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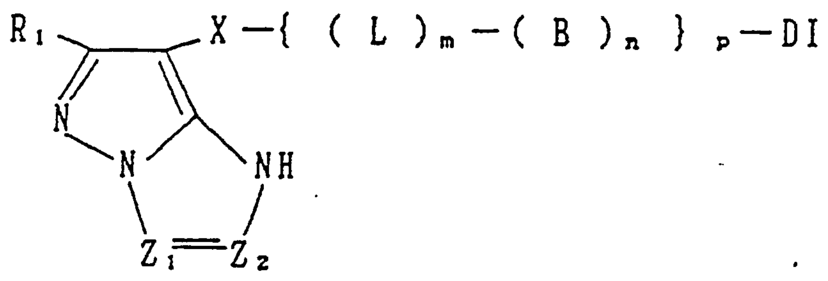
(54) Silver halide color photographic material.

(57) A silver halide color photographic material having at least one silver halide emulsion layer on a support,. wherein said emulsion layer contains a development inhibitor-releasing coupler represented by following formula (I);



wherein R_1 represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxy group, a nitro group, a carboxy group, an amino group, an alkoxy group, an aryloxy group, an acylamino group, an alkylamino group, an anilino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a sulfonyl group, a phosphinyl group, an aryloxycarbonyl group, an aryl group, or an azolyl and when R_1 is a divalent group, the coupler may form a bispcompound at the divalent group; Z_1 and Z_2 each represents a nitrogen atom or $=C\text{-}R_2$ (wherein R_2 has the same meaning as R_1) and when Z_1 and Z_2 are both

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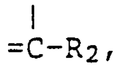
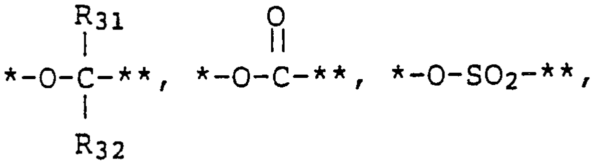
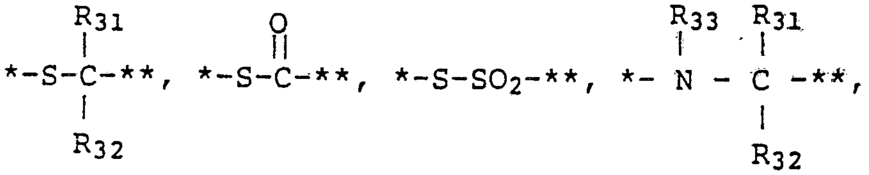


$$=\overset{|}{C}-R_2,$$

two R_2s may be the same or different; X represents

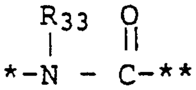


$$*-O-\underset{R_{32}}{\overset{R_{31}}{C}}-**,\quad *-O-\overset{O}{\overset{\|}{C}}-**,\quad *-O-SO_2-**,$$



$$*-S-\underset{R_{32}}{\overset{R_{31}}{C}}-**,\quad *-S-\overset{O}{\overset{\|}{C}}-**,\quad *-S-SO_2-**,\quad *-\overset{R_{33}}{N}-\underset{R_{32}}{\overset{R_{31}}{C}}-**,$$

or



$$*-\overset{R_{33}}{N}-\overset{O}{\overset{\|}{C}}-**$$

(wherein * represents a group bonding to the left side of X; ** represents a group bonding to the right side of X; R_{31} and R_{32} have the same meaning as R_1; and R_{33} represents an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfonyl group, or a sulfamoyl group); L represents a group of cleaving the bond of the right side [the bond to $(B)_m$] after cleaving the left side of L; B represents a group of cleaving the bond at the right side of B by reacting with the oxidation product of a color developing agent; DI represents a development inhibitor; m and n each represents 0 or 1 with the exclusion that m and n are simultaneously 0; and p represents 1 or 2 and when p is 2, two $[(L)_m-(B)_n]$s maybe the same or different.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a silver halide color photographic material containing a compound capable of utilizing a development inhibiting group during the development processing.

BACKGROUND OF THE INVENTION

In a color photographic material by a subtractive color process, a development inhibitor releasing coupler (DIR coupler) is used for improving the photographic performance such as the sharpness, the graininess, the color reproducing property, etc. The photographic action of the DIR couplers is described in T.H. James, The Theory of the Photographic Process, 4th ed., pages 610 to 611, and page 344 (published by Macmillan Publishing Co., New York, 1977).

Now, as the DIR coupler being used for a green-sensitive silver halide emulsion layer, a DIR coupler which releases a development inhibitor by the coupling reaction with the oxidation product of a color developing agent and forms at the same time a magenta dye at development is preferred in the view point of the color reproducing property and the sharpness of the color photographic material.

The reason is as follows. That is, since when a DIR coupler forming a magenta dye is used for a green-sensitive emulsion layer, the dye formed from the DIR coupler can be utilized as a part of the magenta density, the total amount of organic compounds such as couplers being added to the green-sensitive emulsion layer can be reduced as compared to the case of using a DIR coupler which does not form a magenta dye, whereby an effect of improving the sharpness of images by reducing the thickness of the emulsion layer is obtained. Furthermore, the use of a DIR coupler coloring other color than a magenta color for a green-sensitive emulsion layer is undesirable since a color turbidity follows.

As a DIR coupler coloring in magenta color, a coupler having a 5-pyrazolone nucleus is well known but a DIR coupler having a 5-pyrazolone nucleus has a fault that the heat stability is low. A DIR coupler is so designed that the coupler exists in an inactive state until a development occurs by bonding a development inhibitor having a property of largely changing the performance of a color photographic material by strongly acting to a silver halide emulsion to the coupling active position of the coupler directly or via a linkage group such that the active point is protected.

However, if the heat stability of the DIR coupler is low, when the color photographic material containing the coupler is stored for a long period of time or stored under a high-temperature high-humidity condition, the DIR coupler is decomposed to form a material giving had influences on the photographic performance to fatally reduce the photographic performance. This danger is increased as the amount of the DIR coupler is increased and hence in the case of using the DIR coupler of a 5-pyrazolone nucleus having a low heat resistance, there is a restriction that the amount thereof can not be increased too much.

On the other hand, recently, DIR couplers having a pyrazoloazole skeleton as a novel magenta coloring skeleton have been intensely investigated and are disclosed in JP-B-63-22571 (the term "JP-B" as used herein means an "examined published Japanese patent application"), JP-A-60-185950, JP-A-61-177455, JP-A-61-177456, JP-A-61-28947, JP-A-61-231553, JP-A-61-233741, JP-A-61-240240, JP-A-61-236551, JP-A-61-238057, JP-A-61-249052, JP-A-61-251847, JP-A-61-251848, JP-A-61-267046, JP-A-61-267047, JP-61-267048, JP-A-61-272741, JP-A-62-24252, JP-A-62-26962, JP-A-62-81638, JP-A-62-86361, JP-A-62-87958, JP-A-62-103640, JP-A-62-151850, JP-A-63-163454, JP-A-63-259556, JP-A-63-304254, JP-A-60-22034, JP-A-61-80251, JP-A-61-189537,JP-A-62-159144, JP-A-62-166341, JP-A-62-172358, JP-A-1-66646, JP-A-58-42045, and JP-A-63-30847 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), and U.S. Patent 4,248,962.

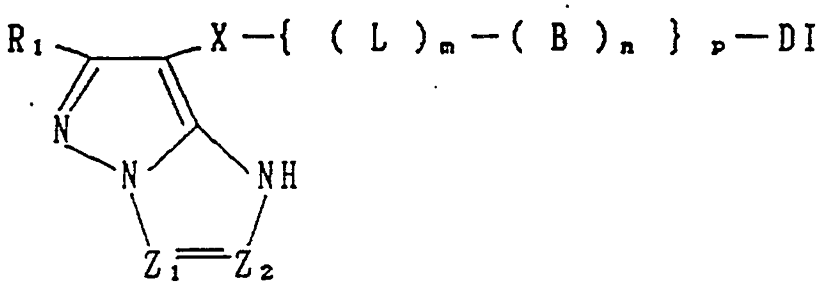
However, these DIR couplers are yet insufficient in the point of improving the sharpness and the color reproducibility.

SUMMARY OF THE INVENTION

The object of this invention is to solve the problem on the heat stability of a conventional magenta coloring DIR coupler and to provide a silver halide color photographic material excellent in sharpness, graininess, and storage stability by developing a magenta coloring DIR coupler having large improving effects of the sharpness and the graininess.

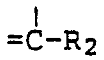
It has now been discovered that the aforesaid object can be attained by the present invention as shown below.

That is, according to this invention, there is provided a silver halide color photographic material containing a development inhibitor releasing coupler (DIR coupler) represented by following formula (I);



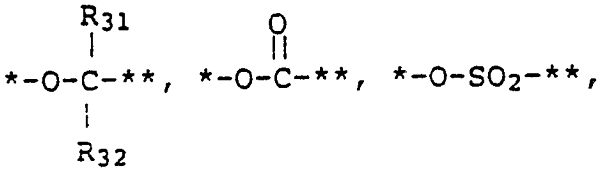
(I)

wherein R_1 represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxy group, a nitro group, a carboxy group, an amino group, an alkoxy group, an aryloxy group, an acylamino group, an alkylamino group, an anilino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a sulfonyl group, an aryloxycarbonyl group, an acyl group, or an azolyl and when R_1 is a divalent group, the coupler may form a bis type coupler; Z_1 and Z_2 each represents a nitrogen atom or

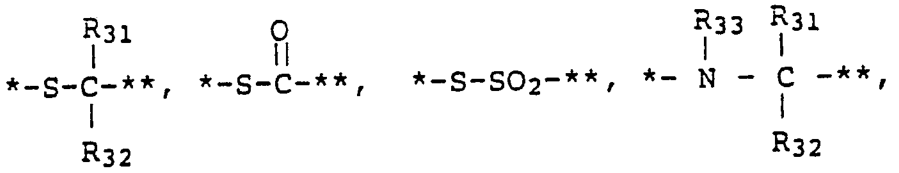


$$=\overset{|}{C}-R_2$$

(wherein R_2 has the same meaning as R_1) and when Z_1 and Z_2 are all $=C-R_2$, two R_2s may be the same or different; X represents

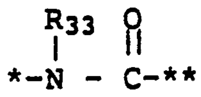


$$*-O-\underset{\underset{R_{32}}{|}}{\overset{\overset{R_{31}}{|}}{C}}-**,\quad *-O-\overset{\overset{O}{\|}}{C}-**,\quad *-O-SO_2-**,$$



$$*-S-\underset{\underset{R_{32}}{|}}{\overset{\overset{R_{31}}{|}}{C}}-**,\quad *-S-\overset{\overset{O}{\|}}{C}-**,\quad *-S-SO_2-**,\quad *-\overset{\overset{R_{33}}{|}}{N}-\underset{\underset{R_{32}}{|}}{\overset{\overset{R_{31}}{|}}{C}}-**,$$

or



$$*-\overset{\overset{R_{33}}{|}}{N}-\overset{\overset{O}{\|}}{C}-**$$

(wherein * represents a group bonding to the left side of X; ** represents a group bonding to the right side of X; R_{31} and R_{32} have the same meaning as R_1; and R_{33} represents an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfonyl group, or sulfamoyl group); L represents a group which cleaves the right side bond, i.e., the bond to $(B)_m$,after cleaving the left side group of L; B represents a group which reacts with the oxidation product of a color developing agent to cleave the bond at the right side of B; DI represents a development inhibitor; m and n each represents 0 or 1 with the exclusion that m and n are all 0; and p represents 1 or 2 and when p is 2, two $((L)_m$- $(B)_n)$s maybe the same or different. DETAILED DESCRIPTION OF THE INVENTION Then, the DIR coupler shown by formula (I) described above is explained in detail.

In formula (I), R_1 represents a hydrogen atom, a halogen atom (e.g., chlorine and bromine), an alkyl group, e.g., a straight chain or branched alkyl group having from 1 to 32 carbon atoms, a C_{7-32} aralkyl group, a C_{2-32} alkenyl group, a C_{2-32} alkinyl group, a C_{3-32} cycloalkyl group, and a C_{3-32} cyclo-alkenyl group; and practically, for example, methyl, ethyl, propyl, isppropyl, t-butyl, tridecyl, 2-methanesulfonylethyl, 3-(3-pentadecylphenoxy)propyl, 3- 4- 2-[4-(4-hydroeyphenylsulfonyl)phenoxy]dodecaneamido phenyl propyl, 2-ethoxytridecyl, trifluoromethyl, cyclopentyl, and 3-(2,4-di-t-amylphenoxy)propyl; a C_{6-30} aryl group (e.g., phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl, and 4-tetradecaneamidophenyl); a C_{1-30} heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pyrimidinyl, and 2-benzothiazolyl, imidazolyl, pyrazolyl, 3-chloropyrazolyl-1-yl, and triazolyl); a cyano group, a hydroxy group, a nitro group, a carboxy group, a C_{1-32} amino group, a C_{1-32} alkoxy group (e. g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecyloxyethoxy, and 2-methanesulfonylethoxy), a C_{6-30} aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-t-butylphenoxy, 3-nitrophenoxy, 3-t-butyloxycarbamoylphenoxy and 2-methoxyphenoxy); a C_{1-32} acylamino group (e.g., acetamido, benzamido, tetradecaneamido, 2-(2,4-di-t-amylphenoxy)-butaneamido, 4-(3-t-butyl-4-hydroxyphenoxy)-butaneamido, and 2-{4-(4-hydroxyphenylsulfonyl)phenoxy}decaneamido)); a C_{1-32} alkylamino group (e.g., methylamino, butylamino, dodecylamino, diethylamino, and methylbutylamino); a C_{6-30} anilino group (e.g., phenylamino, 2-chloroanilino, 2-chloro-5-tetradecaneamidoanilino, 2-chloro-5-{α-(3-t-butyl-4-hydroxyphenoxy)-dodecaneamido}anilino); a C_{1-32} ureido group (e.g., phenylureido, methylureido, and N,N-dibutylureido); a C_{0-30} sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino and N-methyl-N-decylsulfamoylamino); a C_{1-32} alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, and 3-(4-t-butylphenoxy)propylthio); a C_{6-30} arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenyithio, 3-pentadecylphenylthio, 2-carboxyphenylthio, and 4-tetradecaneamidophenylthio); a C_{2-32} alkoxycarbonylamino group (e.g., methoxycarbonylamino, and tetradecyloxycarbonylamino), a C_{1-32} sulfornamido group (e.g., methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido, and 2-methoxy-5-t-butylbenzenesulfonamido); a C_{1-32} carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-dodecyloxyethylethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, and N-{3-(2,4-di-t-aminophenoxy)propyl}carbamoyl); a C_{0-32} sulfamoyl group (e g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-ethyl-N-dodecylsulfamoyl, and N,N-diethylsulfamoyl); a C_{1-32}sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, and toluenesulfonyl); a C_{2-32} alkoxycarbonyl group (e.g., methoxycarbonyl, butoxycarbonyl, dodecyloxycarbonyl, and octadecyloxycarbonyl); a C_{1-32} heterocyclic oxy group (e.g., 1-phenyltetrazol-5-oxy and 2-tetrahydropyranyloxy); a C_{6-30} azo group (e.g., phenylazo, 4-methoxyphenylazo, 4-pivaloylaminophenylazo, and 2-hydroxy-4-propanoylphenylazo); a C_{2-32} acyloxy group (e.g., acetoxy); a carbamoyloxy group (e.g., N-methylcarbamoyloxy and N-phenylcarbamoyloxy); a C_{3-32} silyloxy group (e.g., trimethylsilyloxy and dibutylsilyloxy); a C_{7-30} aryloxycarbonylamino group (e.g., phencxycarbonylamino); a C_{2-32} imido group (e.g., N-succinimido, N-phthalimido, and 3-octadecenylsuccinimido); a C_{1-32} heterocyclic thio group (e.g., 2-benzothiazolythio, 2,4-di-phenoxy-1,3,5-triazine-6-thio, and 2-pyridylthio); a C_{1-32} sulfinyl group (e.g., dodecanesulfinyl, 3-pentadisilphenylsulfinyl, and 3-phenoxypropylsulfinyl); a C_{1-32} phosphinyl group (e.g., phenoxyphosphinyl, octyloxyphosphinyl, and phenylphosphinyl); an aryloxycarbonyl group (e.g., phenoxycarbonyl); a C_{1-32} acyl group (e.g., acetyl, 3-phenylpropane, benzoyl, and 4-dodecyloxybenzoyl).

The aforesaid groups shown by R_1 may further have an organic substituent bonded by a carbon atom, an oxygen atom, a nitrogen atom or a sulfur atom or may have a halogen atom.

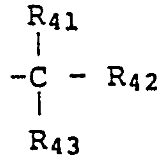
R_1 is preferably a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, a ureido group, a urethane group, or an acylamino group and more preferably a hydrogen atom, an alkyl group, or an aryl group.

When R_1 is a hydrogen atom, an alkyl group or an aryl group, the heat stability of the compound shown by formula (I) is particularly excellent.

R_2 is the same group as illustrated above on R_1 and is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfinyl group, an acyl group, or a cyano group. Also, R_2 is more preferably an alkyl group or an aryl group.

The preferred alkyl group shown by R_2 is shown by following formulae (L - 1) and (L - 2).

$$-CH_2 - R_{21} \qquad (L - 1)$$



$$-\underset{R_{43}}{\overset{R_{41}}{C}} - R_{42} \qquad (L - 2)$$

In formula (L - 1), R_{21} has the same meaning as R_1 in formula (I). In formula (L - 2), R^{41} and R^{42} each represents an alkyl group and R_{43}has the same meaning as R_1 in formula (I).

The alkyl group shown by R_{41} or R_{42} is preferably an alkyl group having from 1 to 20 carbon atoms (e.g., methyl, ethyl, propyl, hexyl, nonyl, undecyl, tridecyl, and hexadecyl) and the alkyl groups each may further have a substituent.

R_{21} and R_{43} each has the same meaning as R_1 in formula (I) and is preferably a hydrogen atom or an alkyl group. Preferred examples of the alkyl group are same as those illustrated above as the preferred examples of the alkyl group shown by R_{41} and further has a substituent.

In formula (I), R_2 is preferably an aryl group or a phenyl group and each group may further has a substituent.

R_2 is most preferably the alkyl group shown by aforesaid formula (L - 2).

In formula (I), R_{31} and R_{32} each represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, or a phenyl group.

R_{33} represents an alkyl group having not more than 6 carbon atoms (e.g., methyl, ethyl, trifluoromethyl, isorpopyl, benzyl, propyl, butyl, and cyclohexyl), an aryl group (e.g., phenyl, p-nitrophenyl, and p-methoxyphenyl), an acyl group (e.g., acetyl, propionyl, butyryl, trilfuoroacetyl, heptafluorobutyryl, benzoyl and pentafluorobutyryl), an alkoxycarbonyl group (e.g., methoxycarbonyl and isobutyloxycarbonyl), a carbamoyl group (e.g., N,N-dimethylcarbamoyl and N,N-diethylcarbamoyl), a sulfonyl group (e.g., methanesulfonyl, trifluoromethanesulfonyl, and benzenesulfonyl), or a sulfamoyl group (e.g., N,N-dimethylsulfamoyl).

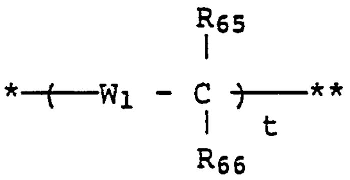
Examples of the linkage group shown by L in formula (I) are the group utilizing a cleavage reaction of hemiacetal described in U.S. Patents 4,146,396, 4,652,516, and 4,698,297, the timing group causing a cleavage reaction by utilizing an intramolecular nucleophilic reaction described in U.S. Patent 4,248,962, the timing group causing a cleavage reaction by utilizing the electron transfer reaction described in U.S. Patents 4,409,323 and 4,421,845, the group causing a cleavage reaction by utilizing the hydrolysis reaction of iminoketal described in U.S. Patent 4,546,073, and the group causing a cleavage reaction by utilizing the hydrolysis reaction of an ester described in West German Patent Publication (OLS) 2,626,317.

In formula (I), L is bonded to X at tge hetero atom included in L, such as, preferably, an oxygen atom, a sulfur atom, or a nitrogen atom.

Preferred examples of the group shown by L are shown below.

