatin solution is described in U.S. Patent 3,451,820. Emulsion polymerization can be carried out by using the methods described in U.S. Patents 4,080,211 and 3,370,952.

The syntheses of the above magenta polymer couplers are carried out by using the compounds described in JP-A-56-5543, JP-A-57-94752, JP-A-57-176038, JP-A-57-204038, JP-A-58-28745, JP-A-58-10738, JP-A-58-42044 and JP-A-58-145944 as polymerization initiators and solvents.

The polymerization temperature is set depending on the molecular weights of polymers to be synthesized, the types of initiators, etc. The polymerization can be conducted at a temperature of from below 0°C to higher than 100°C, but polymerization is usually conducted at a temperature of 30 to 100°C.

Examples of magenta polymer couplers which can be used in the present invention include, but are not limited to, the following compounds (the suffix of parenthesis represents molar ratio).

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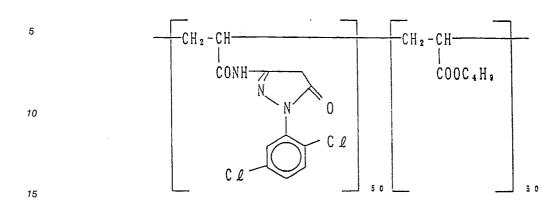
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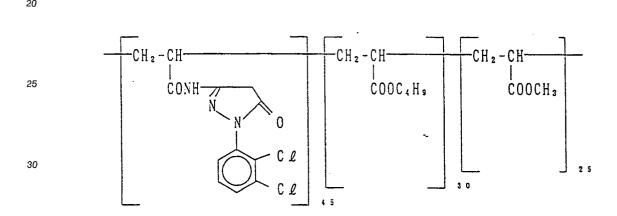
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EP 0 435 334 A2

(P-1)



(P-2)



$$(P - 3)$$

CH<sub>2</sub>-C

CH<sub>2</sub>-CH

CONH

N

O

COOC<sub>4</sub>H<sub>9</sub>

25

CH<sub>2</sub>-C

CH<sub>2</sub>-CH

CONH

CONH

COUC4H

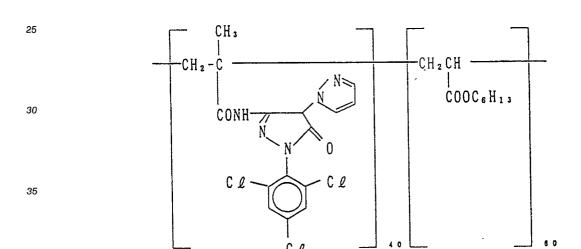
CC L

CC L

$$(P - 5)$$

 $CH_{2}-C$  CONH N  $COOC_{4}H_{9}$   $C\ell$   $C\ell$   $C\ell$   $C\ell$   $CH_{2}CH$   $COOC_{4}H_{9}$   $C\ell$   $C\ell$   $C\ell$   $C\ell$ 

(P - 6)



$$(P - 7)$$

CH<sub>2</sub>-C  $CH_2$ -CH  $COOC_4H_9$  CU C

(P-8).

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25

CH<sub>2</sub>-CH

CONH

N

COOC<sub>6</sub>H<sub>1</sub>;

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EP 0 435 334 A2

(P - 9)

CH<sub>2</sub>-C

CH<sub>2</sub>-C

CH<sub>2</sub>-C

CH<sub>2</sub>CH

COOC<sub>4</sub>H<sub>8</sub>

COOC<sub>4</sub>H<sub>8</sub>

(P-10)

20

40

25

CH 2 - CH

CONH

N

CONH

N

COUC 4 H 9

50

$$(P-11)$$

5

CH<sub>2</sub>-CH

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

CONH

N

O

C<sub>8</sub>H<sub>17</sub>(t)

C

CH<sub>2</sub>CH

COOC<sub>4</sub>H<sub>9</sub>

COOC<sub>4</sub>H<sub>9</sub>

COC<sub>8</sub>H<sub>17</sub>(t)

(P-12)

$$(P-14)$$

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The photographic material of the present invention has a support having thereon at least one blue-sensitive silver halide emulsion layer, green-sensitive silver halide emulsion layer and red-sensitive silver halide emulsion layer. There is no particular limitation with regard to the number of layers of silver halide emulsion layers and non-sensitive layers and the order of the layers. A typical example is a silver halide photographic material having at least one sensitive layer composed of a plurality of silver halide emulsion layers having substantially the same color sensitivity, but different light sensitivity, the sensitive layer being a unit sensitive layer having color sensitivity to any one of blue light, green light and red light. In a multi-layer silver halide color photographic material, the unit sensitive layers are generally arranged in the order of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer from the support. However, the arrangement may be in the reverse order to that described above according to purpose. Further, the arrangement may be such that a different light-sensitive layer is inserted into the same color sensitive layers.

Non-sensitive layers such as various interlayers may be provided between silver halide sensitive layers, or on the uppermost layer or lowermost layer thereof.

The interlayers may contain couplers, or DIR compounds described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038. The inter layers may also contain color mixing inhibitors as used conventionally.

A plurality of silver halide emulsion layers which constitute each unit sensitive layer preferably include a two-layer structure consisting of a high-sensitivity emulsion layer and a low-sensitivity emulsion layer as described in West German Patent 1,121,470 and U.K. Patent 923,045. It is preferred that the layers are disposed such that light sensitivity is lower toward the support. A non-sensitive layer may be provided

between silver halide emulsion layers. The low-sensitivity emulsion layer may be provided on the farther side from the support and the high-sensitivity emulsion layer may be provided on the side nearer to the support as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

In specific embodiments, the layer may be arranged in order of low-sensitivity blue-sensitive layer (BL)-/high-sensitivity blue-sensitive layer (BH)/ high-sensitivity green-sensitive layer (GL)/high-sensitivity red-sensitive layer (RH)/low-sensitivity red-sensitive layer (RL) from the outermost layer, or in order of BH/BL/GH/RH/RL, or in order of BH/BL/GH/RH.

The arrangement may be made in order of blue-sensitive layer/GH/RH/GL/RL from the outermost layer as described in JP-B-55-34932. Further, the arrangement may be made in order of blue-sensitive layer/GL/RL/GH/RH from the outermost layer as described in JP-A-56-25738 and JP-A-62-63936.

In another embodiment, the layer structure contains three layers having different light sensitivity in such an arrangement that the upper layer is a silver halide emulsion layer having the highest light sensitivity, the medium layer is a silver halide emulsion layer having a light sensitivity lower than that of the upper layer and the lower layer is a silver halide emulsion layer having a light sensitivity lower than that of the medium layer so that light sensitivity becomes lower toward the support in order as described in JP-B-49-15495. Even when the layer structure is composed of three layers having different light sensitivity, the arrangement may be made in order of medium-sensitive emulsion layer/high-sensitivity emulsion layer/low-sensitivity emulsion layer from the outermost layer as described in JP-A-59-202464.

In still another embodiment, the arrangement may be made in order of high-sensitivity emulsion layer/low sensitivity emulsion layer/medium-sensitivity emulsion layer or in order of low sensitivity emulsion layer/medium-sensitivity emulsion layer.

When the layer structure is composed of four or more layers, the above-described various arrangements can be made.

It is preferred that a donor layer (CL) having a multilayer effect and different in spectral sensitivity distribution from the principal sensitive layers such as BL, GL and RL are provided adjacent to or near the principal sensitive layers to improve color reproducibility, said donor layer being described in U.S. Patents 4,663,271, 4,705,744 and 4,707,436, JP-A-62-160448 and JP-A-63-89850.

As stated above various layer structures and arrangement can be selected according on he purpose of use.

The preferred silver halide contained in the photographic emulsions of the photographic materials of the present invention is silver iodobromide, silver iodochloride or silver iodochlorobromide, each having a silver iodide content of not higher than about 30 mol%. Particularly preferred is silver iodobromide or silver iodochlorobromide, each having a silver iodide content of about 2 mol% to about 25 mol%.

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Silver halide grains in the photographic emulsions may have a regular crystal form such as cube, octahedron or tetradecahedron, an irregular crystal form such as a sphere or tabular form, a crystal having a defect such as a twinning plane or a composite form thereof.

The size of silver halide grains may be in the range of from fine grains having a grain size of not larger than about 0.2  $\mu$ m to large-size grains having a grain size of about 10  $\mu$ m in terms of the diameter of projected area. Any of a polydisperse emulsion and monodisperse emulsion may be used.

The silver halide photographic emulsions of the present invention can be prepared according to the methods described in Research Disclosure (RD) No. 17643 (December 1978) pp 22-23 <u>I. Emulsion Preparation and Types; ibid. No. 18716 (November 1979)</u>, p. 648; ibid. No. 307105 (November 1989), pp 863-865; P. Glafkides, Chimie et Phisique Photographique (Paul Montel 1967), G.F. Duffin, Photographic Emulsion Chemistry (Focal Press 1966) and V.L. Zelikman et al, Making and Coating Photographic Emulsion (Focal Press 1964).

Monodisperse emulsions described in U.S. Patents 3,574,628 and 3,655,394 and U.K. Patent 1,413,748 are also preferred.