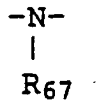
(1) Groups utilizing the cleavage reaction of hemiacetal:

These groups are described, e.g., in U.S. Patent 4,146,396, JP-A-60-249148 and JP-A-60-249149 and are shown by following formula (T - 1):



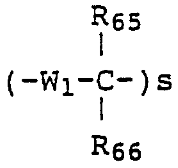
$$*-\!\left(W_1 - \underset{R_{66}}{\overset{R_{65}}{C}}\right)_t\!-** \qquad (T - 1)$$

wherein * represents a bonding hand at the left side of L of the compound shown by formula (I); ** represents a bonding hand at the right side of L of the compound shown by formula (I); W_1 represents an oxygen atom, a, sulfur atom or



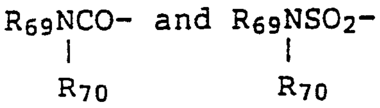
$$-\underset{\displaystyle R_{67}}{\underset{|}{N}}-$$

(wherein R_{67} represents a substituent);
R_{65} and R_{66} each represents a hydrogen atom or a substituent; and t represents 1 or 2, when t is 2, two



$$(-W_1-\overset{\displaystyle R_{65}}{\underset{\displaystyle R_{66}}{\overset{|}{\underset{|}{C}}}}-)s$$

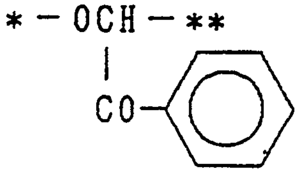
may be same or different.
When R_{65} and R_{66} in formula (T - 1) represent a substituent, typical examples of R_{67} are R_{69}-, $R_{69}SO_2$-,

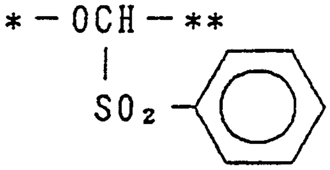


$$R_{69}\underset{\displaystyle R_{70}}{\underset{|}{N}}CO- \text{ and } R_{69}\underset{\displaystyle R_{70}}{\underset{|}{N}}SO_2-$$

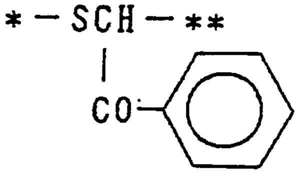
(wherein R_{69} represents an aliphatic group, an aromatic group, or a heterocyclic group and R_{70} represents an aliphatic group, an aromatic group, a heterocyclic group, or a hydrogen atom). R_{65}, R_{66}, and R_{67} each represents a divalent group and includes a case of forming a cyclic structure by the linkage of them.
Specific examples of the group shown by formula (T-1) are as follows:

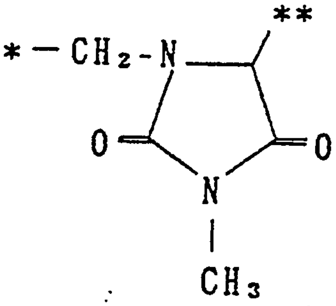
$* - OCH_2 - **$

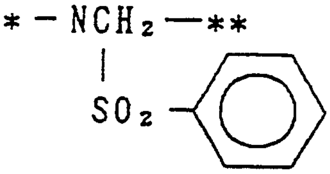


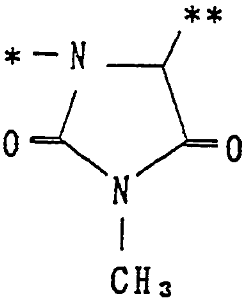


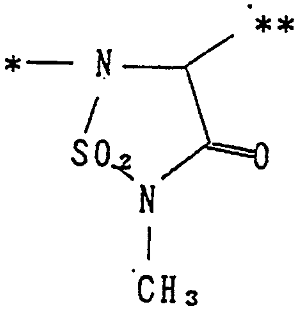
$* - SCH_2 - **$









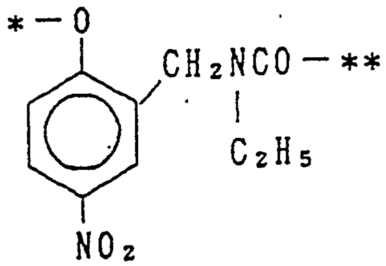


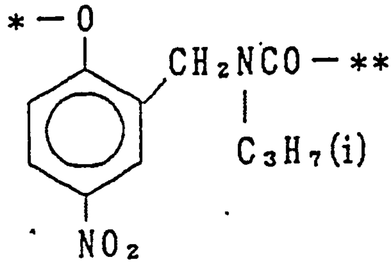
(2) Groups causing a cleavage reaction by utilizing an intramolecular nucleophilic displacement reaction: These groups are described, e.g., in U.S. Patent 4,248,962 and can be shown by following formula (T - 2):

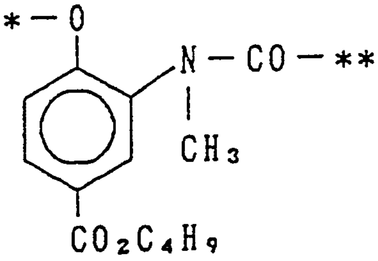
* - Nu - Link - E - II (T - 2)

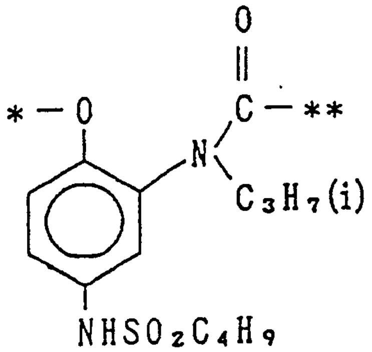
wherein * and ** have the same meaning as explained for aforesaid formula (T - 1); Nu represents a nucleophilic group, examples of the nucleophilic seed being an oxygen atom or a sulfur atom; E represents an electrophilic group which can cleave the bond to ** by the nucleophilic attack from Nu; and Link represents a linkage group which stericallyconnect Nu and E such that they can cause an intramolecular nucleophilic displacement reaction.

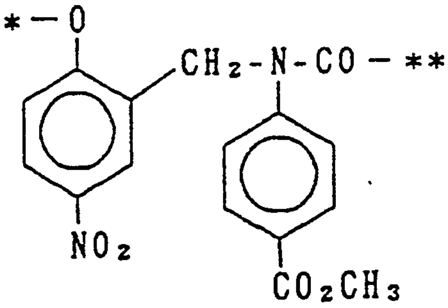
Specific examples of formula (T - 2) are illustrated below:

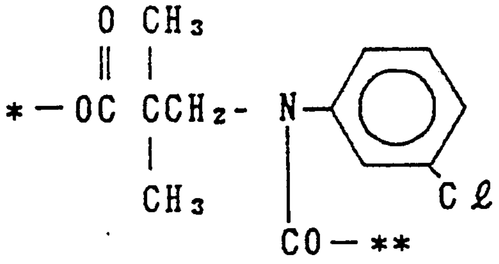










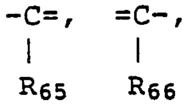


(3) Groups causing a cleavage reaction by utilizing the electron transfer reaction along a conjugated system:

These groups are described, e.g., in U.S. Patents 4,409,323 and 4,421,845 and shown by following formula (T - 3).

$* - W_1 \{ V_1 = v_2 \}_t CH_2 - ** \quad (T - 3)$

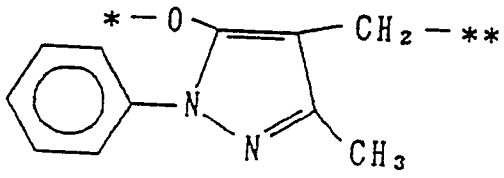
wherein V_1 and Vp2 each represents

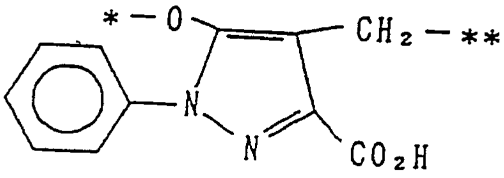


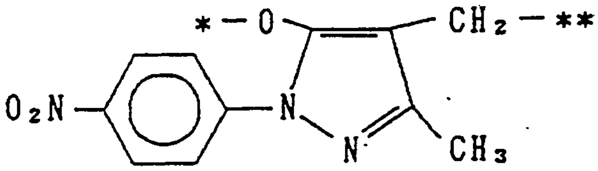
$$\underset{R_{65}}{-C=}, \quad \underset{R_{66}}{=C-},$$

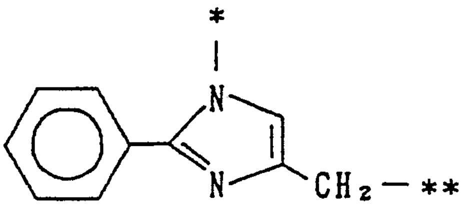
or a nitrogen atom and *, **, W_1, R_{65}, R_{66}, and t have the same meaning as explained above for formula (T - 1).

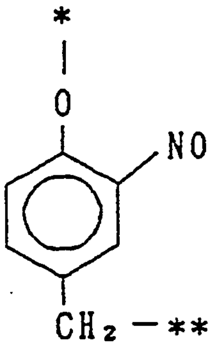
Specific examples of the group are as follows.

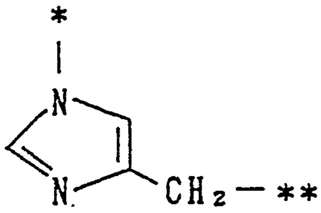


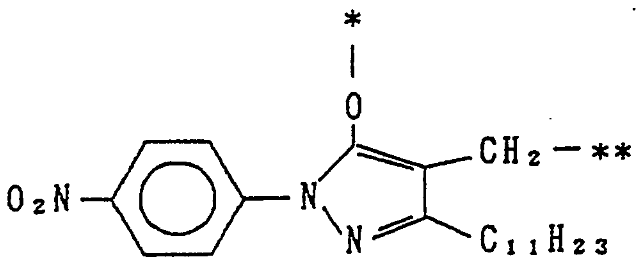






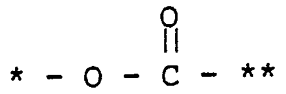






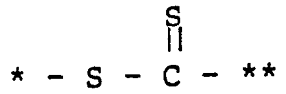
(4) Groups utilizing a cleavage reaction by the hydrolysis of ester:

These groups are linkage groups described in West German Patent Publication (OLS) 2,626,315 and are shown by following formula (T - 4) or (T - 5):



$$*-O-\overset{\overset{O}{\|}}{C}-**$$

(T - 4)



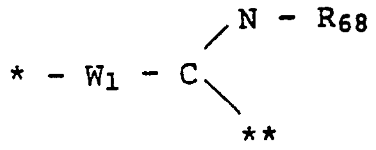
$$*-S-\overset{\overset{S}{\|}}{C}-**$$

(T - 5)

wherein * and ** have the same meaning as explained above for formula (T - 1).

(5) Groups utilizing the cleavage reaction of iminoketal:

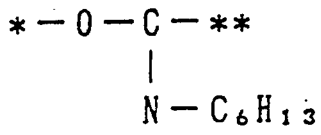
These groups are linkage groups described, e.g., in U.S. Patent 4,546,073 and are shown by following formula (T - 6):

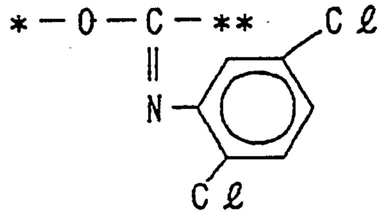


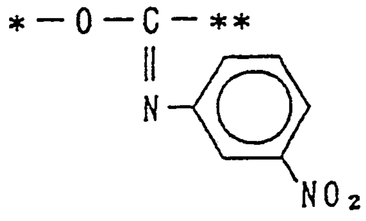
(T - 6)

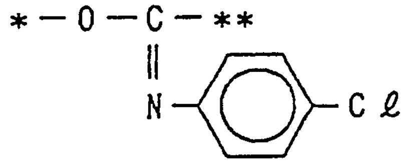
wherein *, **, and W_1 have the same meaning as explained above for formula (T - 1) and R_{68} has the same meaning as R_{67}.

Specific examples of the group shown by formula (T - 6) are as follows.









The group shown by B in formula (I) is the group leading to an oxidation-reduction group or leading to a coupler after cleaving the bond at the left side of B in formula (I).

As the group leading to a coupler, there are a yellow coupler residue (e.g., an open-chain ketomethylene type coupler residue such as acylacetoanilide, malondianilide, etc.), a magenta coupler residue (e.g., a 5-pyrazolone type coupler residue, a pyrazolotriazole type coupler residue, and an imidazopyrazole type coupler residue), a cyan coupler residue (e.g., a phenol type coupler residue, a naphthol type coupler residue, the imidazole type coupler residue described in European Patent Publication (unexamined) 249453, and a pyrazolopyrimidine type coupler residue described in European Patent Publication (unexamined) 304001, and a non-coloring coupler residue (e.g.,an indanone type coupler residue and an acetophenone type coupler residue).

Also, the group becoming a coupler may be the hterocyclic coupler residues described in U.S. Patents 4,315,070, 4,183,752, 4,174,969, 3,961,959,4,171,223 and JP-A-52-82423.

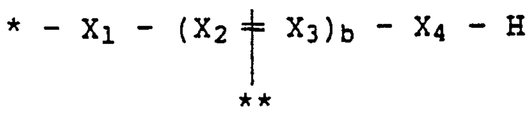
When B represents an oxidation-reduction group, the oxidation-reduction group is a group which can be cross-oxidized by the oxidation product of a color developing agent. Examples thereof are hydroquinones, cetechols, pyrogallols, 1,4-naphthohydroquinones, 1,2-naphthohydroquinones, hydrazines, and sulfonamidonaphthols. Practical examples thereof are described in JP-A-61-230135, JP-A-62-251746, JP-A-61-278852, U.S. Patents 3,364,022, 3379,529, 3,639,417, 4,684,604, and Journal of Organic Chemistry, 29, 588(1964).

The group shown by B has a group releasing by reacting with the oxidation reaction of a color developing agent, that is the group bonded to the right side of B in formula (I).

As the group, shown by B,there are the group shown by B in JP-A-63-6550, the group shown by COUP (B) in U.S. Patent 4,438,139,and the group shown by RED in U.S. Patent 4,618,571.

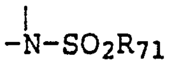
It is preferable that B is bonded to the group of the left side of B at the hetero atom included therein, such as, preferably, an oxygen atom or a nitrogen atom.

A preferred group shown by B is the group shown by following formula (B - 1):



$$* - X_1 - (X_2 \overset{}{\underset{|\,**}{=}} X_3)_b - X_4 - H \qquad (B - 1)$$

wherein * represents a position bonding to the left aide of B in formula (I); ** represents a position bonding to the right side of B in formula (I); X_1 and X_4 each represents an oxygen atom or



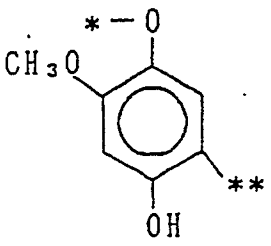
$$\overset{|}{-N}-SO_2R_{71} \quad .$$

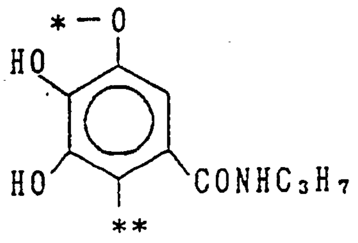
(wherein R_{71} represents an aliphatic group, an aromatic group, or heterocyclic group); X_2 and X_3 each represents a methine group or a nitrogen atom; and b represents an integer of from 1 to 3 and bb represents 0, 1 or 2, at least one of b x X_2 and b x X_3 represents a methine group having a bonding hand shown by **. Also, when b represents 2 or 3, the plural X_2s and X_3s each may be the same or different.

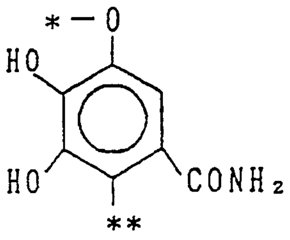
When X_2 and X_3 each represents a methine group having a substituent, they include the case of forming a cyclic structure (e.g., a benzene ring or a pyridine ring) by the combination of them and the case of not forming such a cyclic structure.

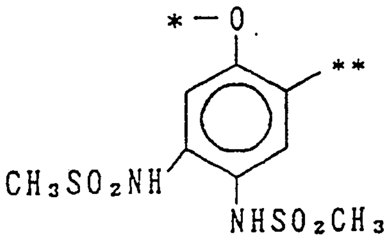
The group shown by formula (B - 1) leads to a compound meeting the Kendall-Pelz rule (see, T.H. James, The Theory of Photographic Process, 4th ed. page 299, published by Macmillan Publishing Co., Ltd., after cleaving the bond of * and is oxidized by the reaction with the oxidation product of a color developing agent.

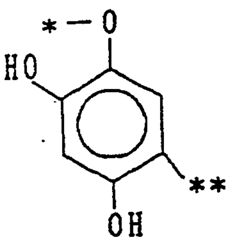
Specific examples of the group shown by formula (B-1) are shown below.

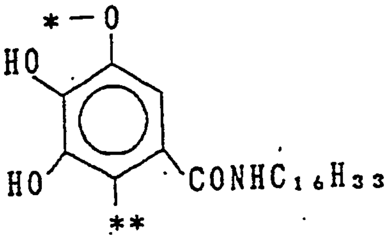

* — O
CH₃O
**
OH

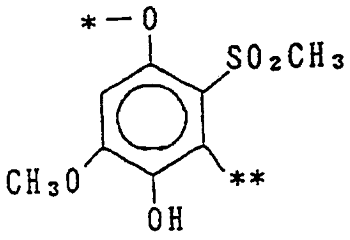

* — O
HO
HO
CONHC₃H₇
**

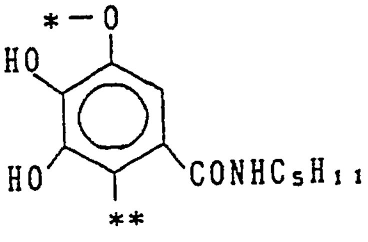

* — O
HO
HO
CONH₂
**

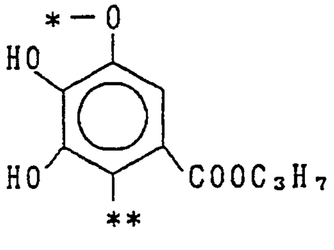

* — O
**
CH₃SO₂NH
NHSO₂CH₃

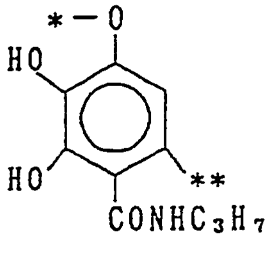

* — O
HO
**
OH


* — O
HO
HO
CONHC₁₆H₃₃
**

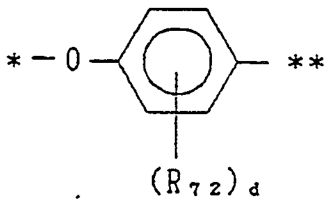

* — O
SO₂CH₃
CH₃O
**
OH


* — O
HO
HO
CONHC₅H₁₁
**

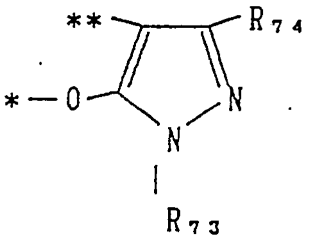

* — O
HO
HO
COOC₃H₇
**

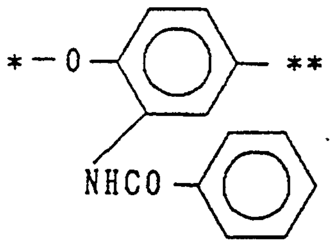

* — O
HO
HO
**
CONHC₃H₇

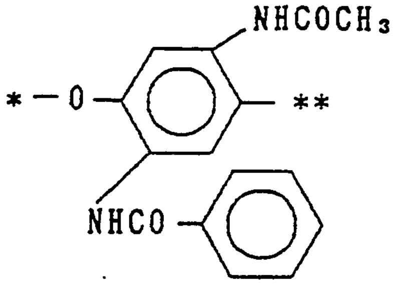
(B - 2)

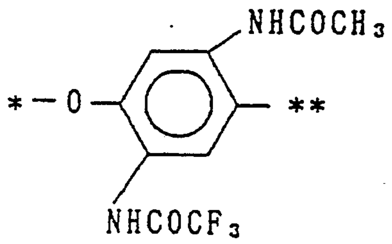


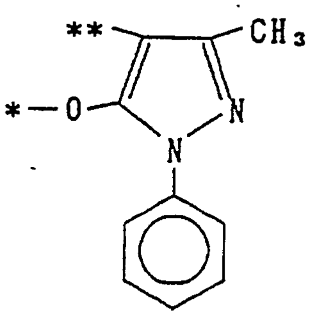
(B - 3)

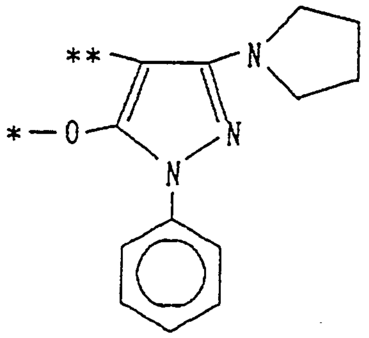




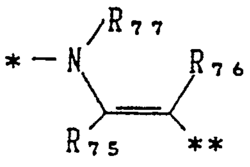






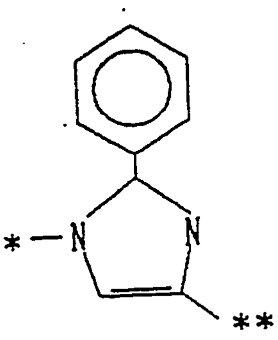


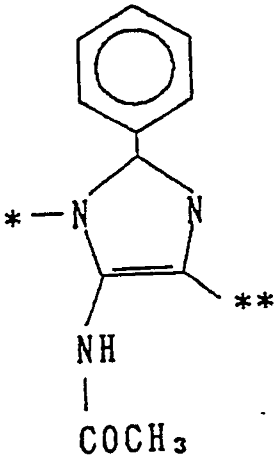
(B - 4)

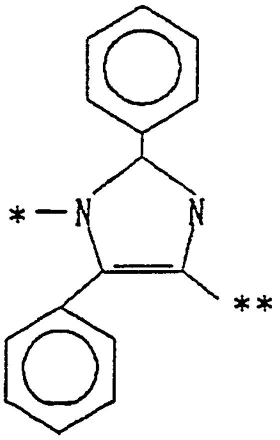


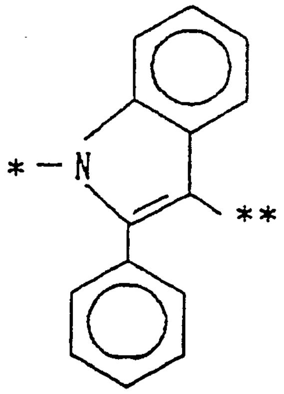
In the aforesaid formulae, * and ** have the same meaning as explained above for formula (B - 1) nd R_{75}, R_{76}, and R_{77} each represents a substituent and they include the case of forming a nitrogen-containing heterocyclic ring by combing R_{77} and R_{76} and the case of forming a nitrogen-containing heterocyclic ring by combining R_{77} and R_{75}. The group shown by aforesaid formula (B - 4) becomes a coupler having a coupling releasable group at ** after cleaving at *.