Tabular grains having an aspect ratio of not lower than about 5 can be used in the present invention. The tabular grains can be easily prepared by the methods described in Gutoff, Photographic Science and Engineering, Vol. 14, pp 248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and U.K. Patent 2,112,157.

Grains having a uniform crystal structure or a crystal structure different in halogen composition between the interior thereof and the surface thereof can be used. Grains having a laminar crystal structure may be used. Silver halide having a different composition may be joined to the grains by epitaxial growth. A compound such as silver rhodanide or lead oxide other than silver halide may be joined to the grains. A mixture of grains having various crystal forms may be used.

Silver halide emulsions are usually subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives used for these stages are described in Research Disclosure No.

17643, ibid. No. 18716 and ibid. No. 30716 and listed in a Table below.

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It is preferred that non-light-sensitive finely divided silver halide grains are used in the present invention. The term "non-sensitive finely divided silver halide grains" as used herein refers to finely divided silver halide grains which are not light-sensitive during imagewise exposure for obtaining a dye image and are substantially not developed in the processing stage. Grains which are previously not fogged are preferable.

Finely divided silver halide grains have a silver bromide content of 0 to 100 mol% and may optionally contain silver chloride and/or silver iodide. Grains containing 0.5 to 10 mol% of silver iodide are preferred.

Finely divided silver halide grains have a mean grain size (the mean value of diameters of the circles having areas corresponding to projected areas) of preferably 0.01 to 0.5  $\mu$ m, more preferably 0.02 to 0.2  $\mu$ m.

Finely divided silver halide grains can be prepared in the same manner as in the preparation of usual light-sensitive silver halides. In the preparation of finely divided silver halide grains, it is not necessary that the surfaces of silver halide grains be optically sensitized or spectrally-sensitized. However, it is preferred that a conventional stabilizer such as triazole, azaindene, benzthiazolium, a mercapto compound or a zinc compound be added before the finely divided silver halide grains are added to coating solutions. Colloidal silver is preferably incorporated in layers containing the finely divided silver halide grains.

Conventional photographic additives which can be used in the present invention are described in the three Research Disclosures are listed in the following Table.

		Additives	RD 17643 (Dec. 1978)	RD 18716 (Nov. 1979)	RD307105 (Nov. 1989)
5	1.	Chemical Sensitizing Agent	Page 23	Page 648 (right column)	Page 866
	2.	Sensitivity Increaser		- ditto -	
10	3.	Spectral Sensitizing Agent Supersensitiz- ing Agent	Pages 23 to 24	Page 648 (right column) to page 649 (right column	Pages 866 to 868
15	4.	Brightening Agent	Page 24	Page 647 (right column)	Page 868
	5.	Anti-fogging Agent, Stabilizer	Pages 24 to 25	Page 649 (right column)	Pages 868 to 870
20	6.	Light Absorber, Filter Dye and U.V. Light Absorber	Pages 25 to 26	Page 649 (right column) to page 650 (left column)	Page 873
25	7.	Stain Inhibitor	Page 25 (right column)	Page 650 (left column to right column)	Page 872
30	8.	Dye Image Stabilizer	Page 25	Page 650 (left column)	Page 872
35	9.	Hardening Agent	Page 26	Page 651 (left column)	Pages 874 to 875
	10.	. Binder	Page 26	- ditto -	Pages 873 to 874
40	11.	. Plasticizer, Lubricant	Page 27	Page 650 (right column	Page 876 )
45		Kind of Additives	<u>RD 17643</u> (Dec. 1978)	RD 18716 (Nov. 1979)	RD307105 (Nov. 1989)
	12.	Coating Aid, Surfactant	Pages 26 to 27	- ditto -	Pages 875 to 876
50	13.	Antistatic Agent	Page 27	- ditto -	Pages 876 to 877
55	14.	Matting Agent			Pages 878 to 879

It is preferred that compounds capable of reacting with formaldehyde to fix it as described in U.S. Patents 4,411,987 and 4,435,503 are added to photographic materials to prevent photographic performance

from being deteriorated by formaldehyde gas.

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Various color couplers can be used in the present invention. Examples thereof are described in patent specifications cited in the above-described Research Disclosure No. 17643, VII-C to G and ibid. No. 307105, VII-C to G.

Preferred examples of yellow couplers include those described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752 and 4,248,961, JP-B-58-10739, U.K. Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023 and 4,511,649 and European Patent 249,473A.

5-Pyrazolone compounds and pyrazoloazole compounds are preferred as magenta couplers. Particularly preferred are magenta couplers described 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, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654 and 4,556,630 and WO88/04795.

As cyan couplers phenol couplers and naphthol couplers may be used. Preferred cyan couplers include those described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011 and 4,327,173, West German Patent Application (Laid-Open) No. 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199 and JP-A-61-42658.

As couplers forming developed dyes with controlled diffusion, there are preferred those described in U.S. Patent 4,366,237,U.K. Patent 2,125,570, European Patent 96,570 and West German Patent Application (Laid-Open) No. 3,234,533.

In addition to the colored couplers of the present invention, there are preferred compounds described in Research Disclosure No. 17643, item VII-G, ibid. No. 307105, item VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258 and U.K. Patent 1,146,368, as colored couplers for correcting the unnecessary absorption of developed dyes. It is also preferred to use couplers for correcting the unnecessary absorption of developed dyes by fluorescent dyes released during coupling as described in U.S. Patent 4,774,181 or couplers having, as an elimination group, a dye precursor group capable of reacting with developing agents to form a dye as described in U.S. Patent 4,777,120.

Compounds which release a photographically useful residue with coupling can be preferably used in the present invention. Preferred DIR couplers which release restrainers are described in patent specifications cited in the above-described RD No. 17643, item VII-F, ibid. No. 307105, item VII-F and in JP-A-57-151944,JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012.

As couplers which release imagewise nucleating agents or development accelerators during development, there are preferred those described in U.K. Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840.

Other examples of compounds which can be used in the present invention include competitive couplers described in U.S. Patent 4,130,427, polyequivalent type couplers described in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, couplers which release dyes capable of again forming color after elimination described in European Patents 173,302A and 313,308A, couplers releasing bleaching accelerators described in RD No. 11449, RD No. 24241 and JP-A-61-201247, couplers releasing ligands described in U.S. Patent 4,555,477, couplers releasing leuco dyes described in JP-A-63-75747, and couplers releasing fluorescent dyes described in U.S. Patent 4,774,181.

Couplers used in the present invention can be introduced into photographic materials by various known dispersion methods.

Examples of high-boiling solvents used for the oil-in-water dispersion method are described in U.S. Patent 2,322,027.

Examples of the high-boiling organic solvents which have a boiling point of not lower than 175 °C at normal pressure used in the oil-in-water dispersion method include phthalic esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, dicyclohexyl phthalate, decyl phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) phosphate, bis(1,1-diethylpropyl) phthalate), phosphoric or phosphonic esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, di-2-ethylhexyl phenyl phosphate,), benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, N-tetradecylpyr-rolidone), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-t-octylaniline) and hydrocarbons (e.g., paraffin, dodecylbenzene, diisopropylnaphthalene). Organic solvents having a boiling point of not lower than about

30°C, preferably not lower than about 50°C, but not higher than about 160°C can be used as co-solvents. Examples of the co-solvents include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

Examples of steps for latex dispersion methods, effects thereof and the impregnating latex are described in U.S. Patent 4,199,363, West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

It is preferred that antiseptic and antifungal agents such as 1,2-benzoisothiazoline-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl)benzimidazole described in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941 and phenethyl alcohol are added to the color photographic materials of the present invention.

The present invention can be applied to various color photographic materials. Typical examples of the color photographic materials according to the present invention include general-purpose and movie color negative films, reversal color films for slide or TV, color paper, color positive films and reversal color paper.

Examples of supports which can be used in the present invention include those described in the above-described RD No. 17643 (page 28), RD No. 18716 (right column of page 647 to left column of page 648) and RD No. 307105 (page 879).

In the photographic material of the present invention, the total of the layer thicknesses of the entire hydrophilic colloid layers on the emulsion layer side thereof is preferably not more than 28  $\mu$ m, more preferably not more than 23  $\mu$ m, still more preferably not more than 18  $\mu$ m, particularly preferably not more than 16  $\mu$ m. The layer-swelling rate  $T_{1/2}$  is preferably not longer than 30 seconds, more preferably not longer than 20 seconds. The layer thickness refers to a layer thickness obtained by measuring the thickness of a layer at 25 °C and 55% RH under air conditioning (2 days). The layer-swelling rate  $T_{1/2}$  can be measured by known method in the field of photography, for example, by using a swellometer described in A. Green et al., Photogr. Sci. Eng., Vol. 19, No. 2, pp. 124-129.  $T_{1/2}$  is defined as the time taken until layer thickness reaches 1/2 of saturated layer thickness when processing is conducted with a color developing solution at 30 °C for 3 min 15 sec and 90% of the attainable maximum swollen layer thickness is referred to as saturated layer thickness.