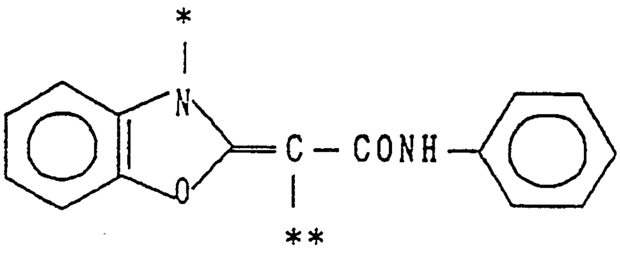
Specific examples of the group shown by formula (B - 4) are shown below.

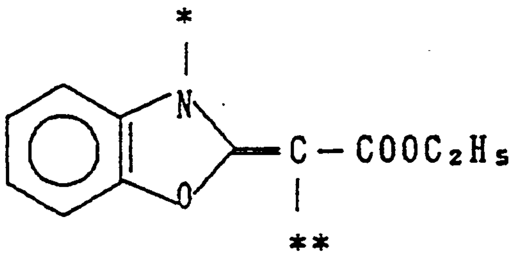

*
N
N
**

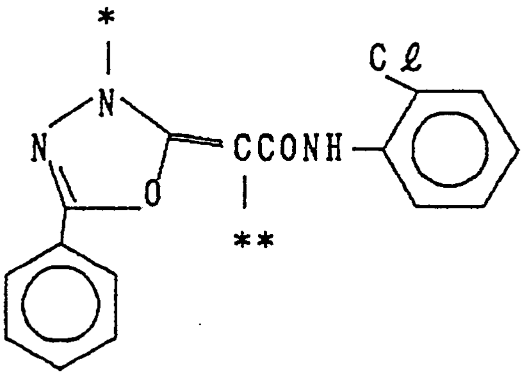

*
N
N
**
NH
COCH3









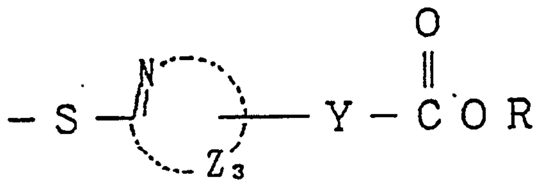


Examples of the group shown by DI in formula (I) are are a tetrazolylthio group, a thiazolylthio group, an oxadiazolylthio group, a triazolylthio group, a benzimidazolylthio group, a benzothiazolylthio group, a tetrazolylseleno group, a benzoxazolylthio group, a benzotriazolyl group, a triazolyl group, and a benzimidazolyl group.

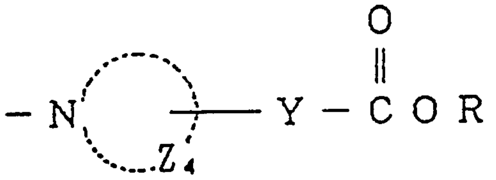
These groups are described, e.g., in U.S. Patents 3,227,554, 3,384,657, 3,615,506, 3,617,291, 3,733,201, 3,933,500, 3,958,993, 3,961,959, 4,149,886, 4,259,437, 4,095,984, 4,477,563, and 4,782,012 and

British Patent 1,450,479.

When the group shown by DI in formula (I) is the group shown by following formula (DI - a) or (DI - b), the effect of this invention is particularly large.



(DI - a)



(DI - b)

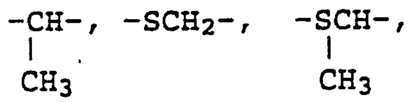
wherein Y represents a divalent linkage group having not more than 8 carbon atoms or a simple bonding hand; R represents an aliphatic group having from 1 to 6 carbon atoms or a heterocyclic group; Z_3 represents a non-metallicatomic group necessary for forming a heterocyclic ring together with carbon atom and nitrogen atom; and Z_4 represents a non-metallic atomic group necessary for forming a heterocyclic ring (a single ring or a condensed ring) together with nitrogen atom.

Z_3 preferably represents a non-metallic atomic group necessary for forming a 5- to 7-membered heterocyclic ring, which may be substituted or may be a condensed ring, together with -C=N-.

Examples of such a heterocyclic ring are triazole, tetrazole, oxadiazole, thiadiazole, benzimidazole, and benzothiazole. In these heterocyclic rings, tetrazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole, and 1,2,4-triazole are particularly preferred.

Z_4 preferably represents a non-metallic atomic group necessary for forming a 5- to 7-membered heterocyclic ring (a single ring or a condensed ring), which may be substituted, together with nitrogen atom. Examples of such a heterocyclic ring are imidazole, 1,2,4-triazole, benztriazole, 1,2,3-triazole, pyrazole, indazole, imidazoline-2-thion, 1,2,4-triazoline-3-thion, and 1,3,4-thiadiazoline-2-thion. In these heterocyclic rings, 1,2,3-triazole and benztriazole are particularly preferred.

When the heterocyclic ring shown by formula (DI - a) or (DI - b) has other substituent than Y-COOR at a position capable of being substituted, examples thereof are an aliphatic group (having from 1 to 6 carbon atoms, e.g., methyl and ethyl), a halogen atom (e.g., chlorine, fluorine, and bromine), a heterocyclic group (having from 1 to 5 carbon atoms, a 3- to 6-membered ring having heteroatoms selected from oxygen atom, sulfur atom, and nitrogen atom, e.g., furyl, thienyl, and imidazolyl), a nitro group, a cyano group, an aromatic group (having from 6 to 10 carbon atoms, e.g., phenyl), an amino group, an alkylthio group (having from 1 to 10 carbon atoms, e.g., methylthio and ethylthio), and an acylamino group (having from 2 to 8 carbon atoms, e.g., acetamide and benzamide). The divalent group shown by Y in formulae (DI - a) and (DI - b) is preferably an aliphatic group which may contain a bonding group having hetero-atom(s), such as an ether condensation, a thioether condensation, -NHCO-, - SO_2-, -CO-, or -$NHSO_2$-; an aromatic divalent linkage group, or a simple bonding hand. Examples of the divalent linkage group shown by Y are methylene, ethylene, propylene,



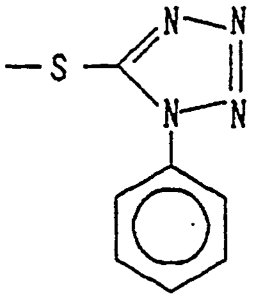
$$\underset{\displaystyle CH_3}{-\underset{|}{C}H-},\quad -SCH_2-,\quad \underset{\displaystyle CH_3}{-S\underset{|}{C}H-},$$

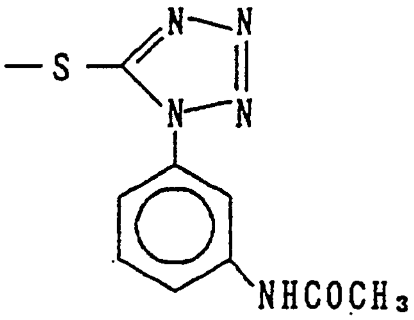
-CH_2O-CH_2-, -SCH_2CH_2-, and -CH_2SCH_2-.

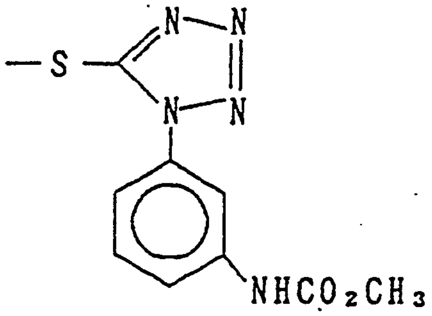
In formulae (DI - a) and (DI - b), the group shown by R is preferably an aliphatic group having from 1 to 6 carbon atoms, which may be substituted. Examples of the aliphatic group are methyl, ethyl, propyl, butyl, isopropyl, isobutyl, isoamyl, sec-amyl, and t-amyl.

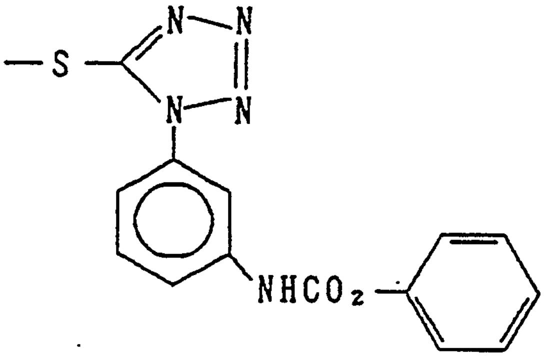
When the group shown by R has a substituent, examples of the substituent are an alkoxycarbonyl group (having from 2 to 6 carbon atoms, e.g., methoxycarbonyl, propoxycarbonyl, butoxycarbonyl, isobutoxycarbonyl, isopropoxycarbonyl, pentyloxycarbonyl, isopentyloxycarbonyl, and 2-methoxyethoxycarbonyl), a carbamoyl group (having from 0 to 6 carbon atoms, e.g., N,N-diethylcarbamyl, N-methyl-N-ethylcarbamoyl, pyrrolidinocarbonyl, and piperidinocarbonyl), a halogen atom (e.g., chlorine and fluorine), a nitro group, a cyano group, an alkoxy group (having from 1 to 4 carbon atoms, e.g., methoxy, ethoxy, and methoxyethoxy), a sulfamoyl group (having from 0 to 6 carbon atoms, e.g., N,N-diethylsulfamoyl and N-methyl-N-ethylsulfamoyl), an aryloxy group (having from 6to 10 carbon atoms, e.g., 4-chlorophenoxy), an acyl group (having from 2 to 6 carbon atoms, e.g., acetyl and benzoyl), a sulfonyl group (having from 1 to 6 carbon atoms, e.g., methanesulfonyl and butanesulfonyl), a heterocyclic group (having from 1 to 5 carbon atoms, a 3- to 6-membered heterocyclic group having hetero-atom(s)selected from nitrogen atom, oxygen atom, and sulfur aton, e.g., 2-pyridyland 3-pyridyl), and a phosphinyl group (having from 2 to 5 carbon atoms, e.g., diethoxyphosphinyl).

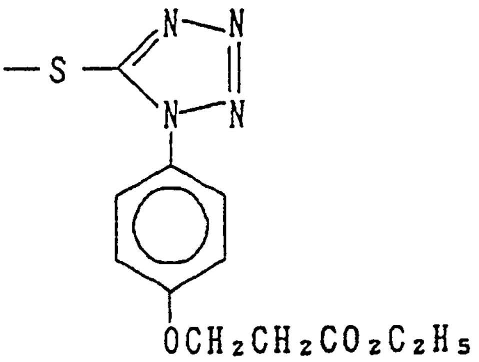
Then, specific examples of the group shown by formula (DI - a) described above are illustrated below.







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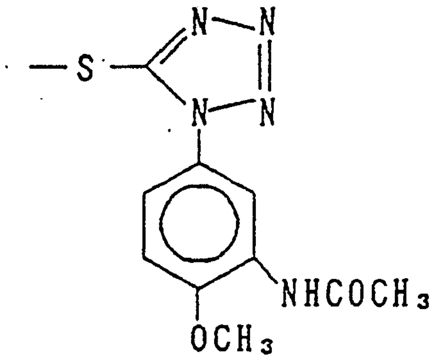
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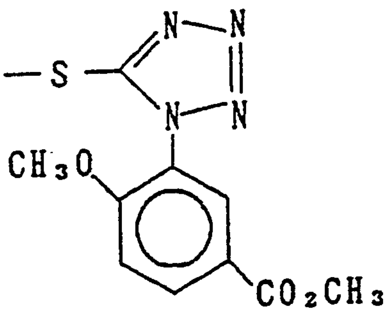
OCH₃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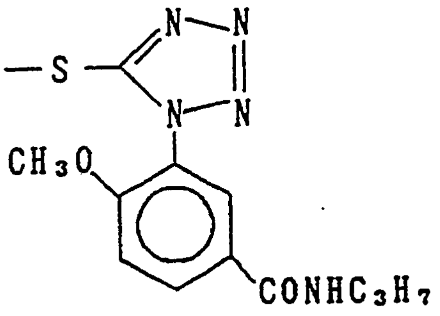
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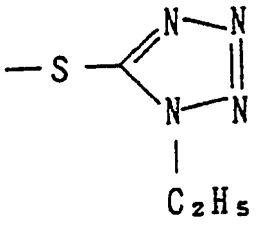
CONHC₃H₇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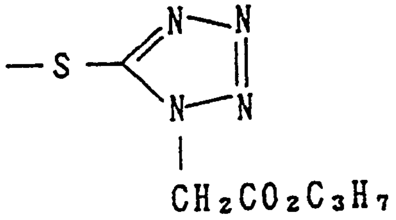
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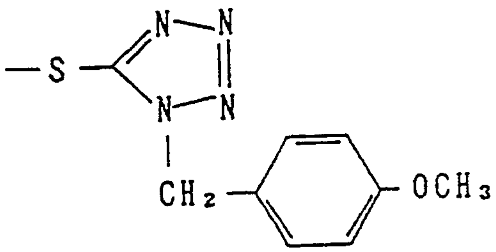
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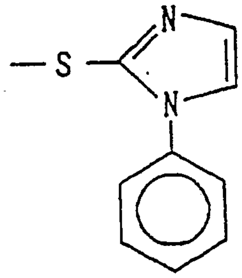
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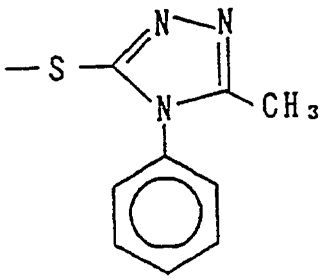
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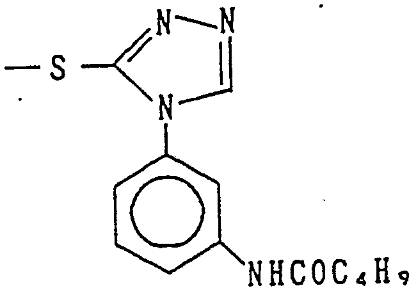
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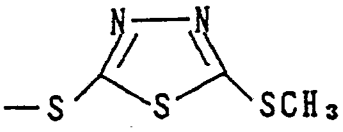
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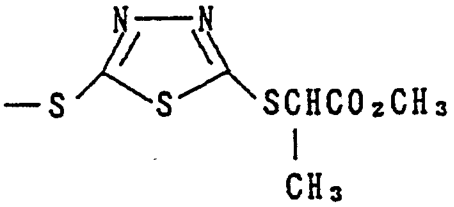
SCH₃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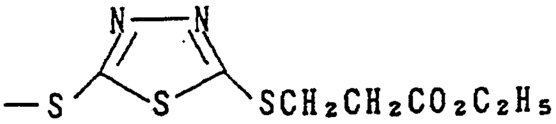
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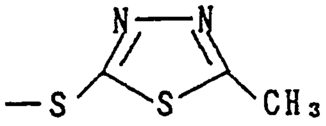
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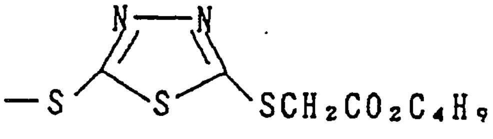
CH₃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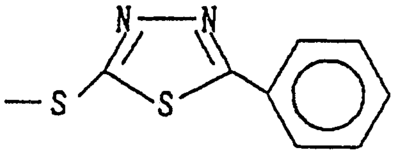
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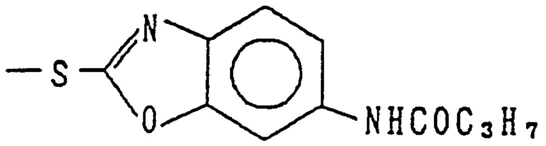
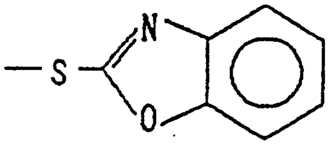
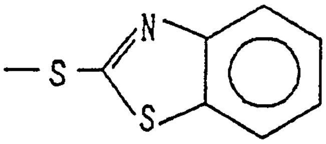
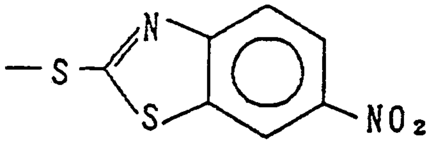
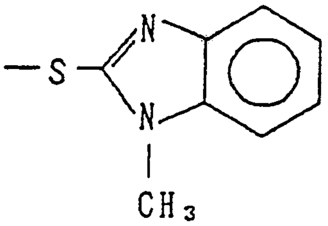
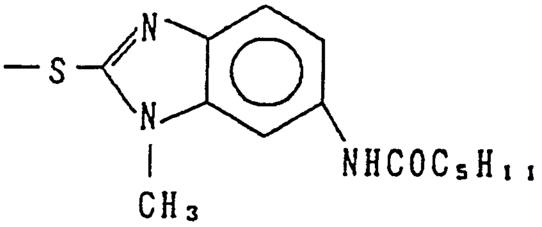


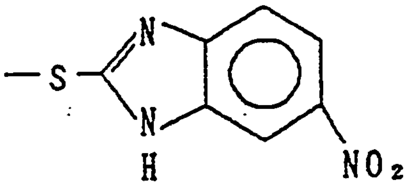


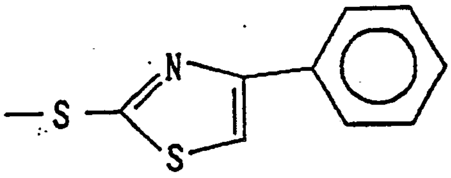


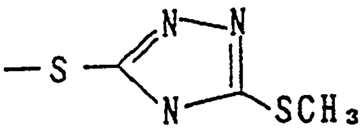


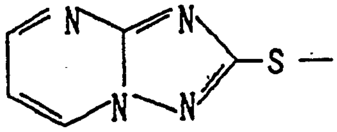


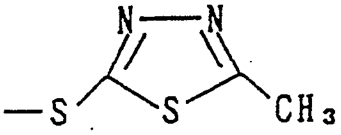




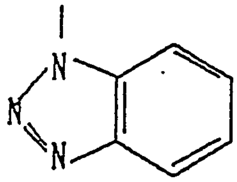


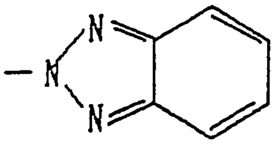


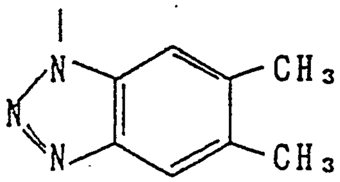


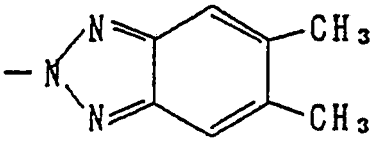


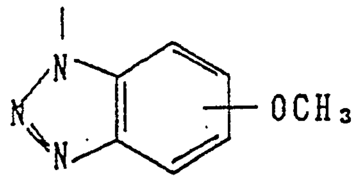
Then, specific examples of the group shown by formula (DI - b) described above are illustrated below.







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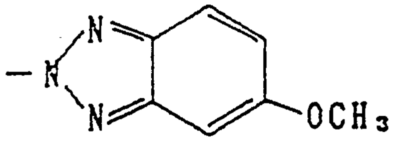
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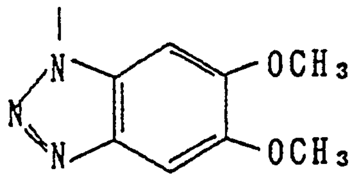
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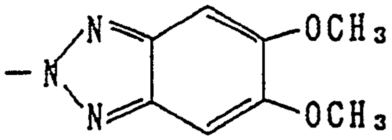
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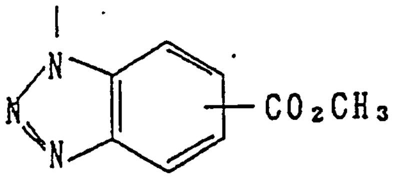
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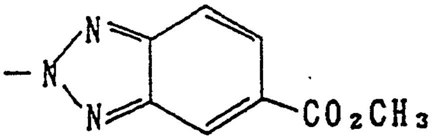
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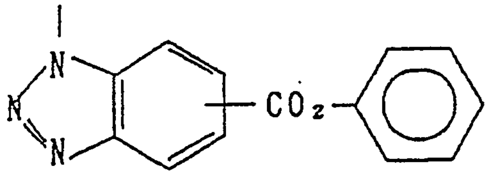
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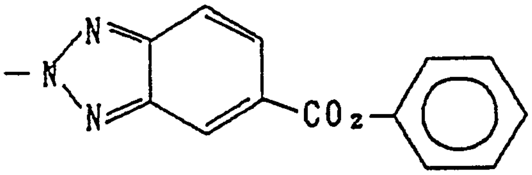
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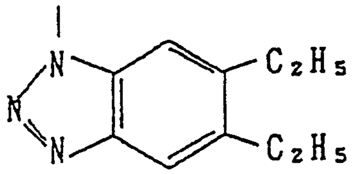
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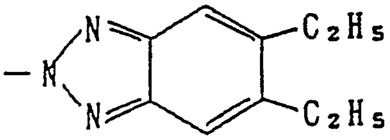
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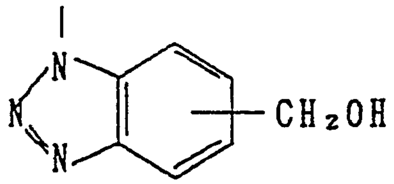
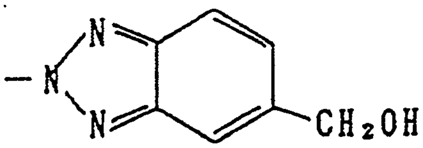
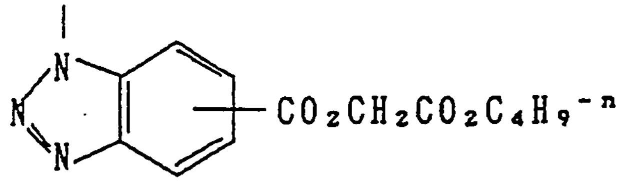
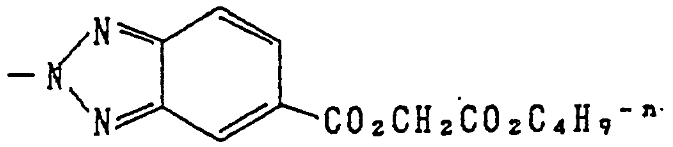
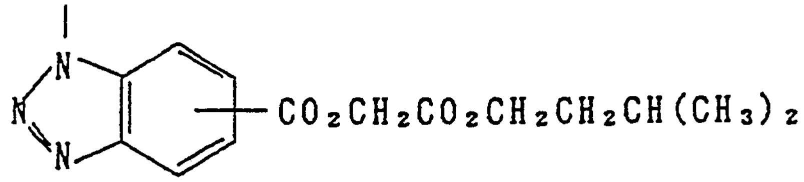
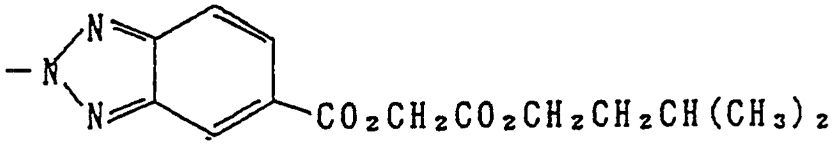










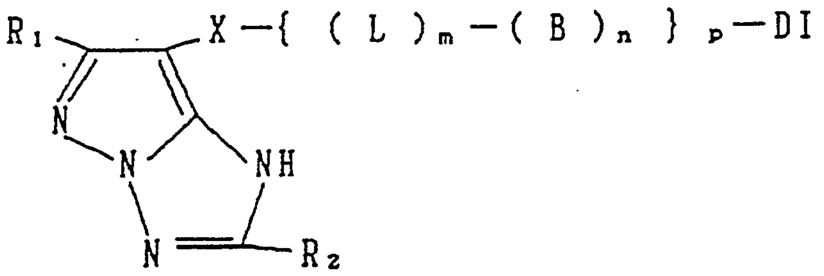


Then, the preferred range of the compound shown by aforesaid formula (I) are explained below.

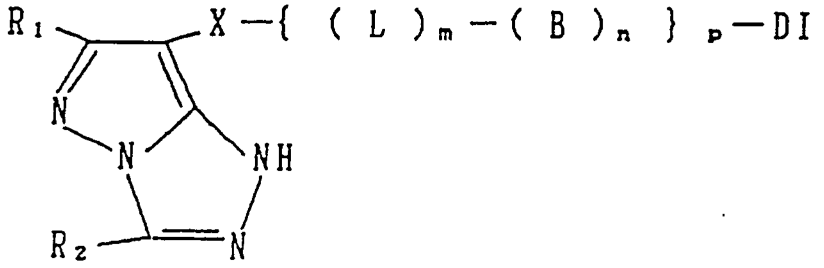
In formula (I), p is preferably 1.

It is preferred that the coupler shown by formula (I) is of a non-diffusible type and it is particularly preferable that the non-diffusible group in included in R_1, R_2, L or B in formula (I).

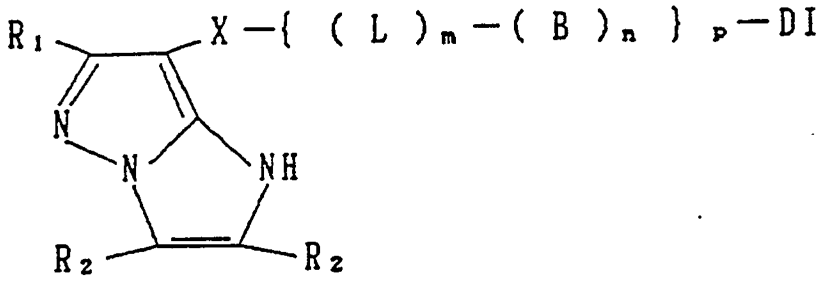
The couplers shown by formula (I) include the couplers shown by following formulae (II), (III), (IV), and (V) but in these couplers, the couplers shown by formulae (II) and (III) are particularly preferred in the point of heat stability and also the coupler shown by formula (II) is particularly preferred in the point of a high reactivity with the oxidation product of a color developing agent.



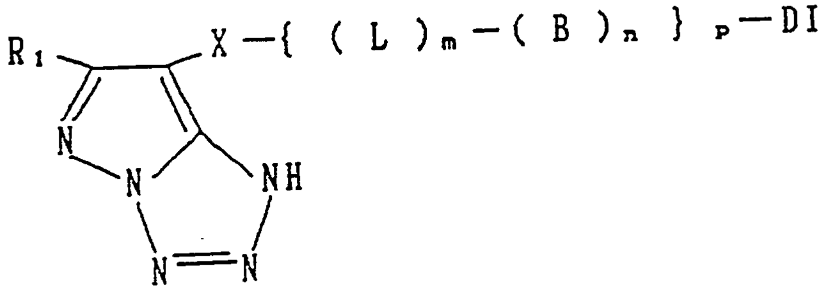
(II)



(III)



(IV)



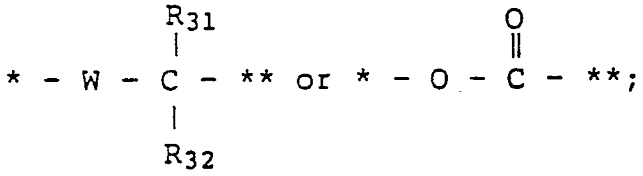
(V)

In formulae (II), (III), (IV), and (V), R_1, R_2, X, L, B, DI, m, n, and p have the same meaning as in formula (I) and also, in formula (IV), it is excluded that two R_2s bond to each other to form an aromatic ring.

In the particularly preferred compound shown in formula (I), p = m = 1 and n = 0, and also in formula (I), the group shown by $-X-\{(L)_m-(B)n\}p-DI$ is shown by following formula (VII), and in this case, the effects of improving the sharpness and the graininess of the color photographic material are large.

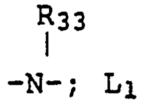
$-X_1-L_1-DI$ (VII)

wherein X_1 represents



$$* - W - \underset{R_{32}}{\overset{R_{31}}{C}} - ** \text{ or } * - O - \overset{O}{\overset{\|}{C}} - **;$$

W represents an oxygen atom, a sulfur atom, or

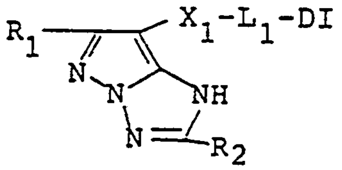


$$-\overset{R_{33}}{N}-;\ L_1$$

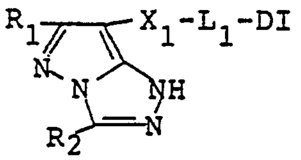
represents a group releasing DI by an electron transfer along the conjugated system; and DI R_{31}, R_{32}, R_{33}, *, and ** have the same meaning as in formula (I).

The compound shown by formula (I) may form a dimer or more polymer via a divalent or higher valent group at R_1 or R_2.

Among those compound, the particularly preferred coupler are shown in formulae (VIII) and (IX).



(VIII)

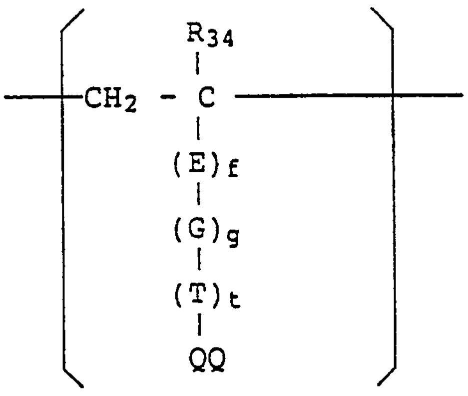


(IX)

In formulae (VIII) and (IX), X_1 and L_1 have the same meaning as in formula (VII) and R_1 and R_2 have the same meaning as in formula (VII) above.

That is, the compounds of formulae (VIII) and (IX) above correspond to the compounds of formula (I) wherein the group represented by "$-X-\{(L)_m-(B)_n\}_P-DI$ is the group of formula (VII).

When the compound shown by formula (I) forms a polymer, the typical example thereof is a homopolymer or a copolymer of an addition polymerizable ethylenically unsaturated compound (coloring monomer) having the aforesaidcompound residue. In this case, the polymer has a recurring unit shown by following formula (VI). The polymer may contain one or more kinds of the aforesaid coloring recurring unit and also ray be a copolymer containing one or more kinds of non-coloring ethylenic monomers.



$$\left(CH_2 - \underset{\underset{\underset{\underset{QQ}{|}}{(T)_t}}{\underset{|}{(G)_g}}}{\underset{|}{\underset{(E)_f}{|}}}}{\overset{R_{34}}{\overset{|}{C}}} \right) \quad \text{(VI)}$$

wherein R_{34} represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, or chlorine atom; E represents -CONH-, -COO-, or a substituted or unsubstituted phenylene group; G represents a substituted or unsubstituted alkylene group, a substituted or unsubstituted phenylene group, or a substituted or unsubstituted aralkylene group; T represents -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, $-SO_2-$, $-NHSO_2-$, or $-SO_2NH-$; f, g, and t each represents 0 or 1; and QQ represents a compound residue formed by releasing a hydrogen atom from the compound shown by formula (I).

As the aforesaid polymer, a copolymer of the compound monomer giving the compound unit show by formula (VI) and a non-coloring ethylecial monomer shown below is preferred.

That is, as the non-coloring ethylenical monomer which does not coupling with the oxidation product of an aromatic primary amine developing agent, there are acrylic acid, α-chloroacrylic acid, α-aracrylic acid (e.g., methacrylic acid), the esters or amides induced from these acrylic acids (e.g., acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, methylenebisacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, uraryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, and β-hydroxymethacrylate), vinyl esters (e.g., vinyl acetate, vinyl propionate, and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and the derivatives thereof, such as vinyltoluene, divinylbenzene, vinylacetophenone, and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (e.g., vinyl ethyl ether), maleic acid esters, N-vinyl-2-pyrrolidone, N-vinylpyridine, and 2- and 4-vinylpyridine.

In the aforesaid compounds, acrylic acid esters, methacrylic acid esters, and maleic acid esters are preferred.

The non-coloring ethylenic monomers described above can be used singly or as a combination thereof.

Examples of the combination are methyl acrylate and butyl acrylate, butyl acrylate and styrene, butyl methacrylate and methacrylic acid, and methyl acrylate and diacetoneacrylamide.

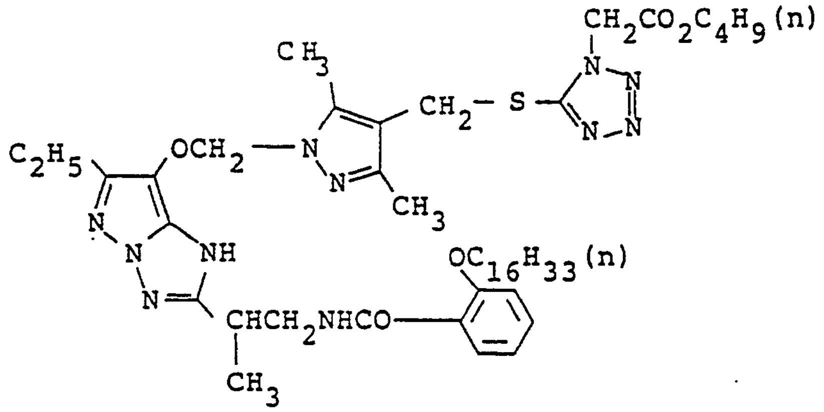
When a polymer has the recurring unit shown by aforesaid formula (VI), as well-known in the field of polymer couplers, for forming the polymer, the non-coloring ethylenical monomer which is copoltmerized with the ethylenical monomer having the dye forming residue in this invention can be selected such that the physical properties and/or the chemical properties of the copolymer formed, such as the compatibility with gelatin, the flexibility, the thermal stability, etc., receive good influences.

The polymer compound for use in this invention, that is an oleophilic polymer compound obtained by the polymerization of a vinylic monomer giving the compound unit shown by aforesaid formula (VI), may be prepared by emulsion-dispersing the solution thereof in an organic solvent in an aqueous gelatin solution as a form of latex or may be directly prepared by a emulsion polymerization method.

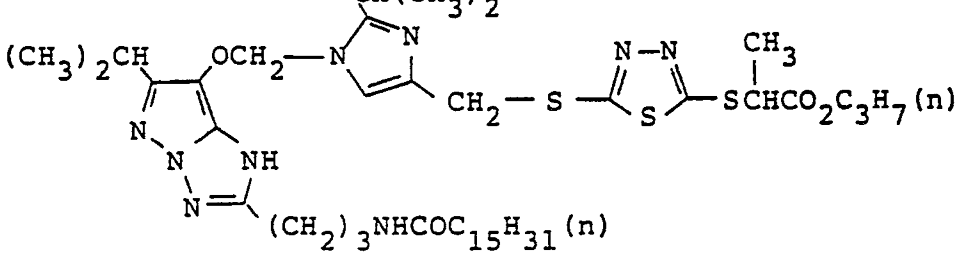
For emulsion-dispersing the oleophilic polymer compound in an aqueous gelatin solution as a form of latex, the method described in U.S. Patent 3,451,820 can be used and for the emulsion polymerization, the method described in U.S. Patents 4,080,211 and 3,370,952 can be used.

Then, specific examples of the compound for use in this invention shown be aforesaid formula (I) are illustrated below but the invention is not limited to these compounds.

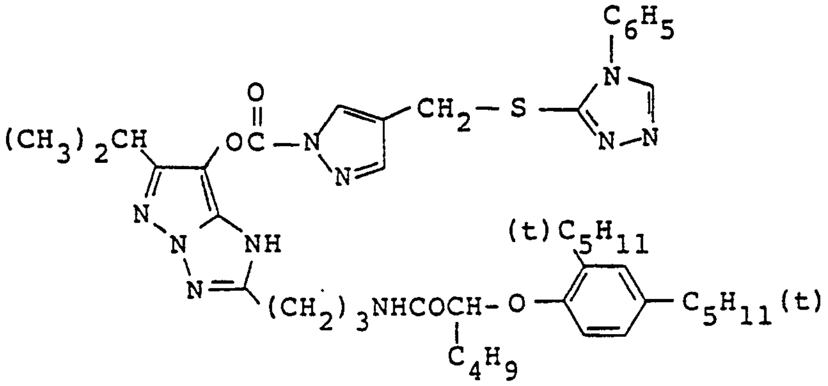
(1)


CH2CO2C4H9(n)
CH3
CH2 — S
C2H5
OCH2
CH3
NH
OC16H33(n)
CHCH2NHCO
CH3

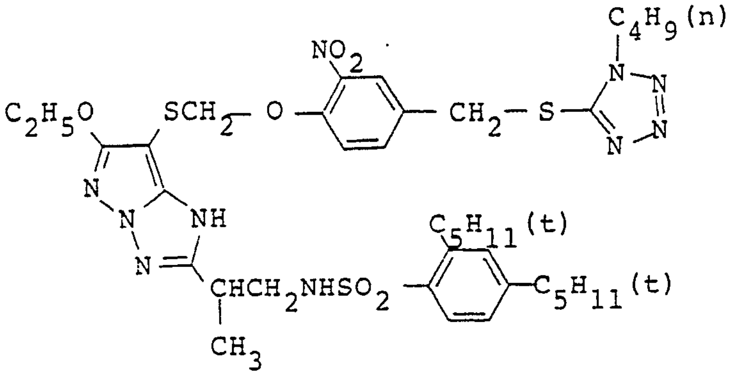
(2)


CH(CH3)2
(CH3)2CH
OCH2
CH3
CH2 — S
SCHCO2C3H7(n)
NH
(CH2)3NHCOC15H31(n)

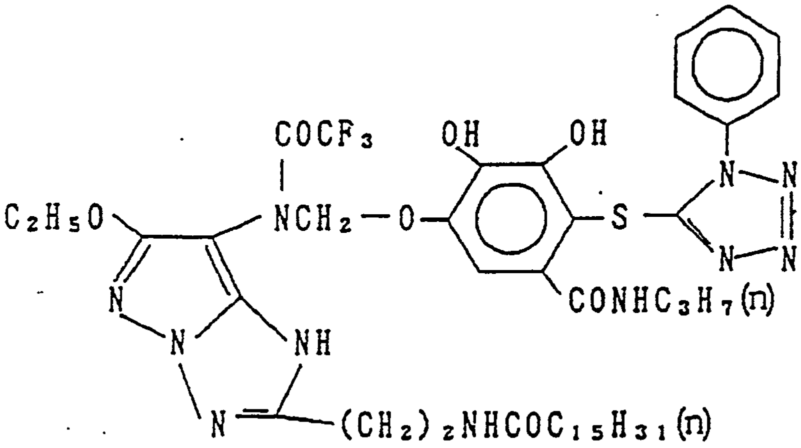
(3)


C6H5
O
(CH3)2CH
OC
CH2 — S
NH
(t)C5H11
(CH2)3NHCOCH- O
C5H11(t)
C4H9

(4)



(5)



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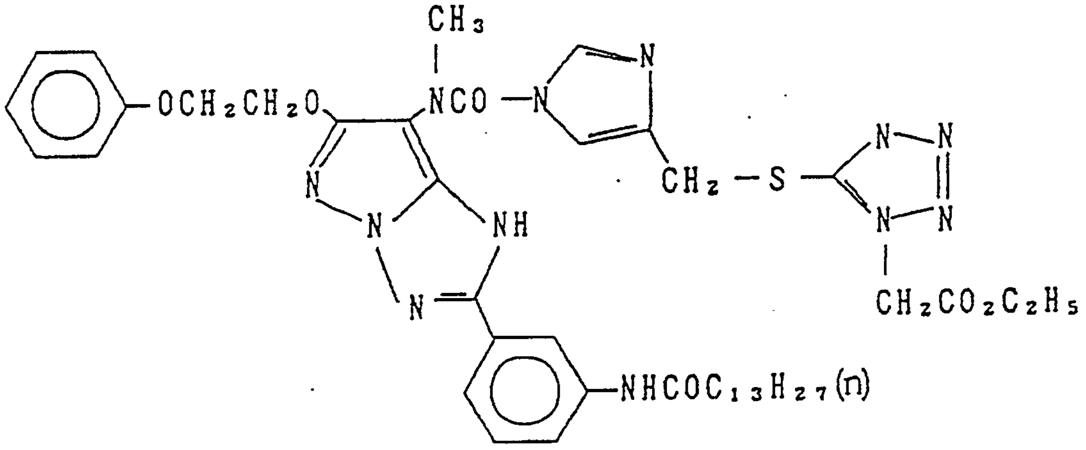
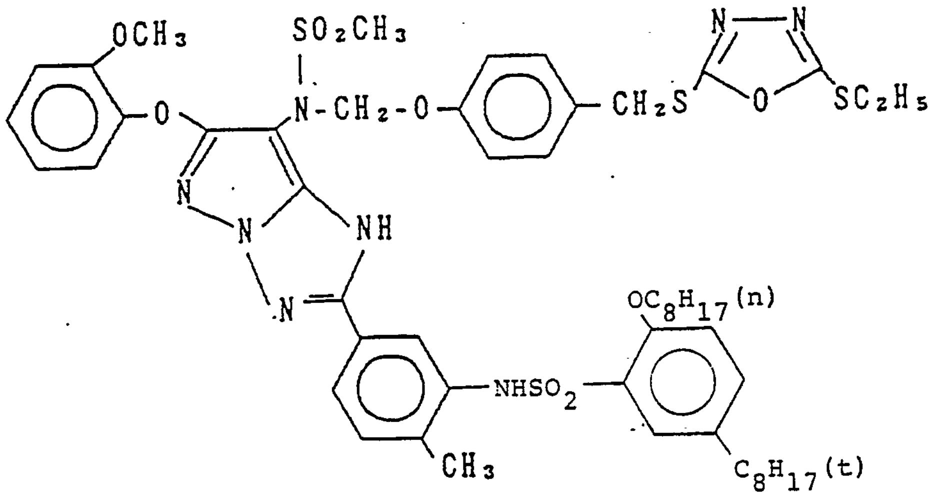
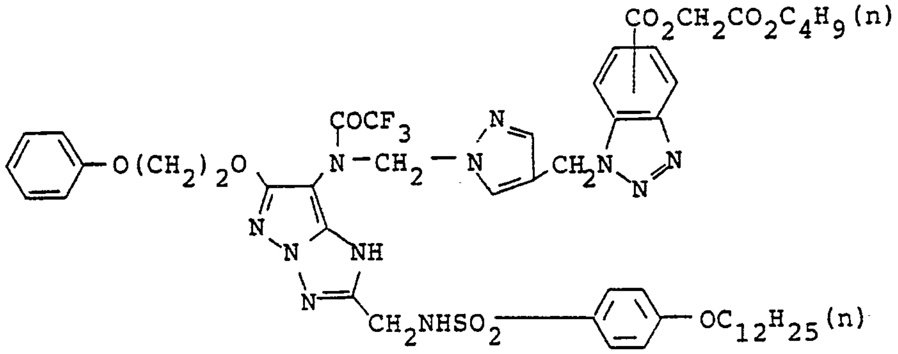