The layer-swelling rate  $T_{1/2}$  can be controlled by adding a hardening agent to gelatin as a binder or by changing conditions with time after coating. A swelling ratio of 150 to 400% is preferred. The swelling ratio can be calculated from the maximum swollen layer thickness under the above conditions by using the formula (maximum swollen layer thickness - layer thickness)/layer thickness.

The color photographic materials of the present invention can be developed according to conventional methods described in RD No. 17643 (pp 28-29), RD No. 18716 (left column to right column of page 651) and RD No. 307105 (pp 880-881).

Color developing solutions which can be used in the processing of the photographic materials of the present invention are preferably aqueous alkaline solutions mainly composed of aromatic primary amine color developing agents. Aminophenol compounds are useful as the color developing agents and p-phenylenediamine compounds are preferred as the color developing agents. Typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline and salts thereof such as sulfate, hydrochloride and p-toluenesulfonate. Among them, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline sulfate is particularly preferred. These compounds may be used either alone or in combination of two or more of them according to purpose.

Generally, the color developing solutions contain pH buffering agents such as alkali metal carbonates, borates and phosphates, developed restrainers such as chlorides, bromides, iodides, benzimidazoles, benzothiazoles and mercapto compounds and anti-fogging agents. If desired, the color developing solutions may optionally contain preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazine such as N,N-biscarboxymethylhydrazine, phenylsemicarbazides, triethanolamine, catecholsulfonic acids; organic solvents such as ethylene glycol and diethylene glycol; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines; color forming couplers, competitive couplers; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; tackifiers; and chelating agents such as aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid and ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof.

Generally, when reversal processing is to be conducted, black-and-white development is first carried out and color development is then carried out. Black-and-white developing solutions may contain conventional developing agents such as dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-

3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol). These developing agents may be used either alone or in combination of two or more of them.

The pH of the color developing solutions and the black-and-white developing solutions is generally in the range of 9 to 12. The replenishment rate of these developing solutions varies depending on the types of the color photographic materials, but is usually not more than 3 £ per m² of the photographic material. The replenishment rate can be reduced to 500 ml or less when the concentration of bromide ion in the replenisher is reduced. When the replenishment is to be reduced, it is desirable that the contact area of the processing solution with air be reduced to prevent the solution from being evaporated or oxidized by air. The contact area of the photographic processing solution with air in the processing tank is represented by opening ratio defined below.

Contact area 
$$(cm^2)$$
 of processing solution with air

Opening ratio = 

Capacity  $(cm^3)$  of processing solution

10

The opening ratio is preferably not higher than 0.1, more preferably 0.001 to 0.05. Methods for reducing the opening ratio include a method wherein a cover such as a floating lid is provided on the surface of the photographic processing solution in the processing tank; a method wherein a movable lid is used as described in JP-A-1-82033; and a slit development method described in JP-A-63-216050. It is preferred the opening ratio be reduced not only for color development and black and white development stages, but also all of the subsequent stages such as bleaching, bleaching-fixing, fixing, rinsing and stabilization stages. The replenishment rate can be reduced by inhibiting the accumulation of bromide ion in the developing solution.

Color development is usually 2 to 5 minutes. However, when a higher temperature and a higher pH are used and the color developing agents are used at a higher concentration, processing time can be shortened

After color development, the photographic emulsion layer is generally bleached. Bleaching may be carried out simultaneously with fixing (bleaching-fixing treatment) or separately carried out. After bleaching, a bleaching-fixing treatment may be conducted to expedite processing. Processing may be conducted with a bleaching-fixing bath composed of two consecutive baths. Fixing may be conducted before the bleachingfixing treatment. After the bleaching-fixing treatment, bleaching may be conducted according to purpose. Examples of bleaching agents include compounds of polyvalent metals such as iron(III), peracids, quinones and nitro compounds. Typical examples of the bleaching agents include organic complex salts of iron(III) such as complex salts of aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid), citric acid, tartaric acid, and malic acid. Among them, iron(III) complex salts of aminopolycarboxylic acids such as (ethylenediaminetetraacetonato)iron(III) complex and (1,3-diaminopropanetetraacetonato)iron(III) complex are preferred for rapid processing and prevention of environmental pollution. Further, iron(III) complex salts of aminopolycarboxylic acids are useful for bleaching solutions and bleaching-fixing solutions. The pH of the bleaching solutions containing the iron(III) complex salts of aminopolycarboxylic acids and the bleaching-fixing solutions containing the iron(III) complex salts is generally in the range of 4.0 to 8. A lower pH may be used to expedite processing.

If desired, the bleaching solution, the bleaching-fixing solution and the pre-bath thereof may contain bleaching accelerators. Examples of the bleaching accelerators include compounds having a mercapto group or disulfide group described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426 and Research Disclosure No. 17129 (July 1978); thiazolidine derivatives described in JP-A-50-140219; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561; iodides described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds described in West German Patents 996,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; compounds described in JP-A-49-40943, JP-A-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and bromide ions. Among them, the compounds having a mercapto group or disulfide group are preferred for their high accelerating effect. Particularly, the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are preferred. Further, the compounds described in U.S. Patent 4,552,834 are preferred. These bleaching accelerators may be incorporated in the photographic materials. These bleach-

ing accelerators are particularly effective in conducting bleaching-fixing of the color photographic materials for photographing.

It is preferred that in addition to the above-described compounds, the bleaching solution and the bleaching-fixing solution contain organic acids to prevent stain from being caused by bleaching. Particularly preferred organic acids are compounds having an acid dissociation constant (pKa) of 2 to 5. Examples of the organic acids include acetic acid and propionic acid.

Examples of fixing agents used in the fixing solution and the bleaching-fixing solution include thiosulfates, thiocyanates, thioether compounds, thioureas and a large amount of an iodide. The thiosulfates are widely used as the fixing agents. Particularly, ammonium thiosulfate is most widely used. A combination of a thiosulfate with a thiocyanate, a thioether compound or a thiourea is also preferred. Sulfites, bisulfites, carbonyl bisulfite adducts and sulfinic acid compounds described in European Patent 294769A are preferred as preservatives for the fixing solution and the bleaching-fixing solution. It is also preferred that aminopolycarboxylic acids or organic phosphonic acids are added to the fixing solution or the bleaching-fixing solution to stabilize the solution.

It is preferred that compounds having a pKa of 6.0 to 9.0, preferably imidazoles such as imidazole, 1-methylimidazole, 1-ethylimidazole and 2-methylimidazole, in an amount of 0.1 to 10 mol/£ are added to the fixing solution or the bleaching-fixing solution to adjust the pH.

Shorter desilvering time (in total) is preferred, so long desilvering failure is not caused. Desilvering time is preferably 1 to 3 min, more preferably 1 to 2 min. Processing temperature is 25 to 50 °C, preferably 35 to 45 °C. When desilvering is carried out at a temperature within the preferred range, the desilvering rate is increased and stain is effectively prevented from being formed after processing.

It is preferred that agitation in the desilvering stage be intensified as much as possible. Methods for intensifying agitation include a method wherein a jet of the processing solution collides with the surfaces of the emulsions of photographic materials as described in JP-A-62-183460; a method wherein stirring is improved by a rotating means as described in JP-A-62-183461; a method wherein a wiper blade provided in the solution is brought into contact with the surfaces of the emulsions, the photographic material is transferred to thereby form a turbulent flow, whereby a stirring effect is improved; and a method wherein the whole amount of the processing solution circulated is increased. Such means for improving agitation are effectively applicable to any of the bleaching solution, the bleaching-fixing solution and the fixing solution into the emulsion layers and as a result, the desilvering rate is enhanced. The above-described means for improving agitation is more effective when the bleaching accelerators are used. The accelerating effect can be greatly increased and the problem of inhibiting fixation caused by the bleaching accelerators can be solved.

It is preferred that automatic processors for use in the processing of the photographic materials of the present invention be provided with photographic material conveying means described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. As stated in JP-A-60-191257 the conveying means can greatly reduce the amount of the processing solution brought over from the previous bath to the subsequent bath so that preservation of the performance of the processing solution is very high. This is particularly effective in shortening the processing time in each stage or reducing the replenishment rate of the processing solution.

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Usually, the silver halide color photographic materials of the present invention are subjected to washing and/or stabilization after desilvering. The amount of rinsing water in the washing stage varies widely depending on the characteristics (e.g., depending on materials used such as couplers) of the photographic materials, their use, the temperature of rinsing water, the number of rinsing tanks (the number of stages), replenishing system (countercurrent, direct flow) and other conditions. The relationship between the amount of water and the number of rinsing tanks in the multi-stage countercurrent system can be determined by the method described in <u>Journal of the Society of Motion Picture and Television Engineers</u>, Vol. 64, p. 248-253 (May 1955).

According to the multi-stage countercurrent system described in the above article, the amount of rinsing water can be greatly reduced. However, the residence time of water in the tanks is prolonged and as a result, bacteria are grown and the resulting suspended matter is deposited on the photographic material. A method for reducing calcium ion and magnesium ion concentrations described in JP-A-62-288838 can be effectively used for the color photographic materials of the present invention to solve this problem. Further, isothiazolone compounds, thiabendazole compounds, chlorine-containing germicides such as sodium chlorinated isocyanurate and benztriazole described in JP-A-57-8542 and germicides described in Chemistry of Germicidal Antifungal Agent, (1986) written by Hiroshi Horiguchi (Sankyo Shuppan), Sterilization, Disinfection, Antifungal Technique, edited by Sanitary Technique Society and Antibacterial and Antifungal

Cyclopedie, (1986) edited by Nippon Antibacterial Antifungal Society, can be used.

The pH of rinsing water in the treatment of the photographic materials of the present invention is in the range of 4 to 9, preferably 5 to 8. The temperature of rinsing water and washing time vary depending on the characteristics of the photographic materials and use, but the temperature and time of washing are generally 15 to 45° C for 20 seconds to 10 minutes, preferably 25 to 40° C for 30 seconds to 5 minutes. The photographic materials of the present invention may be processed directly with stabilizing solutions in place of rinsing water. Such stabilizing treatment can be carried out by conventional methods described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345.

A stabilizing treatment subsequent to rinsing may be conducted. The stabilizing treatment may be used as the final bath for the color photographic materials for photographing. An example thereof include a stabilizing bath containing a dye stabilizer and a surfactant. Examples of the dye stabilizer include aldehydes such as formalin and glutaraldehyde, N-methylol compounds, hexamethylenetetramine and aldehydesulfite adducts.

The stabilizing bath may contain various chelating agents and antifungal agents.

Overflow solution from the replenishment of rinsing water and/or stabilizing can be reused in other stages such as desilvering stage.

When the processing solutions are concentrated by evaporation in processing with automatic processors, it is preferred that water is added thereto to make up the amount of water evaporated.

The color developing agents may be incorporated in the silver halide color photographic materials of the present invention for the purpose of simplifying and expediting processing. It is preferred that precursors for the color developing agents are used for the incorporation thereof in the photographic materials. Examples of the precursors include indoaniline compounds described in U.S. Patent 3,342,597; Schiff base compounds described in U.S. Patent 3,342,599 Research Disclosure No. 14850 and ibid., No. 15159; aldol compounds described in Research Disclosure No. 13924; metal complex salts described in U.S. Patent 3,719,492; and urethane compounds described in JP-A-53-135628.

If desired, 1-phenyl-3-pyrazolidones may be incorporated in the silver halide color photographic materials of the present invention for the purpose of accelerating color development. Typical examples of the compounds include those described in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

In the present invention, various processing solutions are used at a temperature of 10 to 50 °C. Generally, a temperature of 33 to 38 °C is used. However, a higher temperature can be used to accelerate processing and to shorten processing time, while a lower temperature is used to improve image quality and to improve the stability of the processing solutions.

The silver halide photographic materials of the present invention include heat developable photo sensitive materials described in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056 and European Patent 210,660A2.

The present invention is now illustrated in greater detail with reference to the following examples which, however, are not to be construed as limiting the invention in any way. Unless otherwise indicated, all parts, percents and ratios are by weight.

### 40 EXAMPLE 1

The surface of a cellulose triacetate film support having an undercoat applied thereto was coated with the following layers having the following compositions to prepare a multi-layer color photographic material as Sample 101.

#### Compositions of Photographic Layers

The coating weights of silver halide and colloidal silver are represented by g/m² in terms of silver. The coating weights of couplers, additives and gelatin are represented by g/m². The amounts of sensitizing dyes are represented by moles per mole of silver halide in the same layer.

	First Layer: Antihalation Layer	Amount
5	Black colloidal silver	0.15
	Gelatin	1.20
	Second Layer: Interlayer	
10	Gelatin	1.45
15	UV-1	0.03
	UV-2	0.06
	UV-3	0.07
	ExF-1	0.004
20	Solv-2	0.07

# Third Layer: Low-sensitivity Red-sensitive Emulsion Layer

5	Silver iodobromide emulsion [AgI: 6 mol%, interior high AgI type, diameter (in terms of sphere): 0.3 µm, coefficient of variation in diameter (in terms	0.35
10	of sphere): 20%, normal crystal- twin mixed grains, diameter/ thickness ratio: 2.5]: coated silver	
	Gelatin	1.00
15	ExS-1	1.0×10 <sup>-4</sup>
	ExS-2	3.0×10 <sup>-4</sup>
00	ExS-3	1.0×10 <sup>-5</sup>
20	ExC-3	0.22
	ExC-4	0.006
25	Solv-1	0.007
	mounth faces welling and bindle had as	
	Fourth Layer: Medium-sensitivity Red-se Layer	nsitive Emulsion
30	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of	nsitive Emulsion 0.75
	Layer Silver iodobromide emulsion [AgI: 10 mol%, interior high	
30 35	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal— twin mixed grains, diameter/	
30	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal- twin mixed grains, diameter/ thickness ratio: 1]: coated silver	0.75
30 35	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal— twin mixed grains, diameter/ thickness ratio: 1]: coated silver  Gelatin	1.05
30 35	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal- twin mixed grains, diameter/ thickness ratio: 1]: coated silver  Gelatin  ExS-1	0.75 1.05 1.0×10 <sup>-4</sup>
30 35 40	Layer  Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal— twin mixed grains, diameter/ thickness ratio: 1]: coated silver  Gelatin  ExS-1  ExS-2	1.05 1.0×10 <sup>-4</sup> 3.0×10 <sup>-4</sup>

55

	ExY-14	0.015
	ExY-13	0.018
5	ExC-2	0.082
	Cpd-10	1.0×10 <sup>-4</sup>
10	Solv-l	0.05
	Fifth Layer: High-sensitivity Red-sensitive	Emulsion
	Layer	
15 20	Silver iodobromide emulsion [AgI: 14 mol%, interior high AgI type, diameter (in terms of sphere): 0.7 µm, coefficient of variation in diameter (in terms	0.65
	of sphere): 30%, twin mixed grains, diameter/thickness ratio: 2]: coated silver	
25	Gelatin	0.90
	ExS-1	1.0×10 <sup>-4</sup>
	ExS-2	3.0×10 <sup>-4</sup>
30	ExS-3	1.0×10 <sup>-5</sup>
	ExC-5	0.07
35	ExC-6	0.08
	ExY-13	0.03
	Solv-1	0.15
40	Solv-2	0.08
	Sixth Layer: Interlayer	
45	Gelatin	0.50
	P-2	0.17
	Cpd-1	0.10

	Cpd-4	0.17
	Solv-l	0.05
5	Seventh Layer: Low-sensitivity Green-sensitive Layer	Emulsion
10 15	Silver iodobromide emulsion [AgI: 6 mol%, interior high AgI type, diameter (in terms of sphere): 0.3 µm, coefficient of variation in diameter (in terms of sphere): 19%, normal crystaltwin mixed grains, diameter/thickness ratio: 2.5]: coated silver	0.30
	Gelatin	0.30
20	ExS-4	5.0×10 <sup>-4</sup>
	ExS-6	0.3×10 <sup>-4</sup>
	ExS-5	2.0×10 <sup>-4</sup>
25	Preferred polymer coupler (P-13) of invention (molecular weight: 40,000)	0.22
30	ExY-13	0.03
	ExM-8	0.03
	Solv-l	0.15
35	<u>Eighth Layer</u> : Medium-sensitivity Green-sensit Emulsion Layer	ive
40 45	Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 µm, coefficient of variation in diameter (in terms of sphere): 18%, normal crystal- twin mixed grains, diameter/	0.60
	thickness ratio: 4]: coated silver	
	Gelatin	0.90
50	ExS-4	$5.0 \times 10^{-4}$

	ExS-5	2.0×10 <sup>-4</sup>
	ExS-6	0.3×10 <sup>-4</sup>
5	Preferred polymer coupler (P-13) of invention	0.25
	ExM-8	0.03
10	ExM-10	0.015
	ExY-13	0.04
15	Solv-l	0.20
<u>N</u>	<u>inth Layer</u> : High-sensitivity Green-sensitive Layer	Emulsion
20	Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.7 µm, coefficient of variation in diameter (in terms	0.50
25	of sphere): 30%, normal crystal- twin mixed grains, diameter/ thickness ratio: 2.0]: coated silver	
30	Gelatin	0.75
	ExS-4	2.0×10 <sup>-4</sup>
	ExS-5	2.0×10 <sup>-4</sup>
35	ExS-6	0.2×10 <sup>-4</sup>
	ExS-7	3.0×10 <sup>-4</sup>
40	ExM-11	0.06
	ExM-12	0.02
	ExM-8	0.02
45	Cpd-2	0.01
	Cpd-9	2.0×10 <sup>-4</sup>
50	Cpd-10	2.0×10 <sup>-4</sup>