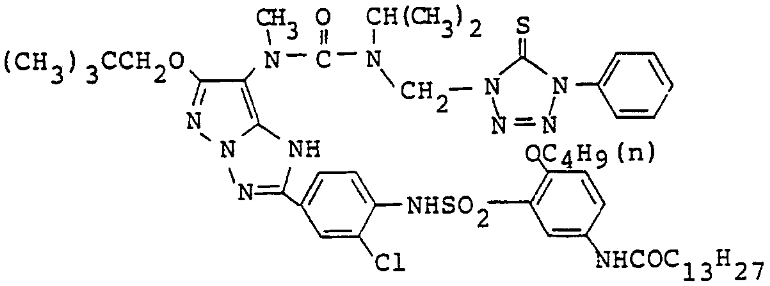
(7)


OCH₃
SO₂CH₃
O
N-CH₂-O
CH₂S
N
N
O
SC₂H₅
N
N
NH
N
OC₈H₁₇(n)
NHSO₂
CH₃
C₈H₁₇(t)

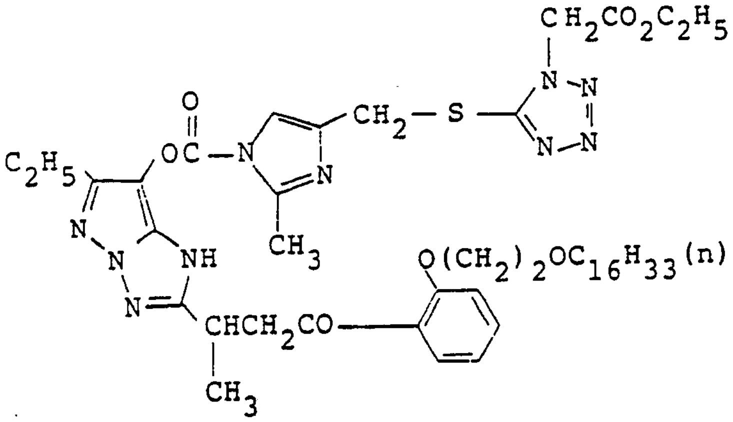
(8)


CO₂CH₂CO₂C₄H₉(n)
COCF₃
O(CH₂)₂O
N-CH₂-
N
N
CH₂N
N
N
N
N
NH
N
CH₂NHSO₂
OC₁₂H₂₅(n)

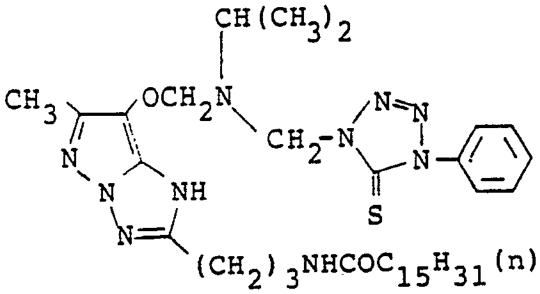
(9)


CH₃
O
CH(CH₃)₂
S
(CH₃)₃CCH₂O
N-C-N
CH₂-
N
N
N=N
N
N
NH
OC₄H₉(n)
N
NHSO₂
Cl
NHCOC₁₃H₂₇

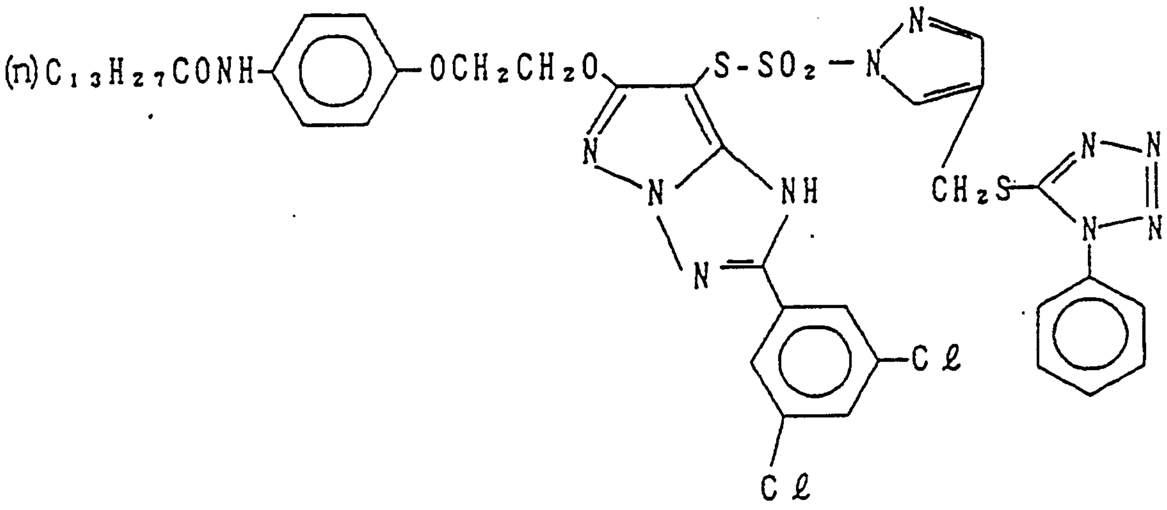
(10)



(11)



(1 2)



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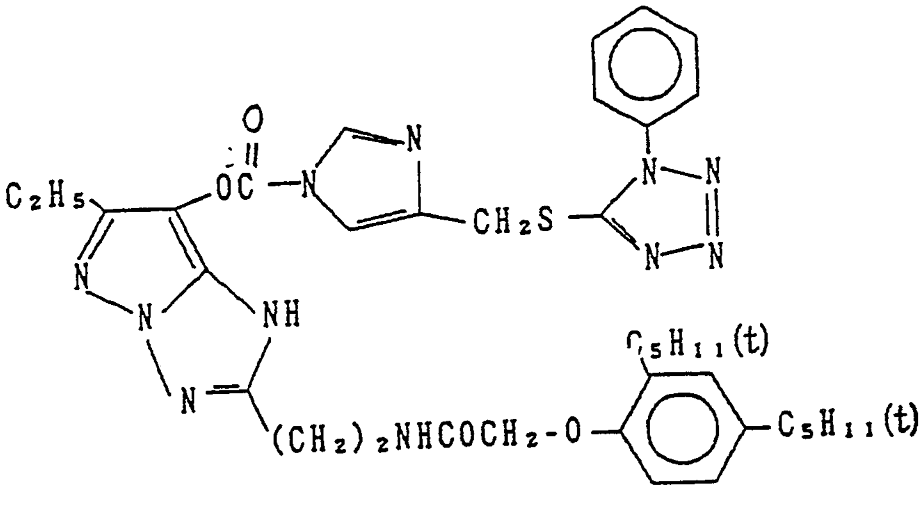
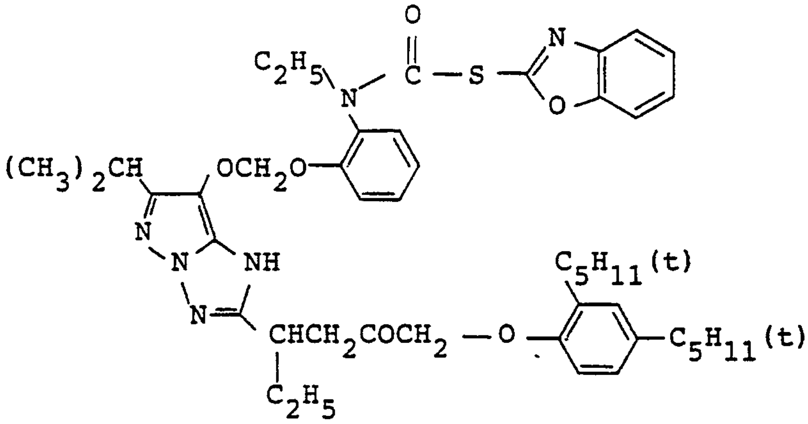
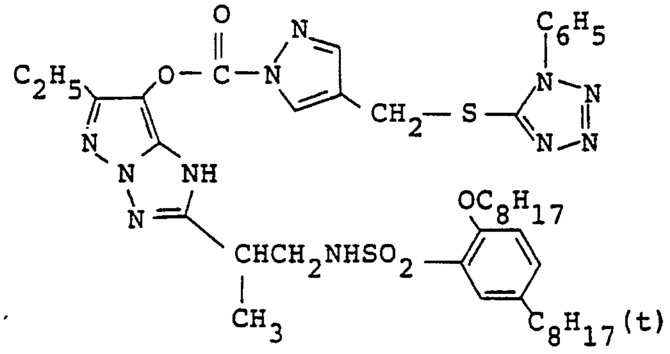

C₂H₅
O
OC
N
N
CH₂S
N
N
N
N
N
N
NH
N
(CH₂)₂NHCOCH₂-O
C₅H₁₁(t)
C₅H₁₁(t)

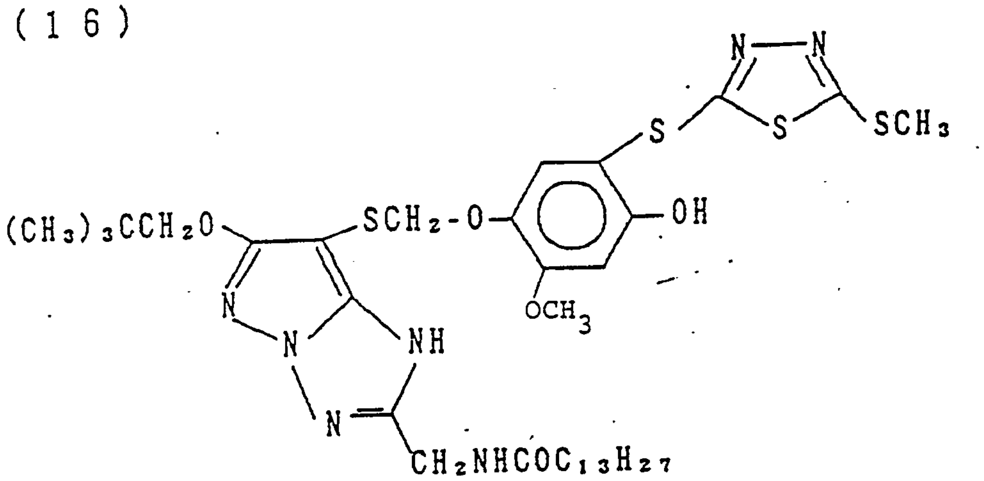
(14)


O
C₂H₅
N
C
S
N
O
(CH₃)₂CH
OCH₂O
N
N
NH
N
CHCH₂COCH₂
O
C₂H₅
C₅H₁₁(t)
C₅H₁₁(t)

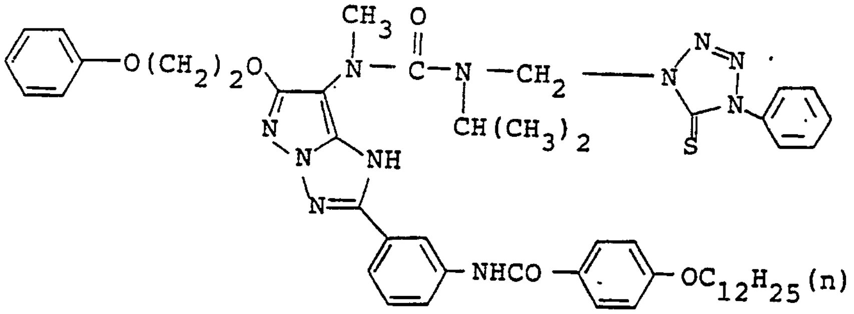
(15)


O
C₂H₅
O
C
N
N
CH₂
S
C₆H₅
N
N
N
N
N
N
NH
N
CHCH₂NHSO₂
CH₃
OC₈H₁₇
C₈H₁₇(t)

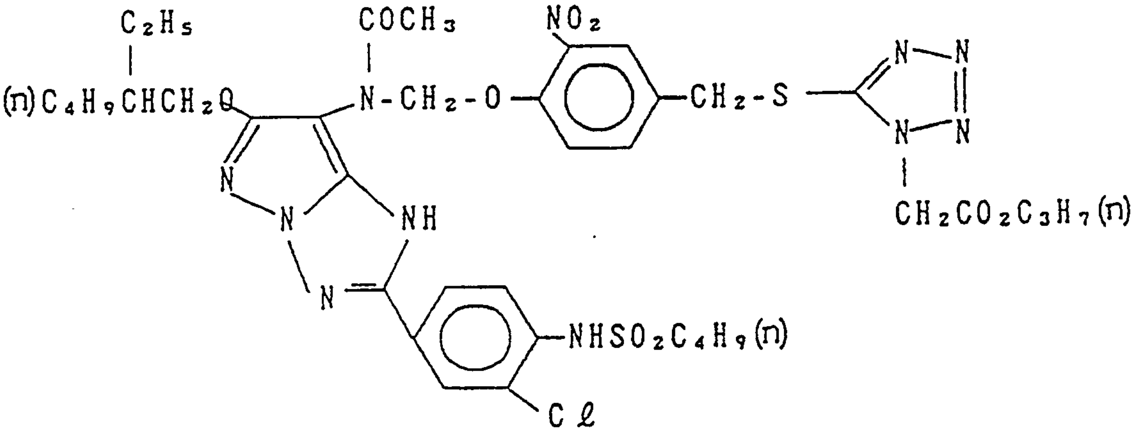
(16)


N
N
S
S
SCH₃
(CH₃)₃CCH₂O
SCH₂-O
OH
OCH₃
N
N
NH
N
CH₂NHCOC₁₃H₂₇

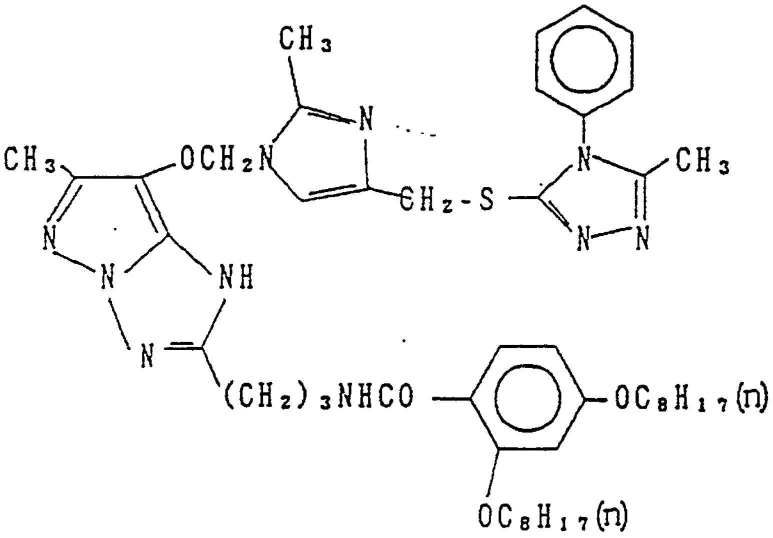
(17)


O(CH₂)₂O
CH₃
O
N
C
N
CH₂
CH(CH₃)₂
N
N
N
N
S
N
N
NH
N
NHCO
OC₁₂H₂₅(n)

(18)


C₂H₅
(n)C₄H₉CHCH₂O
COCH₃
N-CH₂-O
NO₂
CH₂-S
N
N
N
N
CH₂CO₂C₃H₇(n)
N
N
NH
N
NHSO₂C₄H₉(n)
Cℓ

(19)



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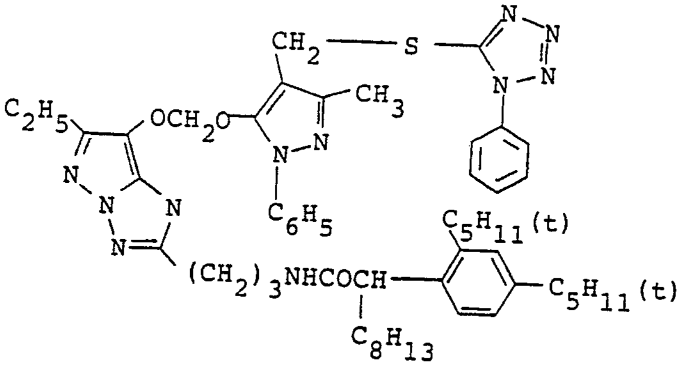

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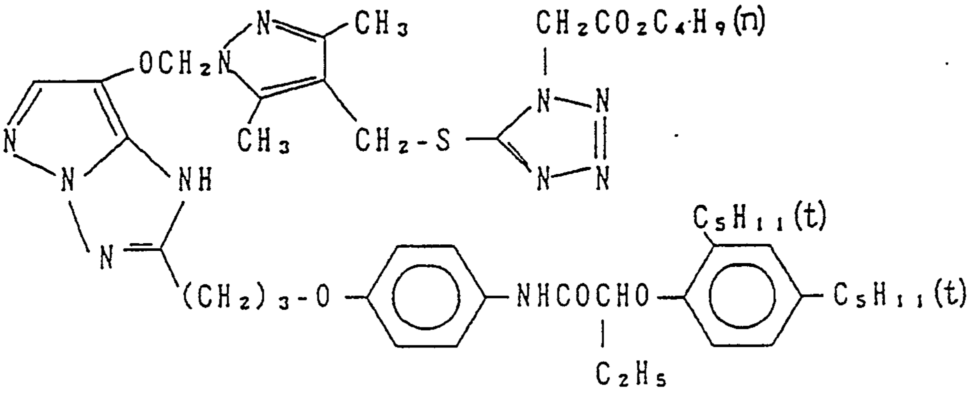

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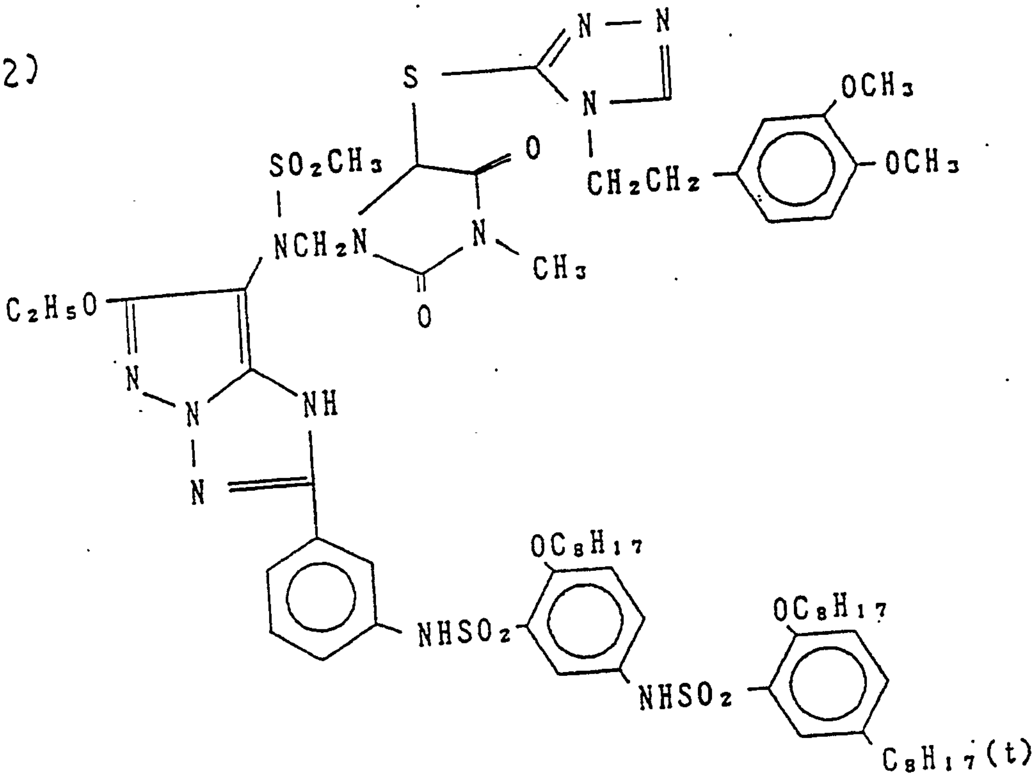
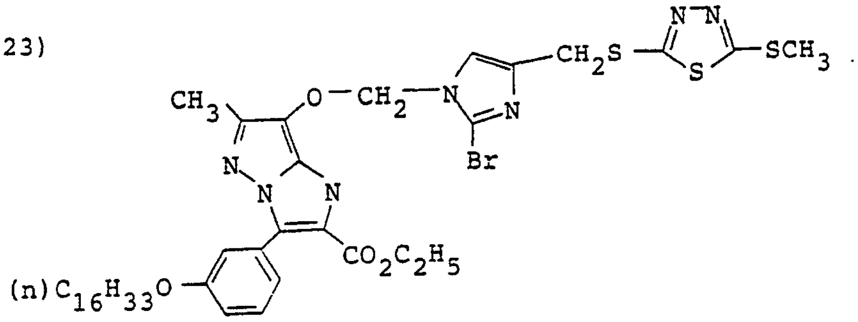
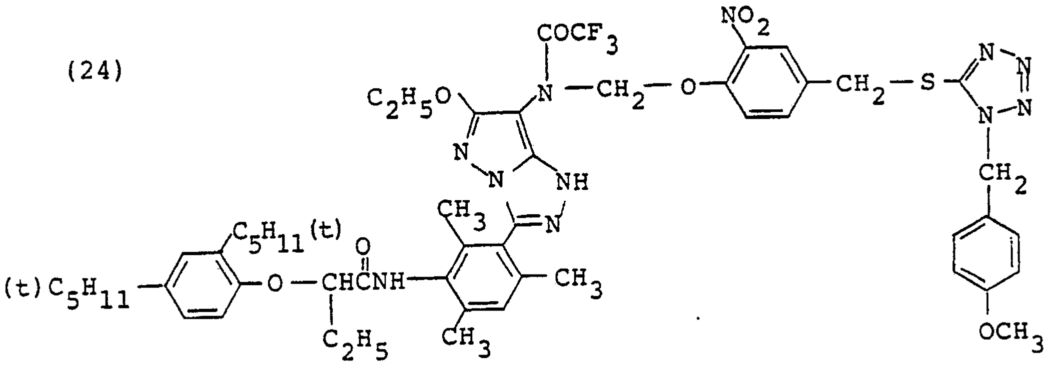

S
N
N
N
OCH₃
OCH₃
O
SO₂CH₃
CH₂CH₂
NCH₂N
N
CH₃
C₂H₅O
O
N
N
NH
N
OC₈H₁₇
OC₈H₁₇
NHSO₂
NHSO₂
C₈H₁₇(t)

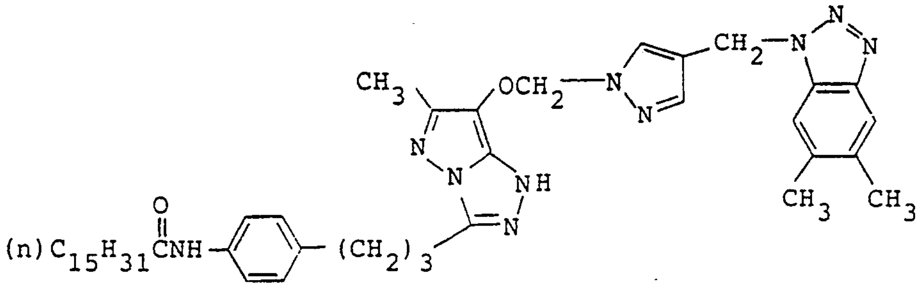
(23)


N
N
CH₂S
SCH₃
S
CH₃
O
CH₂
N
N
Br
N
N
N
CO₂C₂H₅
(n)C₁₆H₃₃O

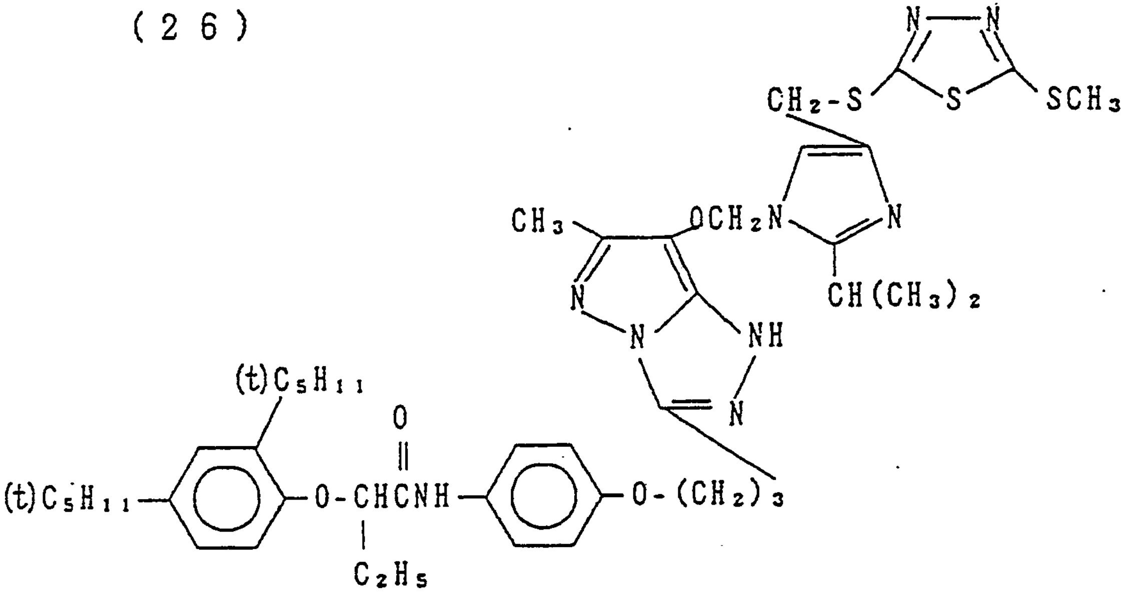
(24)


COCF₃
NO₂
C₂H₅O
N
CH₂
O
CH₂
S
N
N
N
N
N
N
NH
CH₂
CH₃
N
C₅H₁₁(t)
O
(t)C₅H₁₁
O
CHCNH
CH₃
C₂H₅
CH₃
OCH₃

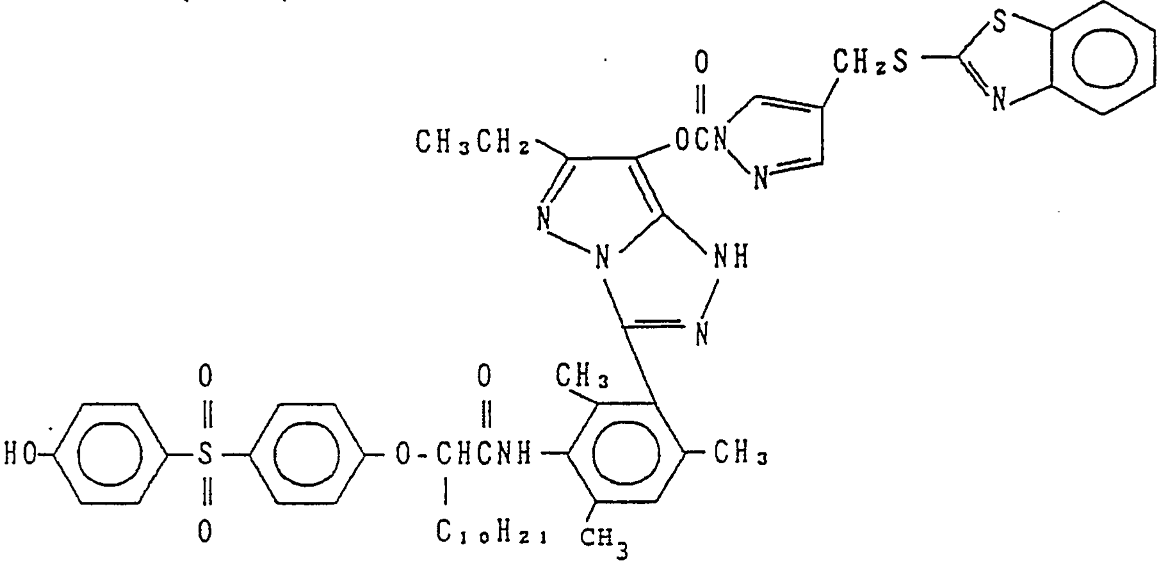
(25)


CH3
OCH2
N
N
CH2
N
N
N
N
N
NH
N
CH3
CH3
O
(n) C15H31CNH
(CH2)3

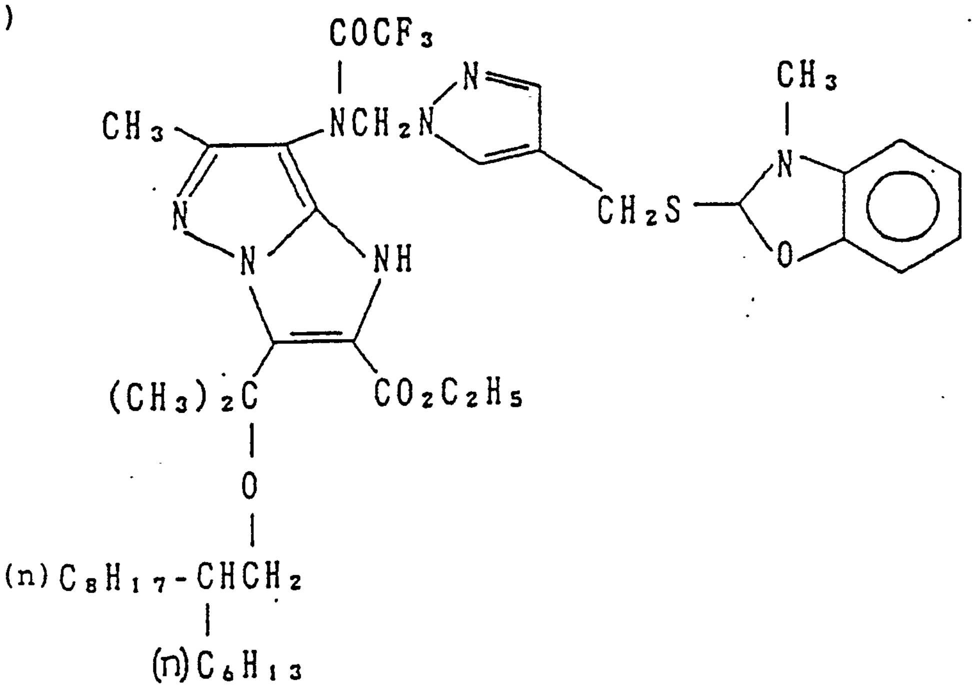
(26)


N
N
CH2-S
S
SCH3
CH3
OCH2N
N
CH(CH3)2
N
N
NH
N
(t)C5H11
O
(t)C5H11
O-CHCNH
O-(CH2)3
C2H5

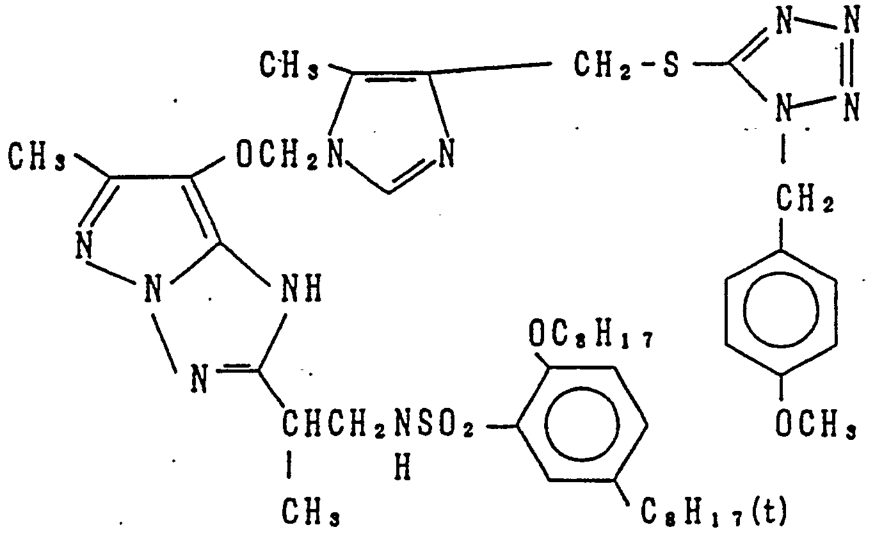
(27)


O
CH2S
S
N
CH3CH2
OCN
N
N
N
NH
N
O
O
CH3
HO
S
O-CHCNH
CH3
O
C10H21
CH3

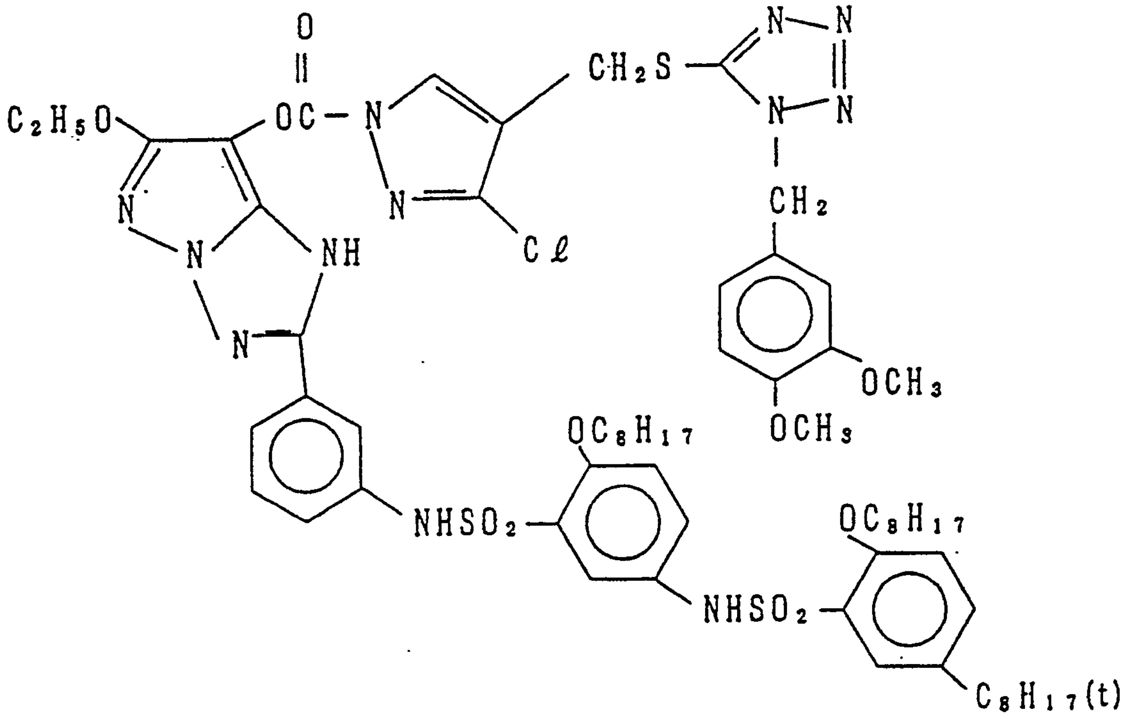
(28)



(29)



(30)



Then, synthesis methods of the compounds shown by formula (I) are explained.

In the compounds shown by formula (I), the 1H-pyrazolo[1,5-b]-1,2,4-triazole skeleton contained in the compound shown by formula (II) can be synthesized by the methods described in U.S. Patent 4,540,654, JP-A-60-172982, JP-A-60-215687, JP-A-60-197688, and JP-A-60-190779.

In the compounds shown by formula (I), the 1H-pyrazolo[5,1-c]-1,2,4-triazole skeleton contained in the compound shown by formula (III) can be synthesized by the methods described in U.S. Patent 3,725,067, JP-B-47-27444, JP-B-48-30895, JP-A-61-18780, JP-A-62-33177, and JP-A-1-233285.

In the compounds shown by formula (I), the 1H-imidazo[1,2-b]pyrazole skeleton contained in the compound shown by formula (IV) can be synthesized by the methods described in JP-A-59-162548, European Patent Publication (unexamined) 11974, and WO 86/02467.

Also, in the compounds shown by formula (I), the 1H-pyrazolo[1,5-d]tetrazole skeleton contained in the compound shown by formula V can be synthesized by the method described in JP-A-60-33552.

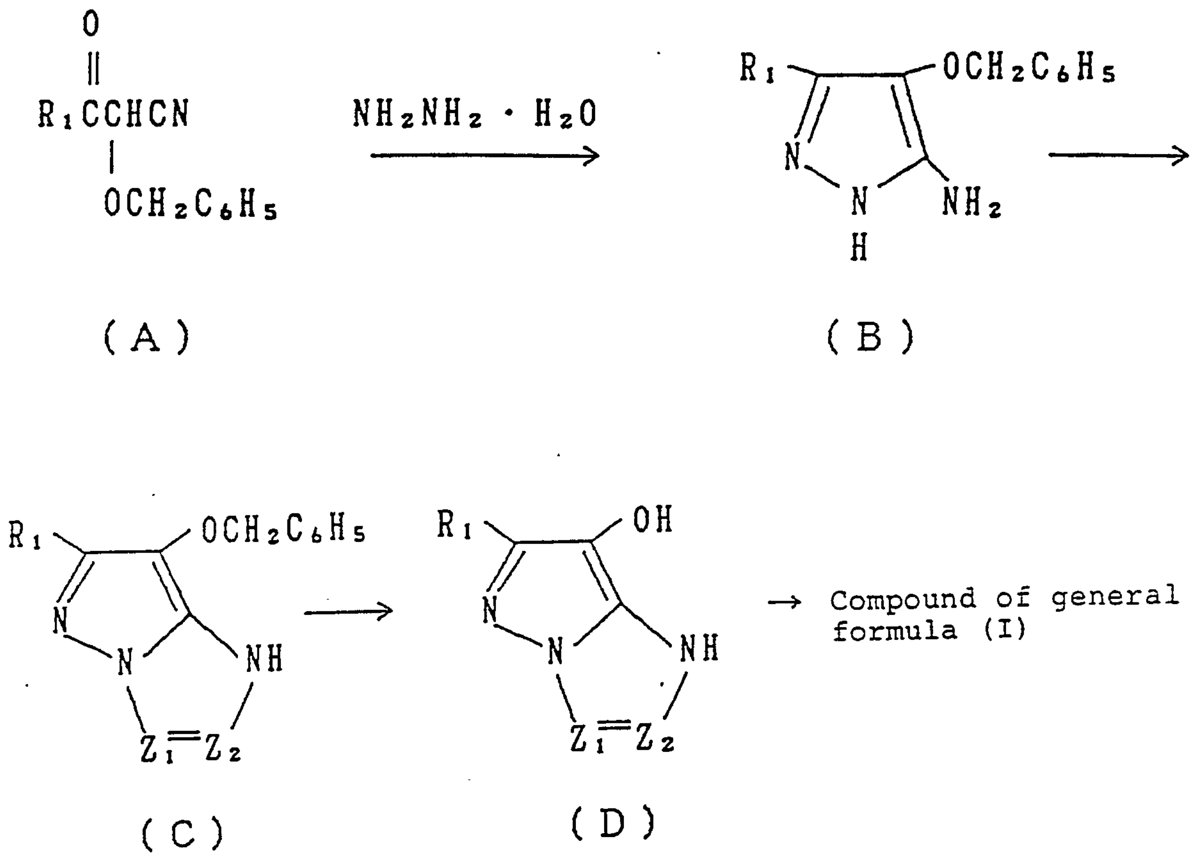
A coupling releasable group can be introduced as follows.

Method of bonding an oxygen atom to the coupling position:

The compound of formula (I) having the coupling releasable group can be synthesized by the method described in JP-A-61-53644 and a method similar to the method.

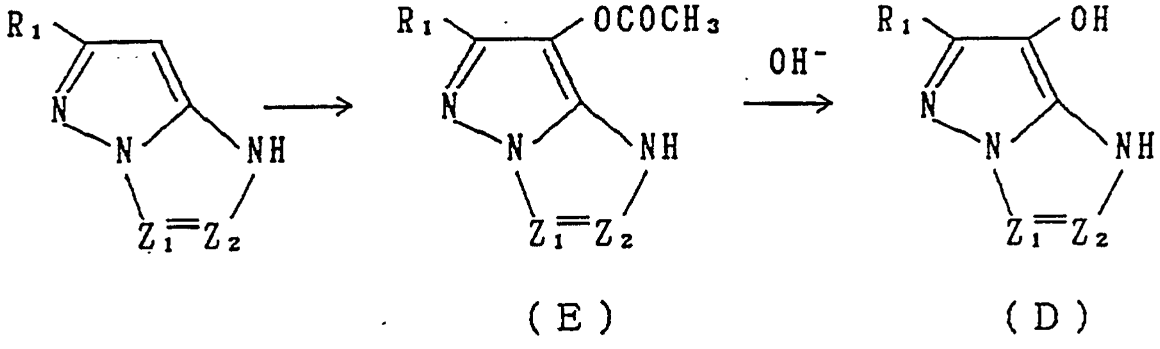
That is, aminopyrazole (B) having a benzyloxy group at the 4-position is synthesized from β-ketonitrile (A) having a benzyloxy group at the α-position, the aminopyrazole (B) is introduced to a pyrazoazole (C) having a benzyloxy group at the coupling position by applying the synthesis method of a pyrazoloazole skeleton described hereinbefore, than pyrazoloazole (D) having a hydroxy group at the coupling position is formed therefrom by a catalytic hydrogegenation or a Lewis acid treatment, and the pyrazoloazole (D) is converted into the compound shown by formula (I).

The scheme of the method is as follows.

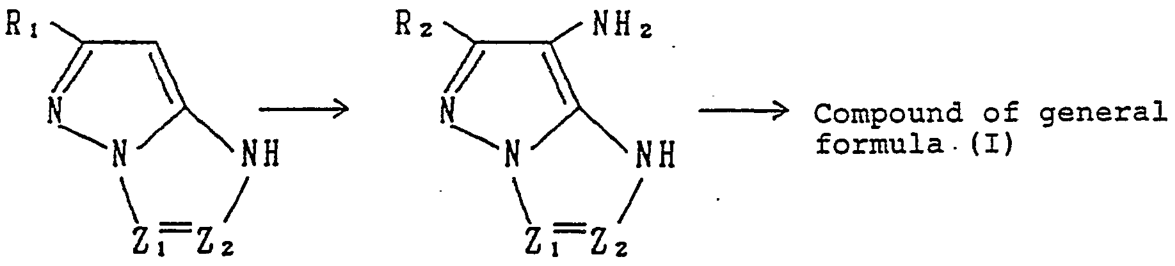


As other method, there is a method of synthesizing pyrazoloazoles (D) having a hydroxyl group at the coupling position by oxidizing pyrazoloazoles the coupling position of which is not substituted.

For example, there is a method of synthesizing pyrazoloazole (E) having an acetoxy group at the coupling position from a pyrazoloazole having no substituent at the coupling position according to the method described in US. Patent 4,914,209 and the pyrazoloazole (E) is hydrolyzed to provide pyrazoloazole (D) as shown by the following scheme.