	Solv-l	0.20
_	Solv-2	0.05
5	Tenth Layer: Yellow Filter Layer	
	Gelatin	0.50
10	Yellow colloidal silver	0.05
	Cpd-1	0.16
15	Solv-l	0.15
	<u>Eleventh Layer</u> : Low-sensitivity Blue-sensitiv Layer	e Emulsion
20	Silver iodobromide emulsion [AgI: 4 mol%, interior high AgI type, diameter (in terms of sphere): 0.5 µm, coefficient of variation in diameter (in terms	0.4
25	of sphere): 15%, octahedral grains]: coated silver	
	Gelatin	1.0
30	ExS-8	2.0×10 <sup>-4</sup>
	ExY-15	0.9
	ExY-13	0.09
35	Cpd-2	0.01
	Solv-l	0.3
40	Twelfth Layer: High-sensitivity Blue-sensitiv Layer	e Emulsion
45	Silver iodobromide emulsion [AgI: 14 mol%, interior high AgI type, diameter (in terms of sphere): 1.3 µm, coefficient of variation in diameter (in terms of sphere): 25%, normal crystal- twin mixed grains, diameter/ thickness ratio: 4.5]: coated silver	0.40
50		

	Gelatin	0.50
5	ExS-8	1.0×10 <sup>-4</sup>
5	ExY-15	0.12
	Cpd-2	0.001
10	Cpd-5	2.0×10 <sup>-4</sup>
	Solv-l	0.04
<u>T</u>	hirteenth Layer: First Protective Layer	
	Finely divided silver iodobromide (mean grain size: 0.07 µm, AgI: 1 mol%)	0.10
20	Gelatin	0.70
	UV-2	0.10
25	UV-3	0.10
	UV-4	0.15
	Solv-3	0.04
<sup>30</sup> <u>F</u>	ourteenth Layer: Second Protective Layer	
	Gelatin	0.80
35	Polymethyl methacrylate particles (diameter: 1.5 µm)	0.15
	H-1	0.30

Further, the following Cpd-3, Cpd-5, Cpd-6, Cpd-7, Cpd-8, P-1, P-2, W-1, W-2, W-3 were added to improve preservability, processability, pressure resistance, mildewproofing and antifungal properties, antistatic properties, and coatability, and the upper layer, the fourteenth layer, was simultaneously coated. Dry film thickness was 16.5 μm when measured by a contact film thickness gauge.

The chemical structural formulas and chemical names of compounds used in the present invention are as follows.

50

UV-l

5 Cl HO  $(t)C_4H_9$   $(t)C_4H_9$ 

15 UV-2

UV-4

10

35

50

55

 $\begin{array}{c|c}
 & \text{HO} \\
 & \text{N} \\
 & \text{N}
\end{array}$   $\begin{array}{c}
 & \text{N} \\
 & \text{N}
\end{array}$   $\begin{array}{c}
 & \text{Otherwise} \\
 & \text{$ 

25 UV-3

 $\begin{array}{c}
\text{HO} \\
\text{(sec)} C_4 H_9 \\
\text{(t)} C_4 H_0
\end{array}$ 

C<sub>2</sub>H<sub>5</sub>  $C_{2}H_{5}$ N-CH=CH-CH=C  $C_{2}H_{5}$ SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

Solv-1: Tricresyl phosphate
Solv-2: Dibutyl phthalate
Solv-3: Tri(2-ethylhexyl) phosphate

ExF-1

 $CH_3$   $CH_3$  C

20 .

ExC-2

OH  $CONHC_{12}H_{25}$ OH  $NHCOCH_3$ OCH  $_2CH_2O$ NaO $_3S$ SO $_3Na$ 

ExC-3

15

30

ExC-4: (DC-1 of West German Patent Laid-Open No. 3815469)

50

ExC-5

5 
$$(n)C_4H_9 \longrightarrow NHCONH \longrightarrow CN$$

$$(t)C_5H_{11} \longrightarrow OCHCONH$$

$$C_5H_{11}(t)$$

ExC-6

OH 
$$CONH(CH_2)_3OC_{12}H_{25}$$

(i)  $C_4H_9OCONH$   $OCH_2CH_2SCH_2COOH$ 

 $E \times M = 8$ 

$$\begin{array}{c|c}
C_2 H_5 \\
\hline
- OCHCONH \\
C_5 H_{11}(t)
\end{array}$$

$$\begin{array}{c|c}
C_2 H_5 \\
\hline
- OCHCONH \\
\hline
N N O \\
C \ell
\end{array}$$

$$\begin{array}{c|c}
C_2 H_5 \\
\hline
- OCHCONH \\
\hline
N O \\
C \ell
\end{array}$$

 $E \times M - 9$ : (M-1 of West German Patent Laid-Open No. 3815469)

# E X M - 1 0 :

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

$$- 0CHCONH$$

$$- C \ell$$

$$N = N$$

$$- NHCOC_{4}H_{5}(t)$$

$$C \ell$$

$$C \ell$$

 $E \times M - 1 1 :$ 

$$\begin{array}{c|c} C_2H_5\\ \hline \\ -OCHCONH \\ \hline \\ (t)C_5H_{11} \\ \hline \\ CONH \\ \hline \\ C \\ \ell \\ \hline \\ C \\ \ell \\ \hline \\ C \\ \ell \\ \hline \end{array}$$

 $E \times M - 1 2 :$ 

$$\begin{array}{c|c} C_2 H_5 \\ \hline \\ (t) C_5 H_{11} \\ \hline \\ \end{array} \begin{array}{c} C_2 H_5 \\ \hline \\ CONH \\ \hline \\ C \\ \end{array} \begin{array}{c} N \\ N \\ O \\ C \\ \mathcal{L} \end{array}$$

 $E \times Y - 1 3 :$ 

 $E \times Y - 1 \ 4 :$ 

$$(CH_3)_3 CCOCHCONH \longrightarrow C_5H_{11}(t)$$

$$C_8H_{11}(t)$$

$$C_8H_{11}(t)$$

$$C_8H_{11}(t)$$

 $E \times Y - 1 5 :$ 

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

$$C = 0$$

$$HC \longrightarrow N$$

$$CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2}$$

E x Y - 1 6 : (DC-2 of West German Patent Laid-Open No. 3815469)

 $E \times M - 1 7$ : (DIR coupler similar to DC-3 in West German Patent Laid-Open No. 3815469)

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NHCOCH<sub>2</sub>O Ć<sub>5</sub>H<sub>11</sub>(t)

Cpd-1:

C<sub>5</sub>H<sub>13</sub>(n)

Cpd-2:

50

45

 $E \times S - 1$ :

$$\begin{array}{c}
C_2 H_5 \\
\downarrow \\
N \\
C = CH - C = CH - \Theta \\
\downarrow \\
C H_2)_3 SO_3 Na \\
C H_2)_4 SO_3 \Theta
\end{array}$$

10  $E \times S - 2$ :

5

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$$\begin{array}{c|c}
C_2H_3\\
C & \\
C$$

 $E \times S - 3$ :

 $E \times S - 4$ : C2H5 35 (ĊH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>⊖ (CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na

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 $E \times S - 5$ :

$$\begin{array}{c} C_2 H_5 \\ O \\ \Theta \\ N \end{array} - CH = C - CH = \begin{array}{c} O \\ N \\ O \\ CH_2 \end{array} )_4 SO_3 \Theta \qquad C_2 H_5 \end{array}$$

$$E \times S - 6$$
:

$$\begin{array}{c|c}
C_2 H_5 \\
O \\
O \\
CH_2 CH = C - CH \\
\hline
CH_2 \\
CH_2 \\
CH_2 \\
CH_3 \\
CH_4 \\
CH_2 \\
CH_2 \\
CH_2 \\
CH_3 \\
CH_3 \\
CH_4 \\
CH_5 \\
CH$$

$$E \times S - 7 :$$

$$E \times S - 8$$
:

S CH 
$$\stackrel{S}{\longrightarrow}$$
 CH  $\stackrel{\Theta}{\longrightarrow}$  CH  $\stackrel{C}{\longrightarrow}$  CH

W-1

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W-2

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$$\begin{array}{c} C_2H_5 \\ \mid \\ (n)C_4H_9CHCH_2COOCH_2 \\ \mid \\ (n)C_4H_9CHCH_2COOCHSO_3Na \\ \mid \\ C_2H_5 \end{array}$$

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W-3  $C_8F_{17}SO_2N(C_3H_7)CH_2COOK$ 

P-1 Cope

Copolymer of vinyl-pyrrolidone and vinyl alcohol

(copolymerization ratio = 70:30 by weight)

P-2 Polyethyl acrylate

### Samples 102 to 106

Each of Samples 102 and 103 was prepared in the same way as Sample 101, except that ExY-16 in an amount of twice by mol that of ExC-4 or ExM-17 in an amount of 1.4 times by mol that of ExC-4 was used in place of ExC-4 in each of the third and fourth layers of the Sample 101. Each of Samples 104, 105 and 106 was prepared in the same way as Sample 101 except that Compound (5) of the present invention in an

amount of 4 times by mol that of ExC-4, Compound (7) of the present invention in an amount of 3 times by mol that of ExC-4, or Compound (14) of the present invention in an amount of 4 times by mol ExC-4 was

used in place of ExC-4 in each of the third and fourth layers of Sample 101.

## Samples 107 to 124

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Each of Samples 107 to 124 was prepared by adding the yellow colored coupler (YC-26) of the present invention in an amount of  $0.025~\rm g/m^2$  and  $0.008~\rm g/m^2$  to the fourth and fifth layers of each of the Samples 101 to 106, respectively. Similarly, (YC-32) and (YC-47) were added to prepare Samples 113 to 124.

## 45 Samples 125 to 131

Each of Samples 125 to 131 was prepared in the same way as Sample 101 except that each of (YC-3), (YC-24), (YC-25), (YC-1). )YC-85), (YC-86), and (YC-89) was used in place of (YC-26).

#### 50 Samples 132 and 133

Sample 132 was prepared in the same way as Sample 110, except that ExM-9 in an amount of twice by weight that of the preferred Coupler (P-13) of the present invention was used in place of Coupler (P-13) in each of the seventh and eighth layers of Sample 110, the amount of Solv-1 was increased to 1.8 times that used in Sample 110 and the amount of gelatin was increased to 1.5 times that used in Sample 110. A sample 133 was prepared in the same way as Sample 132 except that an equimolar amount of ExM-11 was used in place of ExM-9.

The relative sensitivity of the green-sensitive layer of Samples 132 and 133 obtained by color

development described hereinafter was the same as that of Sample 110. Scratch strength was measured by using a sapphire stylus of 0.05 mm diameter. There was little difference in scratch strength between these samples. Further, it was confirmed that the film strength and photographic performance of these samples were nearly the same.

The samples prepared above were subjected to imagewise red exposure and then to the following color development (Condition A). Separately, the samples were subjected to uniform blue exposure so that the yellow density of the red unexposed area of Sample 101 in the following color development became 1.2 after imagewise red exposure, and the samples were then subjected to imagewise red exposure and developed (Condition B).

Relative sensitivity was determined from the logarithm of the reciprocal of exposure amount giving a density of (Fog + 0.2) under the Condition A. Color turbidity was determined from a value obtained by subtracting the yellow density in the red unexposed area from the yellow density in an exposure amount giving a cyan density of (Fog + 0.3) and (Fog + 0.1) under the Conditions A and B.

The sharpness of these samples was determined by the conventional MTF method.

The development was carried out at 38 °C under the following conditions.

	1.	Color development	3	min	15	sec
20	2.	Bleaching	6	min	30	sec
	3.	Rinse with water	3	min	15	sec
25	4.	Fixing	6	min	30	sec
20	5.	Rinse with water	3	min	15	sec
	6.	Stabilization	3	min	15	sec

Each processing solution used in each stage had the following composition.

### Color Developing Solution

35	Sodium nitrilotriacetate	1.0	g
	Sodium sulfite	4.0	g
40	Sodium carbonate	30.0	g
	Potassium bromide	1.3	g
45	Hydroxylamine sulfate	2.4	g
45	4-(N-Ethyl-N-β-hydroxyethylamino)- 2-methylaniline sulfate	4.5	g
50	Add water to make	1 13	iter

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# Bleaching Solution

	Ammonium bromide	160.0 g
5	Ammonia water (28%)	25.0 ml
	Sodium iron salt of ethylenediaminetetraacetic acid	130 g
10	Glacial acetic acid	14 ml
	Add water to make	l liter
15	Fixing Solution	
	Sodium tetrapolyphosphate	2.0 g
	Sodium sulfite	4.0 g
20	Ammonium thiosulfate (70% aqueous solution)	175.0 ml
	Sodium bisulfite	4.6 g
25	Add water to make	l liter
	Stabilizing Solution	
30	Formalin	2.0 ml
	Add water to make	l liter

		alue e/mm)	Image	0.64	0.64	0.64	0.67	0.67	0.67	0.65	0.65	0.65	0.68
5		MTF Value (20 cycle/mm)	Image	0.86	0.85	0.86	0.87	0.87	0.87	0.89	0.88	0.89	0.91
10		a .	Fog+1.0	+0.19	+0.21	+0.20	. +0.07	+0.10	+0.08	+0.11	+0.13	+0.12	-0.01
15		Color Turbidity	124	+0.04	+0.06	+0.04	+0.02	+0.03	+0.03	+0.01	+0.03	+0.01	-0.01
		Color T	Fog+0.3 Fog+1.0	+0.21	+0.24	+0.22	+0.13	+0.15	+0.14	+0.13	+0.16	+0.14	+0.05
		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Fog+0.3	+0.04	+0.06	+0.04	+0.03	+0.04	+0.04	+0.01	+0.03	+0.01	00.00
25	Table 1	Rela- tive	Sensi- tivity	00.00	+0.01	0.00	+0.07	+0.06	90.0+	+0.01	+0.01	00.0	+0.08
30		Magenta Coupler in	7th, and 8th Layers	P-13	=	=	*	=	=	=	=	=	=
35		Yellow Colored Coupler	in 4th and 5th Layers	ı	ŀ	I	1	ì	ı	YC-26	=	=	=
40			3rd, and 4th Layers	ExC-4	ExY-16	ExM-17	(2)	(7)	(14)	ExC-4	ExY-16	ExM-17	(5)
45			Sample	101 (Comparison)	( "	(	(	(	( :	-	<u> </u>	<u> </u>	110 (Invention)
50			Sa	101 (	102 (	103 (	104 (	105 (	106 (	107 (	108 (	) 601	) 011

			lue e/mm) Cyan	Image	0.68	0.68	0.65	0.65	0.65	0.68	0.68	0.68	0.65	0.65
5			MTF Value (20 cycle/mm)	Image	06.0	06.0	0.89	0.88	0.89	06.0	06.0	06.0	0.89	0.88
10			on B	Fog+1.0	+0.02	0.00	+0.12	. +0.14	+0.13	00.00	+0.03	+0.01	+0.14	+0.16
15			Turbidity Condition B	Fog+0.3	00.00	00.00	+0.02	+0.04	+0.02	00.00	+0.01	00.00	+0.03	+0.05
20			Color To	Fog+1.0	+0.08	+0.06	+0.14	+0.16	+0.14	+0.06	+0.08	+0.06	+0.16	+0.17
		(d)	Condil	Fog+0.3	+0.01	+0.01	+0.02	+0.04	+0.02	+0.01	+0.02	+0.01	+0.03	+0.05
25		Table 1 (cont'd)	Rela- tive Sensi-	tivity	+0.07	+0.07	-0.01	00.0	-0.01	+0.06	+0.05	+0.05	-0.02	-0.01
30	-	Table	Magenta Coupler in 7th, and	8th Layers	P-13	=	z	=	2	=	=	=	=	E
35			Yellow Colored Coupler	5th Layers	YC-26	2	¥C-32	=	=	z.	=	ž	¥C-47	=
40			DIR Com- pound in	4th Layers	(7)	(14)	ExC-4	ExY-16	ExM-17	(2)	(7)	(14)	ExC-4	ExY-16
45				ole	lll (Invention)	·	113 (Comparison)	<u>.</u>	· .	(Invention)	· .	<u> </u>	(Comparison)	<u> </u>
50				Sample	יוו (ונ	112 ("	113 (Co	114 ( " )	115 (")	116 (In	117 ("	118 ("	119 (Co	120 (")

		lue e/mm) Cyan Image	0.65	. 89.0	0.67	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	99.0	99.0
5		MTF Value (20 cycle/mm) Yellow Cyal	0.89	06.0	06.0	06.0	06.0	06.0	06.0	06.0	06.0	06.0	06.0	0.87	0.87
10		on B Fog+1.0	+0.15	+0.02	+0.05	.+0.03	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	+0.03	+0.03
15		Color Turbidity ion A Condition B Fog+1.0 Fog+0.3 Fog	+0.03	+0.01	+0.02	+0.01	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	+0.02	+0.02
20			+0.16	+0.08	+0.10	+0.08	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.06	+0.06
	t'd)	Condit Fog+0.3	+0.03	+0.02	+0.04	+0.03	-0.01	00.00	00.00	00.00	0.00	00.00	0.00	+0.01	+0.01
25	Table 1 (cont'd)	Rela- tive Sensi-	-0.02	+0.05	+0.04	+0.05	+0.09	+0.08	-0.08	+0.08	+0.09	+0.09	+0.09	+0.06	+0.05
30	Table	Magenta Coupler in 7th, and 8th Layers	P-13	=	=	=	=	=	=	=	=	=	=	EXM-9	ExM-11
35		Yellow Colored Coupler in 4th and 5th Layers	XC-47	:	z	=	¥C-3	YC-24	¥C-25	YC-1	¥C-85	YC-86	YC-89	¥C-26	±
40		DIR Com- pound in 3rd, and	EM-17	(5)	(7)	(14)	(2)	=	=	=	=	=	=	=	5
45			121 (Comparison)	(Invention)	<u> </u>	^ =	<u> </u>	<u> </u>	<u> </u>	<u>.</u>	<b>(</b> :	<u> </u>	<u> </u>	<u> </u>	<u>^</u> :
50		Sample	121 (Cc	122 (Ir	123 ("	124 (	125 ("	126 ("	127 ("	128 ("	129 ("	130 ("	131 ( "	132 ("	133 ("

It is apparent from Table 1 that Samples of the present invention provided superior results to Samples 104 to 106 obtained by using only the compounds of formula (I) according to the present invention and no yellow colored coupler low color turbidity, in color reproducibility, high MTF values and in sharpness in any exposure amounts under both the Conditions A and B. Further, it is apparent that the samples of the present invention are highly sensitive and are excellent in color reproducibility in terms of color turbidity as

well as in sharpness in terms of MTF value in comparison with Samples 107 to 109, 113 to 115 and 119 to 121 obtained by using DIR couplers described in West German Patent 3815469 without using any compound of formula (I) according to the present invention. Namely, it is shown in Table 1 that when the present invention is applied to photographic materials, photographic materials which have improved color reproducibility under various exposure conditions and which are highly sensitive and have excellent sharpness can be obtained.