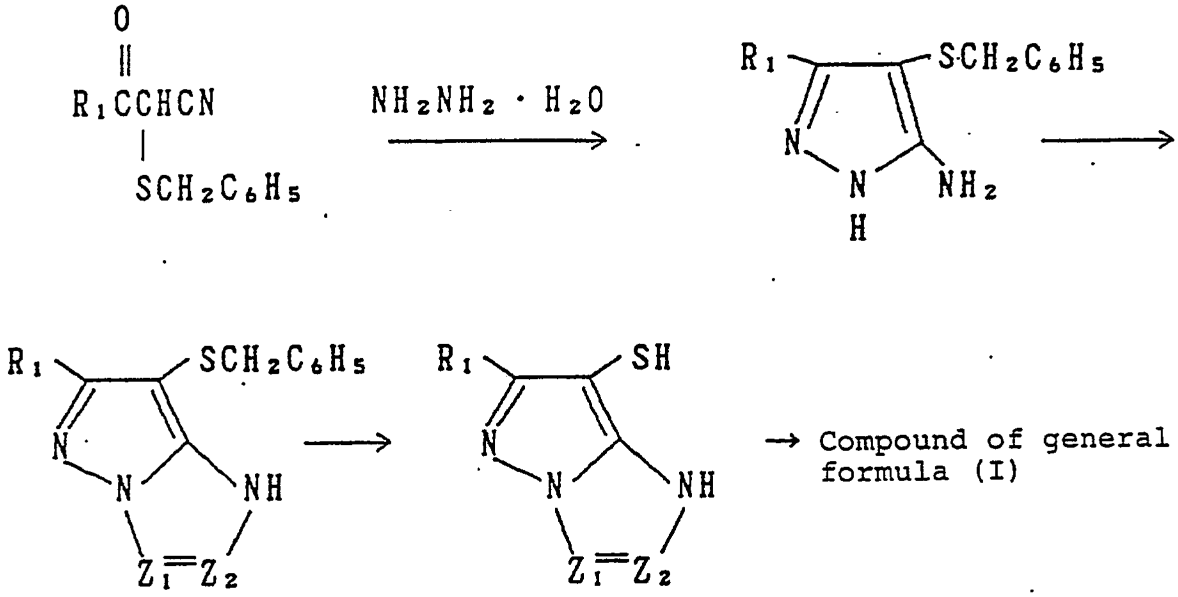
Method of bonding a nitrogen atom to the coupling position:
a pyrazoloazole having no substituent at the coupling position is converted to pyrazoloazole (F) having an amino group at the coupling position by the method described in JP-A-60-140241 and the pyrazoloazole (F) can be induced to the compound shown by formula (I) as shown in the following scheme.



(F)

Method of bonding a sulfur atom to the coupling position:

The compound shown by formula (I) having the coupling releasable group can be synthesized as shown by the following scheme starting from β-ketonitrile having a benzylthio group at the α-position by the same manner as the method of boding an oxygen to the coupling position described above.

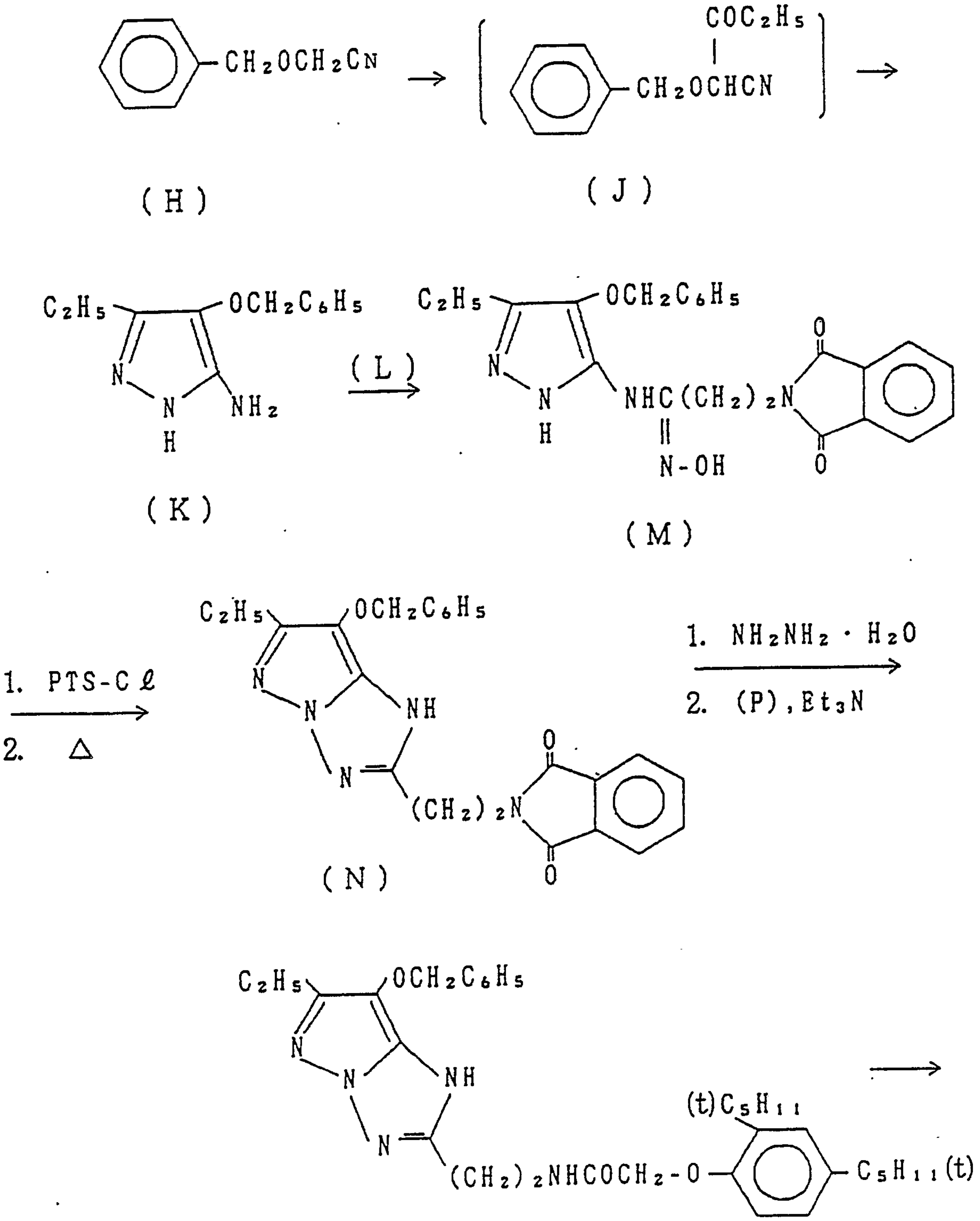


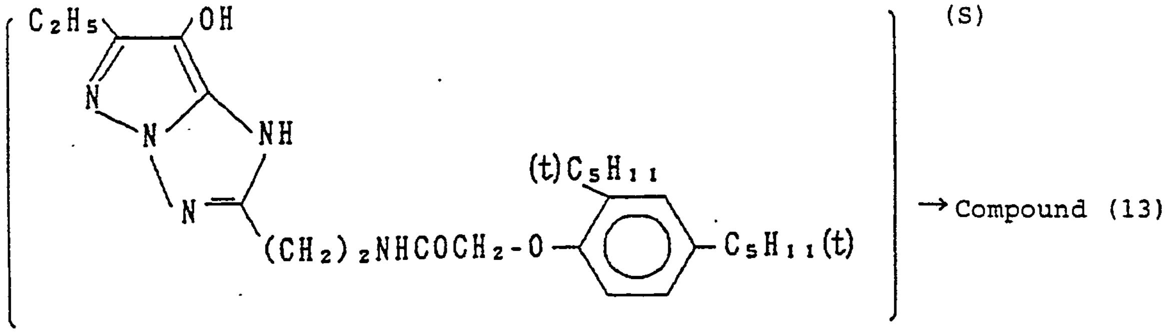
(G)

Also, compound (G) can be synthesized by treating a pyrazoloazole having no substituent at the coupling position with sulfur monochloride.

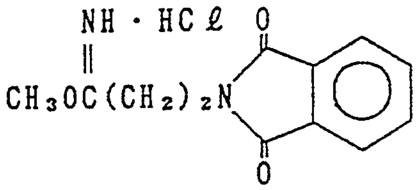
Then, practical synthesis examples of the compounds of formula (I) for use in this invention are shown below.

Synthesis Example 1 (Synthesis of Compound (13)):

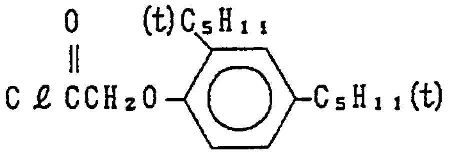

(H)
(J)
(K)
(L)
(M)
1. PTS-Cℓ
2. △
(N)
1. NH₂NH₂ · H₂O
2. (P), Et₃N
(Q)



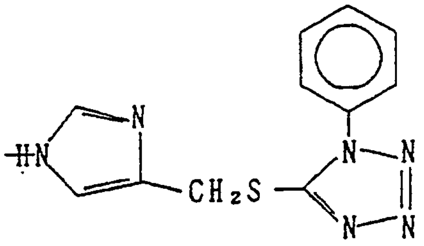
Intermediate (R)



Intermediate (L)



Intermediate (P)



Intermediate (S)

Synthesis of Intermediate (K):

After cooling 201 g of methyl propionate to -10° C, 56.2 g of potassium tert-butoxide was gradually added thereto with stirring. Then, benzyloxyacetonitrile (H) was added dropwise to the mixture at a temperature of lower than 0° C over a period of 10 minutes. Thereafter, cooling was stopped and the temperature of the mixture was allowed to raise to room temperature with stirring.

To the reaction mixture obtained were added 300 ml of water and 500 ml of hexane followed by extraction. To the aqueous layer thus formed were added 250 ml of ethyl acetate and 43ml of concentrated hydrochloric acid followed by extraction. an aqueous layer formed was collected, washed with a saturated aqueous sodium chloride solution, and concentrated under reduced pressure to provide 42.3 g of Intermediate (J) as a crude product.

To the intermediate (J) was added 100 ml of isopropyl alcohol followed by stirring and after adding thereto 12.1 ml of hydrazine hydrate, the mixture was refluxed for 30 minutes. After distilling off the solvent under reduced pressure, 200 ml of ethyl acetate and 200 ml of water were added thereto followed by extraction and an organic solvent formed was collected and washed with a saturated aqueous sodium chloride solution. Then, after drying the organic layer on anhydrous magnesium sulfate, the organic layer was concentrated under reduced pressure to provide 29.7 g of Intermediate (K) as an oily product.

^{1}H NMR Spectra ($CDCl_3$, ppm) δ: 7.36(s, 5H), 5.92(br, 3H), 4.83(s, 2H), 2.40(q, 2H, J = 7.0Hz), 1.10(t, 3H, J = 7.0Hz).

Synthesis of Intermediate (M):

To 120 ml of acetonitrile was added 22.3 g of Intermediate (K) and the mixture was stirred at room temperature. To the mixture was added 27.7 g of Intermediate (L) and the mixture was stirred for 3 hours.

Crystals thus deposited were collected by filtration and after cleaning the crystals with acetonitrile, they were dried to provide crystals (T).

In 90 ml of methanol was dissolved 8.69 g of hydroxylamine hydrochloride, 25.1 ml of an methanol solution of 28% sodium methoxide was added to the solution, and sodium chloride deposited was filtered off.

To the methanol solution of hydroxylamine thus obtained was added crystals (T) obtained above and the mixture was stirred for 3hours at room temperature. After adding 5 ml of acetic acid to the mixture, 100 ml of water was added dropwise to the mixture. Crystals deposited were collected by filtration and after washing with water, were dried to provide 27.7 g of Intermediate (M).

Synthesis of Intermediate (N):

To 80 ml of N,N-dimethylacetamide was added 55.0 g of Intermediate (M) and the mixture was stirred while cooling with ice water. To the mixture was added 25.4 g of p-toluenesulfonyl chloride divided into five segments over a period of 20 minutes and then 10.7 ml of pyridine was added dropwise to the mixture over a period of 5 minutes. The cooling bath was removed and after stirring the mixture for 20 minutes, the reaction mixture obtained was added to 800 ml of ice-water with stirring.

Crystals deposited were collected by filrtation, immediately added to 1.0 liters of methanol, and after adding thereto 10.7 ml of pyridine, the resultant mixture was stirred for 4.5, hours at 50° C. Methanol was distilled off under reduced pressure to reduce the volume of the mixture to about 300 ml and crystals thus deposited were collected by filtration and after washing with methanol, were dried to provide 23.0 g of Intermediate (N).

^{1}H NMR spectra (CMSO$_{\text{-d6}}$, ppm) δ: 12.66(s, 1H), 7.85(m, 4H), 7.35(s, 5H), 4.89(s, 2H), 3,97(t, 2H, J = 6.7Hz), 3.06(t, 2H, J = 6.7Hz), 2.44(q, 2H, J = 7.0Hz), 1.06 (t, 3H, J = 7.0Hz).

Synthesis of Intermediate (Q):

Tp 100 ml of isopropyl alcohol was added 20.8 g of Intermediate (N), after added thereto 4.8 ml of hydrazine hydrate, the mixture was stirred for 3 hours at room temperature and then for 3 hours at 50° C. After cooling, insoluble matters were removed by filtration and the filtrate obtained was concentrated under reduced pressure. To the crystallized residue obtained were added 30 ml of acetonitrile and 5 ml of methanol to disperse the residue and after collecting the crystals by filtration, the crystals were washed with acetontrile and dried by air to provide 8.8 g of the crystals. The crystals were added to 40 ml of N,N-dimethylacetamide followed by stirring. Then, after adding thereto 4.9 ml of triethylamine, 10.9 g of Intermediate (P) shown above was added dropwise to the mixture. After stirring the resultant mixture for 20 minutes, 10 ml of aqueous ammonia (28 to 30%) was added to the mixture followed by stirring for 5 minutes. The mixture was added to 200 ml of ethyl acetate and then 200 ml of water and 2 ml of concentrated hydrochloric acid were added thereto followed by extraction.

The organic layer formed was collected, washed with a saturated aqueous sodium chloride solution, and dried on anhydrous magnesium sulfate. After concentrating the aqueous solution under reduced pressure, the product was separated by silica gel column chromatography (eluent: a mixture of chloroform and methanol) to provide 11.1 g of Intermediate (Q) as an oily product. By crystallizing the product from hexane, light yellow crystals having a melting point of from 112° C to 113° C were obtained.

^{1}H NMR (CDCl$_3$, ppm)

δ: 10.83(brs, 1H), 7.33(s, 5H) , 7.16(d, 1H, J = 2.7Hz), 7.12(brt, 1H, J = 6.7Hz), 7.05(dd, 1H, J = 8.0, 2.7Hz), 6.61(d, 1H, ,J = 8.0Hz), 4.88(s, 2H), 4.45(s, 2H), 3.74(dt,2H), 2.95(t, 2H), 2.67(g, 2H, J = 7.3Hz), 1.68(g, 2H, J = 7.3Hz), 1.58(g, 2H, J = 7.3Hz), 1.24(m, 15H), 0.64(t, 3H, J = 7.3Hz), 0.56(t, 3H, J = 7.3Hz).

Synthesis of Compound (13):

In 100 ml of dichloromethane was dissolved 11.2 g of Intermediate (Q) and the solution was stirred while cooling with ice-water. To the solution was added dropwise 12.0 g of boron tribromide over a period of about 10 minutes and the mixture was stirred for 12 minutes under cooling. To the mixture was added 100 ml of water followed by extraction and the organic layer formed was collected, dried on anhydrous magnesium sulfate, and concentrated under reduced pressure to provide a crude product of Intermediate (R).

On the other hand, 5.7 g of Intermediate (S) and 4.4 g of p-nitrophenyl chloroformate were added to 50 ml of dichloromethane and after stirring the mixture for 30 minutes at room temperature, 50 ml of an ethyl acetate solution of Intermediate (R) prepared above and then 3.8 ml of diisopropylethylamine were added to the mixture followed by stirring for 1.5 hours at room temperature.

The reaction mixture was extracted with the addition of ethyl acetate and 1N hydrochloric acid and the organic layer formed was collected, washed with a saturated aqueous sodium chloride solution, and dried on anhydrous magnesium sulfate. After concentrating the product, the residue was purified by silica gel column chromatography (eluent: a mixture of chloroform and methanol) to provide 4:1 g of compound (13) as a glassy solid.

The development inhibitor releasing coupler in this invention may be incorporated in any layer(s) of a color photographic material but is preferably incorporated in a light-sensitive silver halide emulsion layer and/or a layer adhacent thereto. The coupler is more preferably incorporated in a light-sensitive silver halide emulsion layer, and particularly preferably incorporated in a green-sensitive silver halide emulsion layer.

The total addition amount of the coupler(s) in the color photographic material is usually from 3×10^{-7} to 1×10^{-3} mol/m^2, preferably from 3×10^{-6} to 5×10^{-4} mol/m^2, and more preferably from 1×10^{-5} to 3×10^{-4} mol/m^2.

The compound of formula (I) for use in this invention can be incorporated in a color photographic material by the same manner as the case of ordinary coupler as described below.

The color photographic material of this invention has at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one red-sensitive silver halide emulsion layer on a support and there is no specific restriction on the number of the silver halide emulsion layers and light-insensitive emulsion layers and also the arrangement order of these layers. In a typical embodiment, the silver halide color photographic material of this invention has at least one light-sensitive layer composed of plural silver halide emulsion layers each having a substantially same color sensitivity but having a different light sensitivity on a support, and the light-sensitive layer if a unit light-sensitive layer having a color sensitivity for any one one of blue light, green light, and red light. In a multilayer silver halide color photographic material, a red-sensitive emulsion layer, a green-sensitive emulsion layer, and a blue-sensitive emulsion layer are disposed on a support in this order from the support side in the arrangement of the unit light-sensitive layers. However, the order of the arrangement may be reversed depending on the application. Alternatively, an arrangement that a different unit light-sensitive layer is disposed between two light-sensitive layers each having the same color sensitivity can be employed.

Also, light-insensitive layer(s) such as interlayer, etc., may be formed between the aforesaid silver halide.

The interlayer(s) may contain couplers, DIR compounds, etc., as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038 and further may contain a color mixing inhibitor as usually used.

As the plural silver halide emulsion layers constituting each unit light-sensitive layer, a double layer structure composed of a high-sensitive emulsion layer and a low-sensitive emulsion layer as described in West German Patent 1,121,470 or British Patent 923,045 can be preferably used. Usually, these layers are preferably arranged in such an order that the light sensitivity becomes lower towards the support and also a light-insensitive layer may be formed between these silver halide emulsion layers.

Also, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, a low-sensitiveemulsion layer may be disposed at aside far from a support and a high-sensitive emulsion layer may be disposed at a side near the support.

In a practical embodiment of this invention, a low-sensitive blue-sensitive emulsion layer (BL), a high-sensitive blue-sensitive emulsion layer (BH), a high-sensitive green-sensitive emulsion layer (GH), a low-sensitive green-sensitive emulsion layer (GL), a high-sensitive red-sensitive emulsion layer (RH), and a low-sensitive red-sensitive emulsion layer (RL) can be disposed on a support in this order from the farthest side of the support. In other embodiments, the order of embodiments, the order of BH/BL/GL/GH/RH/RL or the order of BH/BL/GH/GL/RL/RH can be employed.

Also, as described in JP-B-55-34932 (the term "JP-B" as used herein means an "examined published Japanese patent application"), the order of a blue-sensitive emulsion layer, GH, RH, GL, and RL from the farthest side of the support can be employed. Furthermore, as described in JP-A-56-25738 and JP-A-62-63936, the order of a blue-sensitive emulsion layer, GL, RL, GH, and RH from the farthest side of the support can be also employed.

Also, as described in JP-B-49-15495, a unit light-sensitive layer of three layer structure that the uppermost layer is a silver halide emulsion layer having the highest light sensitivity, an intermediate layer is a silver halide emulsion layer having a lower than that of the uppermost layer, and the lowermost layer is a silver halide emulsion layer having a lower light-sensitivity than that of the intermediate layer, that is, the light sensitivities of the three silver halide emulsion layers become successively lower towards the support may be employed. Even in the case of the aforesaid three layers each having a different light sensitivity, as described in JP-A-59-202464, a same color-sensitive layer may be composed of an intermediate-sensitive emulsion layer, a high-sensitive emulsion layer, and a low-sensitive emulsion layer in this order from the farthest side of a support may be employed.

Furthermore, the disposition order of a high-sensitive emulsion layer, a low-sensitive emulsion layer, and an intermediate emulsion layer or the disposition order of a high-sensitive emulsion layer may be employed.

When a same color-sensitive layer is composed of four or more layers, the arrangement of the layers can be varied as described above.

As described above, various layer structures and arrangements can be selected according to the purpose of the color photographic material.

The silver halide contained in the photographic emulsion layers of the color photographic material of this invention is preferably is silver iodobromide, silver iodochloride, or silver iodochloro-bromide containing about not more than about 30 mol% silver iodide. Silver iodibromide or silver iodovhloro-bromide containing from about 2 mol% to about 10 mol% silver iodide.

The silver halide grains in the photographic emulsion may be those having a regular crystal form such as a cubic form, an octahedral form and a tetradecahedral form, those having an irregular crystal form such as a pherical form or a tabular from, those having a crystal defect such as twin planes, or those having the composite form of them.

The silver halide grains may be either fine grains having grain sizes of less than about 0.2 microns or coarse grains having large grain sizes up to about 10 microns in the projected area diameter. Also, the silver halide emulsion for use in this invention may be a polydisperse emulsion or a monodisperse emulsion.

The silver halide photographic emulsions for use in this invention can be prepared by a method described, for example, in Research Disclosure (RD), No. 17643 (December, 1978), pages 22-23, "I. Emulsion Preparation and Types", ibid., No. 18716 (November, 1979), age 648, ibid., No. 307105 (November, 1989), pages 863-865, P. Glafkides, Chemie et Phisique Photographique, Paul Montel, 1967, C.F. Duffin, Photographic Emulsion Chemistry, published by Focal Press, 1966, and V. L. Zelikman et al, Making and Coating Photographic Emulsion, published by Focal Press, 1964.

Furthermore, monodisperse emulsions as described in U.S. Patents 3,574,628 and 3,655,394 can be preferably used in this invention.

Tabular grains having an aspect ratio of at least about 3 can be used in this invention. Tabular grain silver halide emulsions can be easily prepared by the methods described, e.g., in Gotoff, Photographic Science and Engineering, Vol. 14, pages 248-257(1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048, 4,439,520, and British Patent 2,112,157.