Further, Sample 110 obtained by using the polymer coupler (P-13) is highly sensitive and has good sharpness and color reproducibility in comparison with Samples 132 and 133 obtained by using ExM-9 and ExM-11, respectively. Accordingly, it is clear that the use of the polymer coupler in the present invention is preferable.

# EXAMPLE 2

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An evaluation of color turbidity of Samples 101 to 128, 132 and 133 was made in the same manner as in Example 1 except that the following developing solution (model exhausted solution) was used in place of the color developing solution used in Example 1, the developing solution being a model exhausted solution in which the evaporation of the solution proceeded and was deteriorated by oxidation, because the processing amount was small.

20	Color Developing Solution (Model exhausted	solution	1)
25	Sodium nitrilotriacetate	1.0	g
	Sodium sulfite	2.0	g
	Sodium carbonate	30.0	g
30	Potassium bromide	1.6	g
	Hydroxylamine sulfate	1.2	g
35	$4-(N-Ethyl-N-\beta-hydroxyethylamino)-2-methylaniline sulfate$	4.5	g
	Add water to make	1 1i	iter

The difference in development results between Examples 1 and 2 is shown in Table 2 (a minus sign indicates that the color turbidity of the photographic material developed with the exhausted solution is high).

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Table 2

		Color Turbidity							
5	Sample	Condi Foq+0.3	tion A Fog+1.0	Condi Fog+0.3	tion B Fog+1.0				
	101 (Comparison)	-0.02	-0.04	-0.01	-0.06				
10	102 ( " )	-0.02	-0.05	-0.01	-0.06				
70	103 ( " )	-0.01	-0.04	0.00	-0.05				
	104 ( " )	0.00	-0.02	0.00	-0.03				
15	105 ( " )	0.00	-0.03	0.00	-0.04				
	106 (")	0.00	-0.02	0.00	-0.03				
20	107 ( " )	-0.01	-0.03	-0.01	-0.05				
	108 ( " )	-0.01	-0.04	-0.01	-0.05				
	109 ( " )	0.00	-0.03	0.00	-0.04				
25	110 (Invention)	0.00	0.00	0.00	-0.01				
	111 ( " )	0.00	0.00	0.00	-0.01				
30	112 ( " )	+0.01	+0.01	+0.01	0.00				
	113 (Comparison	) -0.01	-0.03	-0.01	-0.05				
	114 ( " )	-0.01	-0.04	-0.01	-0.05				
35	115 ( " )	0.00	-0.03	-0.01	-0.05				
	116 (Invention)	0.00	0.00	+0.01	0.00				
40	117 ( " )	0.00	0.00	+0.01	0.00				
	118 ( " )	+0.01	+0.01	+0.02	+0.01				
	119 (Comparison	) -0.02	-0.03	-0.01	-0.04				
45	120 (")	-0.02	-0.04	-0.01	-0.04				
	121 ( " )	-0.01	-0.03	0.00	-0.04				
50	122 (Invention)	0.00	-0.01	0.00	-0.01				

### Table 2 (cont'd)

		Color Turbidity						
		Cond:	ition A	Condi	tion B			
5	Sample	Fog+0.3	Fog+1.0	Fog+0.3	Fog+1.0			
	123 (Invention)	0.00	-0.02	0.00	-0.02			
10	124 (")	+0.01	-0.01	0.00	-0.01			
	125 ( " )	+0.01	+0.01	+0.01	0.00			
	126 ( " )	0.00	0.00	0.00	-0.01			
15	127 (")	0.00	0.00	0.00	-0.01			
	128 (")	0.00	-0.01	-0.01	-0.01			
20	132 ( " )	0.00	-0.01	-0.01	-0.01			
	133 ( " )	0.00	-0.01	-0.01	-0.01			

It is apparent from Table 2 that even when the samples of the present invention are processed with a model exhausted solution, the change in color turbidity is small, while when samples outside the scope of the invention are processed with the model exhausted solution, the change in color turbidity is large. Accordingly, it is clear that the color turbidity of samples of the present invention are little processing-dependent.

# 80 EXAMPLE 3

A yellow colored coupler (YC-3) of the present invention in an amount of 0.004 g/m², 0.013 g/m² and 0.008 g/m² was added to the third layer, the fourth layer and the fifth layer of Sample 105 (Compound (26) being the same as Compound (4) of the present invention and containing no any yellow colored cyan coupler) of JP-A-1-214849 to prepare Sample 201. Similarly, (YC-26), (YC-28) and (YC-59) were added to prepare Samples 202, 203 and 204.

The color turbidity of these samples was evaluated in the same manner as in Example 1. The following color development was carried out, and the MTF value was measured.

It will be understood from Table 3 that Samples 201 to 204 of the present invention are highly sensitive, exhibit low color turbidity under any exposure conditions and are excellent in sharpness in comparison with Sample 105 of JP-A-1-214849.

Color development was conducted at 38 °C with an automatic processor under the following conditions.

45	Color development	3 min 15 sec
40	Bleaching	l min
50	Bleaching-fixing	3 min 15 sec
	Rinse with water (1)	40 sec
	Rinse with water (2)	l min
55	Stabilization	40 sec
	Drying (50°C)	1 min 15 sec

In the above processing, rinses (1) and (2) were carried out by a countercurrent system flowing from (2) to (1). Each processing solution had the following composition.

The replenishment rate of each processing solution was such that the replenishment rate in the color development was 1200 ml per m² of photographic material and that in each of the other stages including rinse was 800 ml. The amount of the processing solution brought over from the previous bath to the rinse stage was 50 ml per m² of photographic material.

# Color Developing Solution

10		Mother Solution	Replenisher
15	Diethylenetriaminepentaacetic acid	1.0 g	1.1 g
	<pre>l-Hydroxyethylidene-1,1- diphosphonic acid</pre>	2.0 g	2.2 g
20	Sodium sulfite	4.0 g	4.4 g
	Potassium carbonate	30.0 g	32.0 g
	Potassium bromide	1.4 g	0.7 g
25	Potassium iodide	1.3 mg	-
	Hydroxylamine sulfate	2.4 g	2.6 g
30	4-(N-Ethyl-N-β-hydroxyethyl-amino)-2-methylaniline sulfate	4.5 g	5.0 g
	Add water to make	l liter	l liter
35	рН	10.0	10.05

# Bleaching Solution

Mother solution and replenisher being the same.

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	Ethylenediaminetetraacetic acid iron(III) ammonium salt	120.0 g
5	Disodium ethylenediaminetetraacetate	10.0 g
	Ammonium nitrate	10.0 g
	Ammonium bromide	100.0 g
10	Bleaching accelerator	$5 \times 10^{-3}$ mo:
15	$\begin{pmatrix} H_3C \\ H_3C \end{pmatrix} N-(CH_2)_2-S-S-(CH_2)_2 N \begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$	
20	Add ammonia water to make	рН 6.3
	Add water to make	l liter
25	Bleaching-fixing Solution	
20	Mother solution and replenisher being the	same.
30	Ethylenediaminetetraacetic acid iron(III) ammonium salt	<b>50.</b> 0 g
	Disodium ethylenediaminetetraacetate	5.0 g
	Sodium sulfite	12.0 g
35	Aqueous solution of ammonium thiosulfate (70%)	240 ml
	Add ammonia water to make	рн 7.3

# Rinsing Water

Add water to make

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Tap water containing calcium ions (32 mg/ $\ell$ ) and magnesium ions (7.3 mg/ $\ell$ ) was passed through a column packed with an H-type strongly acidic cation exchange resin and an OH-type strongly basic anion exchange resin to reduce calcium ion concentration to 1.2 mg/ $\ell$  and magnesium ion concentration to 0.4 mg/ $\ell$ . Sodium isocyanurate dichloride in an amount of 20 mg/ $\ell$  was then added to the treated water.

l liter

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# Stabilizing Solution

Mother solution and replenisher being the same.

5	Formalin (37% w/v)	2.0 ml		
10	Polyoxyethylene p-monononylphenyl ether (average degree of polymerization: 10)	0.3 g		
	Disodium ethylenediamintetraacetate	0.05 g		
15	Add water to make	l liter		
	рН	5.8		

# 20 Drying

Drying temperature was 50°C.

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		lue Le/mm) Cyan Image	0.82	0.84	0.84	0.84	0.84											
5		MTF Va 10 cyc Yellow Image	0.98	1.00	1.00	1.00	0.99											
10											E L	+0.07	-0.03	-0.03	-0.03	0.00		
15			bidity Condition Fog+0.3 Fog	+0.01	-0.03	-0.03	-0.03	-0.02										
20		Color Turbidity Condition A Cond 9+0.3 Fog+1.0 Fog+0.	+0.12	+0.02	+0.02	+0.02	+0.04		r.									
				Condit Fog+0.3	+0.02	-0.02	-0.02	-0.02	-0.01		inventio							
30	Table 3	Relative Sensitivity	00.0	0.03	0.03	0.03	0.01		he present invention.									
35		Yellow Colored Cyan Coupler in 3rd, 4th and	1	YC-3	YC-26	YC-28	YC-59	JP-A-1-214849	(4) is the compound No. of the									
40		Compound in 3rd and 4th Layers	(4)2)	=	z	Ξ	=	Sample 105 of	is the com									
45			nparison)	ntion)			_	l) Samp	2) (4)									
50		Sample	$105^{1)}$ (Comparison) $(4)^{2}$	201 (Invention)	202 (")	203 (")	204 (")											

# EXAMPLE 4

The yellow colored cyan coupler (YC-31) of the present invention in an amount of  $0.012~g/m^2$  and the compound (12) of formula (I) according to the present invention in an amount of  $0.010~g/m^2$  were added to

the fourth layer of Sample 108 (containing no compound represented by formula (I) and yellow colored coupler of the present invention) of JP-A-61-51146. The sample was processed in the same manner as in Example 1 of JP-A-61-51146. The yellow color turbidity of the resulting sample was small in comparison with Sample 108 of JP-61-51146.

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 a support having thereon at least one redsensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, wherein said photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:

$$A-(L_1)_v-B-(L_2)_v-DI$$
 (I)

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wherein A represents a group which is cleaved from  $(L_1)_V$ -B- $(L_2)_w$ -DI by a reaction of the compound of formula (I) with an oxidation product of a developing agent;  $L_1$  represents a bonding group which is cleaved from B after the cleavage of the bond between  $L_1$  and A; B represents a group which reacts with an oxidation product of a developing agent to release  $(L_2)_W$ -DI;  $L_2$  is a group which is cleaved from DI after the cleavage of the bond between B and  $L_2$ ; DI represents a development inhibitor; v and w each represents an integer of 0 to 2; and when v or w is 2, the two  $L_1$  groups or the two  $L_2$  groups may be the same or different groups.

- 2. The silver halide color photographic material as in claim 1, wherein the compound represented by formula (I) and the yellow colored cyan coupler each is incroporated in at least one of said silver halide emulsion layers and a light-insensitive intermediate layer adjacent thereto.
- 3. The silver halide color photographic material as in claim 1, wherein the compound represented by formula (I) is incorporated in the layer having the same color sensitivity as that of the layer containing the yellow colored cyan coupler.
  - 4. The silver halide color photographic material as in claim 1, wherein the layer containing the compound represented by formula (I) is a red sensitive layer.

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- 5. The silver halide color photographic material as in claim 1, wherein the yellow colored cyan coupler is contained in the red-sensitive layer.
- 6. The silver halide color photographic material as in claim 1, wherein the compound represented by general formula (I) and the yellow colored cyan coupler are contained in the same red-sensitive silver halide emulsion layer.
  - 7. The silver halide color photographic material as in claim 1, wherein a magenta polymer coupler is contained in the green-sensitive silver halide emulsion layer or in a light-insensitive layer adjacent thereto.
  - 8. The silver halide color photographic material as in claim 1, wherein the order of the layers is red-, green- and blue-sensitive silver halide emulsion layers from the support and a magenta polymer coupler is contained in the green sensitive silver halide emulsion layer.

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9. The silver halide color photographic material as in claim 1, wherein the amount of the compound represented by formula (I) is from 1  $\times$  10<sup>-6</sup> to 1  $\times$  10<sup>-3</sup> mol/m<sup>2</sup>.

- 10. The silver halide color photographic material as in claim 1, wherein the amount of the yellow colored cyan coupler is from 0.05 to 0.30 g/m<sup>2</sup>.
- 11. The silver halide color photographic material as in claim 1, wherein the yellow colored cyan coupler has an absorption maximum at 400 nm to 500 nm and forms a cyan dye having an absorption maximum at 630 nm to 750 nm by coupling with the oxidation product of an aromatic primary amine developing agent.
- 12. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is capable of releasing a moiety of a water-soluble dye having a group selected from the group consisting of a 6-hydroxy-2-pyridone-5-ylazogroup, a pyrazolone-4-ylazo group, a 2-acylaminophenylazo group, a 2-sulfonamidophenylazo group, 5-aminopyrazole-4-ylazo group by a coupling reaction with an oxidation product of an aromatic primary amine developing agent.
- 13. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is selected from the group consisting of couplers represented by formulas (CI) to (CIV):

$$Cp-(T)_{k}-X-Q-N=N \xrightarrow{R_{1}} R_{2}$$
HO
$$R_{3}$$

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Cp-(T)<sub>k</sub>-X-Q-N=N
$$\stackrel{R_9}{\longrightarrow}$$
HN $\stackrel{N}{\longrightarrow}$ 
R<sub>10</sub>

Cp-(T)<sub>k</sub>-X-Q-N=N
$$\stackrel{R_9}{\longrightarrow}$$
N (CIV)

wherein Cp represents a cyan coupler moiety (T is bonded to the coupling site thereof); T represents a timing group; k represents 0 or 1; X represents an N-, O- or S-containing bivalent group which is

bonded to  $(T)_k$  through the N, O or S atom and which also is bonded to Q; Q represents an arylene group or a bivalent heterocyclic group;

R<sub>1</sub> and R<sub>2</sub> each represents a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group; R<sub>3</sub> is a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; the group of

$$-N=N$$

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may be in the form of at least one of other tautomeric form thereof;

 $R_4$  is an acyl group or a sulfonyl group;  $R_5$  is a group which can be attached to the benzene ring; j is an integer of 0 to 4; when j is 2 or greater, the two or more  $R_5$  groups may be the same or different;  $R_9$  is a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, a cycloalkyloxy group, an aryloxy group, a heterocyclic group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group;  $R_{10}$  is hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; the group

may be in the tautomeric form thereof; and said coupler has at least one water-solubilizing group at T, X, Q,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_9$  and  $R_{10}$ .

- **14.** The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is added to a silver halide emulsion layer or a light-insensitive intermediate light-insensitive intermediate layer adjacent thereto.
  - **15.** The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is added to a red sensitive silver halide emulsion layer.
  - **16.** The silver halide color photographic material as in claim 7, wherein the magenta polymer coupler is a polymer derived from at least one monomer selected from the group consisting of monomers represented by formula (P):

$$CH_{2} = C$$

$$(P)$$

$$CH_{2} = C$$

$$(D)_{p} (E)_{q} (F)_{r} T$$

wherein R<sub>121</sub> represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms or a chlorine

atom; -D-represents -COO-, -CONR $_{122}$ - or a substituted or unsubstituted phenylene group; -E- represents a substituted or unsubstituted alkylene, phenylene or aralkylene group; -F- represents -CONR $_{122}$ -, -NR $_{122}$ CONR $_{122}$ -, -NR $_{122}$ COO-, -NR $_{122}$ COO-, -OCONR $_{122}$ -, -NR $_{122}$ -, -COO-, -OCO-, -CO-, -O-, -S-, -SO $_{2}$ -, -NR $_{122}$ SO $_{2}$ -, or -SO $_{2}$ NR $_{122}$ -; R $_{122}$  represents a hydrogen atom or a substituted or unsubstituted, saturated or unsaturated aliphatic group or a substituted or unsubstituted aryl group and when two or more R $_{122}$  groups per molecule exist, they may be the same or different groups; and p, q and r each represents 0 or 1 with the proviso that there is no case where p, q and r are 0 simultaneously;

T represents a moiety (which is bonded to  $\{F\}_{r}$ - at any one site of Ar, Z and R<sub>133</sub>) of a magenta coupler represented by formula (Q)

 $\begin{array}{c|c}
R_{133} & Z \\
N & \\
N & \\
\end{array}$ 

wherein Ar represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted aryl group, an alkoxy group, an aryloxy group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylsulfonamido group, an arylsulfonamido group, an alkylsulfonamido group, an arylsulfonamido group, a sulfamoyl group, an alkylsulfamoyl group, a dialkylsulfamoyl group, an alkylthio group, an arylthio group, a cyano group, a nitro group and a halogen atom; R<sub>133</sub> represents an anilino group, an acylamino group, a ureido group or a sulfonamido group, said groups may be substituted;

Z represents a halogen atom, and a group which is bonded through an oxygen atom, nitrogen atom or a sulfur atom and eliminated by a coupling reaction.

- 17. The silver halide color photographic material as in claim 16, wherein the polymer is a copolymer with a non-color forming ethylenic monomer.
- 18. The silver halide color photographic material as in claim 7, wherein a magenta polymer coupler is used in the green-sensitive silver halide emulsion layer in an amount of from 0.005 to 0.5 mol per mol of silver used in the same layer.
- 19. The silver halide color photographic material as in claim 7, wherein a coupler is used in the light-sensitive layer in an amount of from 0.01 to 1.0 g/m².

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