The individual silver halide grains may have either a homogeneous structure or a heterogeneous structure composed of a core and an outer shell differing in halogen composition or may have a layered structure. Furthermore, the silver halide grains may junctioned to other silver halide having a different halogen composition by epitaxial junction or to other compound than silver halide, e.g., silver thiocyanate, lead oxide, etc. Also, a mixture of silver, halide grains having various crystal forms may be used.

The aforesaid silver halide emulsion may be of a surface latent image type of forming a latent image mainly on the surface thereof, an internal latent image type of forming a latent image in the inside of the grain, or a type of forming latent images on the surface and the inside of it. However, it is necessary that the silver halide emulsion for use in this invention is a negative-working emulsion. The internal latent image type emulsion may be a core/shell type internal latent image emulsion described in JP-A-63-264740. The preparation method of the core/shell type internal latent image emulsion described in JP-A-59-133542. The thickness of the shell of the core/shell type silver halide gains differs according to the manner of the development process, etc., but us preferably from 3 to 40 nm, and particularly preferably from 5 to 20 nm.

The silver halide emulsion is usually physically ripened, chemically ripened, and spectrally sensitized for use. Additives which are used in the aforesaid steps are described in Research' Disclosure, No. 17643, ibid., No. 18716, and ibid., No. 307105 as tabulated below.

In the color photographic material of this invention, two or more kinds of silver halide emulsions each having at least one different characters in terms) of the grain sizes, the grain size distribution, the halogen composition, the grain form, and the sensitivity can be used in a same layer as a mixture thereof.

Also, silver halide grains having the fogged grain surface described in U.S. Patent 4,082,553, silver halide grains having the fogged grain inside described in U.S. Patent 4,626,498 and JP-A-59-214852, or colloidal silver can be preferably used for a light-sensitive silver halide emulsion layer and/or a substantially light-insensitive hydrophylic colloid layer.

Silver halide grains having the fogged grain inside or fogged grain surface mean silver halide grains which can be unoformly (non-imagewise) developed regardless of non-exposed and exposed portions of the photographic material. The preparation methods of the silver halide grains having the fogged grain size or grain surface are described in U.S. Patent 4,626,498 and JP-A-59-214852.

The silver halide forming the inner nucleus of the core/shell type silver halide grain having fogged grain side may be one having a same halogen composition as that of the shell portion or a different halogen composition of the latter. As the silver halide having the fogged grain inside or surface, silver chloride, silver chlorobromide, silver iodobromide, or silver chloroiodo-bromide can be used.

There is no particular restriction on the grain sizes of these fogged silver halide grains but the mean grain size is preferably from 0.01 to 0.75 μm, and particularly preferably from 0.05 to 0.6 μm.

Also, there is no particular restriction on the form of the fogged silver halide grains and the silver halide grains may be regular grains. Also, the emulsion of the fogged silver halide grains may be a polydisperse emulsion but is preferably monodisperse emulsion (at least 95% of the weight or the grain number of the silver halide grains have grain sizes within ± 40% of the mean grain size thereof).

In this invention, a light-insensitive fine grain silver halide is preferably used. The light-insensitive fine grain silver halide is a silver halide fine grain which is not exposed at an imagewise exposure for obtaining dye images and is not substantially developed at development processing and it is preferred that the silver halide is not previously fogged.

The fine grain silver halide has a silver bromide content of from 0 to 100% and, if necessary, contains silver chloride and/or silver iodide. The fine grain silver halide containing from 0.5 to 10 mol% of silver iodide is preferred.

The mean grain size (the mean value of the circle-corresponding diameters of the projected areas) of the fine grain silver halide is preferably from 0.01 to 0.5 μm, and more particularly preferably from 0.02 to 0.2 μm.

The fine grain silver halide can be prepared by a same method of preparing ordinary light-sensitive silver halide. In this case, the surface of the silver halide grains is not necessary optically sensitized and also is not necessarily spectrally sensitized. However, it is preferred that before adding the fine grain silver halide to a coating composition, a known additive such as a triazole series compound, an azaindene series compound, a benzothiazolium series compound or a mercapto series compound is previously added to the silver halide. The layer containing the fine grain silver halide can preferably contain colloidal silver.

The amount of the coated silver in the color photographic material of this invention is preferably not more than 6.0 g/m^2, and most preferably not more than 4.5 g/m^2.

Known photographic additives which can be used in this invention are also described in the aforesaid 3 Research Disclosures and they are shown in the following table.

	Additives	RD 17643 (December, 1978)	RD 18716 (November, 1979)	RD 307105 (November, 1989)
1.	Chemical Sensitizers	Page 23	Page 648, right column	Page 866
2.	Sensitivity Increasing Agents	___	Page 648, right column	___
3.	Spectral Sensitizers and Supersensitizers	Pages 23-24	Page 648, right column to page 649, right column	Pages 866-868
4.	Brightening Agents	Page 24	Page 647, right column	Page 868
5.	Antifoggants and Stabilizers	Pages 24-25	Page 649, right column	Pages 868-870
6.	Light Absorbers, Filter Dyes and Ultraviolet Absorbents	Pages 25-26	Page 649, right column to page 650, left column	Page 873
7.	Stain Inhibitors	Pages 25, right column	Page 650, left to right columns	Page 872
8.	Dye Images Stabilizers	Page 25	Page 650, left column	Page 872
9.	Hardeners	Page 26	Page 651, left column	Pages 874-875

Additives	RD 17643 (December, 1978)	RD 18716 (November, 1979)	RD 307105 (November, 1989)
10. Binders	Page 26	Page 651, left column	Pages 873-874
11. Plasticizers and Lubricants	Page 27	Page 650, right column	Page 876
12. Coating Aids and Surface Active Agents	Pages 26-27	Page 650, right column	Pages 875-876
13. Antistatic Agents	Page 27	Page 650, right column	Pages 876-877

In this invention, it is preferred to incorporate a compound capable of fixing formaldehyde by reacting therewith described in U.S. Patents 4,411,987 and 4,435,503 in the color photographic material for inhibiting the photographic performance from being deteriorated with a formaldehyde gas.

It is also preferred that the color photographic material of this invention contains a mercapto compound described in U.S. Patent 4,740,454, 4,788,132, JP-A-62-18539 and JP-A-1-283551:

Furthermore, it is preferred that the color photographic material of this invention contains a compound releasing a fogging agent, a development accelerator, a silver halide solvent, or each precursor thereof regardless of the amount of developed silver formed by development processing disclosed in JP-A-1-106052.

Moreover, it is preferred that the color photographic material of this invention further contains a dye dispersed by the method described in WO(PCT) 88/04794A and Toku Hyo 1-502912 (the term "Toku Hyo" as used herein means an "unexamined published PCT patent application translated into Japanese language") or a dye described in EP 317,308A, U.S. Patent 4,421,555, and JP-A-1-259358.

In this invention, various kinds of color couplers can be used and practical examples are described in aforesaid Research Disclosure, No. 17643, VII-C to G and ibid., No. 307105, VII-C to G.

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

As magenta couplers, 5-pyrazolone series compounds and pyrazoloazole series compounds are preferred and those described in U.S. Patents 4,310,619, 4,351,897, 3,061,432, 3,725,064, 4,500,630, 4,540,654, and 4,556,630, European Patent 73,636,JP-A-60-33552, JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, WO(PCT) 88/04795, Research Disclosure,No. 24220 (June, 1984), and ibid., No. 24230 (June, 1984) are particularly preferred.

Cyan couplers which can be used in this invention include phenolic and naphtholic couplers. Preferred cyan couplers are 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, 4,327,173, 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, West German Patent Publication (OLS) 3,329,729, European Patents 121,365A and 249,453A, and JP-A-61-42658.

Furthermore, pyrazoloazole series cyan couplers described in JP-A-74-553, JP-A-64-554, JP-A-64-555, and JP-A-556 and imidazole series cyan couplers described in U.S. Patent 4,818,672 can be also used in this invention.

Typical examples of polymerized dye forming couplers are described in U.S. Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, British Patent 2,102,173, and European Patent 341,188A.

Couplers which form dyes having a moderate diffusibility can be used in this invention and preferred such couplers are described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Patent Publication (OLS) 3,234,533.

Colored couplers for correcting unnecessary absorptions of colored dyes can be also used in this invention and preferred such couplers are described in Research Disclosure, No. 17643, VII-G, ibid., No. 307105, VII-G, U.S. Patents 4,163,670, 4,004,929, and 4,138,258, JP-B-57-39413, and British Patent 1,146,368. Furthermore, couplers for correcting unnecessary absorptions of colored dyes by fluorescent dyes released upon coupling described in U.S. Patent 4,774,181 and couplers having a dye precursor group capable of forming a dye by reacting with a developing agent as a releasable group described in U.S. Patent 4,777,120 are preferably used.

Compouns releasing photographically useful residues with coupling can be preferably used in this invention.

DIR couplers releasing a development inhibitor other than the DIR coupler of formula (I) for use in this invention can be also used in this invention and .preferred examples of such other DIR couplers are described in the patents described in Research Disclosure, No. 17643, VII-F and ibid., No. 307105, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, and JP-A-63-37350, U.S. Patents 4,248,962 and 4,782,012.

Couplers releasing bleach accelerators described in Research Disclosure, No. 11449, ibid., No. 24241, JP-A-61-201247 are effective for shortening the time of a processing step having a bleach faculty and, in particular, the effect of using such couplers is large in the case of adding the couplers to the color photographic material using aforesaid tabular silver halide grains.

Couplers capable of imagewise releasing a nucleating agent or a development accelerator can be also used in this invention and preferred examples thereof are described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840.

Also, couplers releasing a fogging agent, a development accelerator, a silver halide solvent, etc., by the oxidation reduction reaction with the oxidation product of a color developing agent described in JP-A-60-107029, JP-A-60-252340, JP-A-1-44940, and JP-A-1-45687 are preferably used in this invention.

Other compounds which can be used for the color photographic materials of this invention are competing couplers described in U.S. Patent 4,130,427, polyequivalent couplers described in U.S. Patents 4,283,472, 4,338,393, and 4,310,618, DIR redox compound-releasing couplers, DIR coupler-releasing couplers, DIR coupler-releasing redox compounds, or DIR redox-releasing redox compouns described in JP-A-60-185950 and JP-A-62-24252, couplers releasing a dye recoloring after releasing described in European Patents 173,302A and 313,308A, ligand-releasing couplers described in U.S. Patent 4,555,477, couplers releasing a leuco dye described in JP-A-63-75747, and couplers releasing a fluorescent dye described in U.S. Patent 4,774,181.

The couplers for use in this invention can be introduced into the color photographic materials of this invention by various dispersion methods.

For example, the couplers can be incorporated in the silver halide emulsion by an oil drop-in-water dispersion method and examples of a high-boiling solvent which is used for the oil drop-in-water dispersion method are described in U.S. Patent 2,322,027.

Specific examples of the high-boiling organic solvent having a boiling point at normal pressure of higher than 175° C, which is used for the oil drop-in-water dispersion method are phthalic acid esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-5-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, and bis(1,1-diethylpropyl) phthalate), phosphoric acid esters or phosphonic acid esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexydiphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, and di-2-ethylhexyl-phenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azerate, glycerol tributyrate, isostearyl lactate, and trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline),and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene).

Also, an organic solvent having a boiling point of higher than about 30° C, and preferably from 50° C to about 160° C can be used as an auxiliary solvent. Typical examples of the solvent are ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate, and dimethylformamide.

A latex dispersion method can be also used for incorporating the couplers in the emulsions in this invention and specific examples of the latex dispersion method, the effects thereof, and latexes for impregnation are described in U.S. Patent 4,199,363, West German Patent Publications (OLS) 2,541,274 and 2,541,230.

It is preferred to incorporate phenethyl alcohol or various kinds of preservatives or antimolds such as 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxy ethanol, 2-(4-thiazolyl)benzimidazole, etc., described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941 to the color photographic material of this invention.

This invention can be applied to various color photographic materials. For example, the invention can be applied for ordinary or cinne color negative films, color reversal films for slide or television, color photographic papers, color positive films, and color reversal papers.

Suitable supports which can be used for the color photographic materials of this invention are described in Research Disclosure, No. 17643, page 28, ibid., No. 18716, page 647, right column to page 648, left column, and ibid., No. 307105, page 879.

In the color photographic material of this invention, the total thickness of all hydrophilic colloid layers on the emulsion side is preferably 28 μm or less, more preferably 23 μm or less, particularly preferably 18 μm or less and the most preferably 16 μm or less. The film swelling rate $T_{1/2}$ is preferably 30 seconds or less, and more preferably 20 seconds or less. The film thickness is determined after being stored at a temperature of 25° C and a relative humidity of 55% (for 2 days). The film swelling rate $T_{1/2}$ can be determined by a method known in the art, e.g., by means of a swellometer of the type as described in A. Green et al Photographic Science Engineering, vol. 19, No. 2, pages 124 to 129. $T_{1/2}$ is defined as the time taken until reaching 1/2 of the saturated film thickness, wherein the saturated film thickness of 90% of the most swollen film thickness reached when the light-sensitive material is processed with a color developer for 3 minutes and 15 seconds at 30° C.

The film swelling rate $T_{1/2}$ can be adjusted by adding a hardening agent to gelatin as a binder or by changing the storing condition after coating. Also, the swelling ratio of the color photographic material of this invention is preferably in the range of from 150 to 400%. The swelling ratio can be calculated according to the equation of (most swollen film thickness - film thickness)/film thickness from the most swollen film thickness under the aforesaid condition.

In the color photographic material of this invention, it is preferred to form a hydrophilic colloid layer (back layer) having the total dry layer thickness of from 2 μm to 20 μm at the opposite side of the support to the emulsion layer-carrying side. It is also preferred that the back layer contains a light absorbent, a filter dye, a ultraviolet absorbent, an antistatic agent, a hardening agent, a binder, a plasticizer, a lubricant, a coating aid, a surface active agent. The swelling ratio of the back layer is preferably in the range of from 150 to 500%.

The color photographic material of this invention can be processed by the ordinary process described in Research Disclosure, No. 17643, pages 28 to 29, ibid., No. 18716, page 651,left column to right column and ibid., No. 307105, pages 880 to 881.

A color developer which is used for developing the color photographic material of this invention is an alkaline aqueous solution containing an aromatic primary amino color developing agent as the main component.

As the color developing agent, an aminophenol series compound is useful but a p-phenylenediamine series compound is preferably used.

Typical examples of the color developing agent are 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-3-amino-N-ethyl-N--hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N--methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline, and the sulfates, hydrochlorides, or p-toluenesulfonates of them.

In the aforesaid compounds, 3-methyl-4-amin-N-ethyl-N-β-hydroxyethylaniline sulfate is particularly preferred. The aforesaid compounds can be used as a mixture thereof according to the purpose.

The color developer generally contains a pH buffer agent such as a carbonate, a borate, or a phosphate of an alkali metal and a development inhibitor or an antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole, or a mercapto compound.

Also, if necessary, the color developer can further contain various kinds of preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines (such as N,N-biscarboxymethylhydrazine), phyenylsemicarbazides, triethanolamine, catecholsulfonic acids, etc.; organic solvents such as ethylene glycol, diethylene glycol, etc.; development accelerators such as benzyl alcohol, polyethyleneglycol, quaternary ammonium salts, amines, etc.; auxiliary developing agents such as 1-phenyl-3-pyrazolidone, etc.; dye-forming couplers; competing couplers; viscosity imparting agents; chelating agents represented by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid, phosphonocarboxylic acid, etc., for example, ethylenediaminetetraacetic nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethhylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, nitrilo-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and the salts of them.

In the case of practicing a reversal process, a color development is usually carried out after carrying out a black-and-white development. For the black-and-white developer, known black-and-white developing agents such as dihydroxybenes (such as hydroquinone, etc.), 3-pyrazolidones (such as 1-phenyl-3-pyrazolidone, etc.), or aminophenols (such as N-methyl-p-aminophenol, etc.) can be used singly or as a combination thereof.

The pH of these color developer and black-and-white developer is generally from 9 to 12. Also, the replenishing amount for these developers depends upon the kind of the color photographic material being processed but is generally less than about 3 liters per one square meter of the color photographic material. The amount thereof can be reduced below 500 ml by reducing the bromide ion concentration in the replenisher. In the case of reducing the replenishing amount, it is preferred to prevent the occurrence of the evaporation and the air oxidation of the liquid by reducing the contact area of the processing bath with air.

The contact area of the photographic processing liquid in a processing bath with air can be referred to as the opening ratio defined as follows.

Opening ratio = A (cm^2)/B (cm^3)

A: Contract area of the processing liquid with air

B: Volume of the processing liquid.

The aforesaid opening ratio is preferably less than 0.1, and more preferably from 0.001 to 0.05.

As a method of reducing the opening ratio, there are a method of forming a cover such as a floating lid on the surface of the photographic processing liquid in the processing bath, a method of using a mobile lid described in JP-A-1-82033, and a slit development processing method described in JP-A-63-216050.

The reduction of the opening ratio can be preferably applied not only to both the color development and black-and-white development but also to subsequent many steps such as the steps of bleach, bleach-fix (blix), fix, wash, stabilization, etc. Also, the replenishing amount can be reduced by using a means of restraining the accumulation of bromide ions in the developers.

The time for the color development process is usually in the range of from 2 to 5 minutes but the processing time can be further shortened by employing a high temperature and high pH and using a color developing agent at a high concentration.

The photographic emulsion layers are usually bleached after color development. The bleach process may be carried out simultaneously with a fix process (blix process) or may be carried out separately from a fix process. Furthermore, for quickening processing, a process of applying a blix process after bleach process may be employed. Moreover, it can be optionally practiced according to the purpose to practice the blix process using two baths, to practice a fix process before a blix process, or practice a bleach process after a blix process.

As a bleaching agent, for example, compounds of polyvalent metals such as iron(III), etc., peracids, quinones, nitro compounds, etc., can be used. Typical examples of the bleaching agent are organic complex salts of iron (III), e.g., the complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminipropanetetraacetic acid, glycol ether diaminetetraacetic acid, etc., or the complex salts of citric acid, tartaric acid, malic acid, etc., can be used. In these compounds, aminopolycarboxylic acid iron(III) complex salts as ethylenediaminetetraacetic acid iron(III) complex salt and 1,3-diaminopropanetetraacetic acid iron(III) complex salt are preferably used form the view points of quick processing and the prevention of environmental pollution. Furthermore, the aminopolycarboxylic acid iron(III) complex salt is particularly useful in both a bleach solution and a blix solution. The pH of the bleach solution or blix solution using such an aminopolycarboxylic acid iron(III) complex salt is usually from 4.0 to 8 but a lower pH may be employed for quickening the processing.

For the bleach solution, the blix solution, and a prebath thereof can be used a bleach accelerator if necessary.

Practical examples of the useful bleach accelerator are compounds having a mercapto group or a 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-53-104232, JP-A-53-124424, JP-A-53-141623, and JP-A-53-28426, and Research Disclosure, No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; 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 Patent 966,410 and 2,748,430; polyamine compounds described described in JP-B-45-8836, other compounds described in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and bromide ions.

In these compounds, the compounds having a mercapto group or a disulfide group are preferred in the view point of showing a large acceleration effect and the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are particularly preferred. Furthermore, the compounds described in U.S. Patent 4,552,834 are preferred.

The aforesaid bleaching accelerator may be incorporated in the color photographic material. When a color photographic material for camera use is blixed, the bleach accelerator is particularly effective.

It is preferred that the bleach solution or the blix solution further contains an organic acid for preventing the occurrence of bleach stain in addition of the aforesaid compounds. A particularly preferred organic acid is a compound having an acid association constant (pKa) of from 2 to 5, such as acetic acid, propionic acid, hydroxyacetic acid, etc.

As a fixing agent which is used for a fix solution or a blix solution, there are thiosulfates, thiocyanates, thioether series compounds, thioureas, a large amount of iodides, etc., but thiosulfates are generally used and in particular, ammonium thiosulfate is most widely used. Also, a combination of a thiosulfate and a thiocyanate, a thioether series compound, or a thiourea can be preferably used.

As a preservative for the fix solution or the blix solution, sulfites, hydrogensulfites, carbonyl-hydrogensulfide addition products or the sulfinic compounds described in European Patent 294,769A are preferred. Furthermore, it is preferred that the fix solution or the blix solution contains various kinds of aminopolycarboxylic acids or organic solfonic acids for stabilizing the liquid.

In this invention, it is also preferred to add a compound having pka of from 6.0 to 9.0, preferably an imidazole such as imidazole, 1-methylimidazole, 1-ethylimidazole, 2-methylimidazole, etc., in an amount of from 0.1 to 10 mol/liter for adjusting the pH thereof.

The total time for the desilvering step is preferably as short as possible in the range of not causing poor desilvering. The time is preferably from one minute to 3 minutes, and more preferably from one minute to 2 minutes. Also, the processing temperature is from 25°C to 50°C, and preferably from 35°C to 45°C. In the aforesaid preferred temperature range, the desilvering rate is improved and the occurrence of stains after processing can be effectively prevented.

In the desilvering step, it is preferred that stirring is strengthened as strong as possible. As a practical method of strengthening stirring, there are a method of applying jet stream of a processing liquid onto the surface of the emulsion layer of the color photographic material described in JP-A-62-183460, a method of increasing the stirring effect by using the rotation means described in JP-A-62-183461, a method of improving the stirring effect by transferring the color photographic material while contacting the surface of the emulsion layer with a wiper blade formed in a processing liquid to form turbid stream over the surface of the emulsion layer, and a method of increasing the circulating stream amount of the whole processing liquid. Such a means of improving stirring is effect in any of the bleach solution, the blix solution, and the fix solution.

It is considered that the improvement of stirring increases the rate of supplying a bleaching agent and a fixing agent into the emulsion layers, which results in increasing the desilvering rate. Also, the aforesaid means for improving stirring is more effective in the case of using a bleach accelerator and can greatly increase the bleach accelerating effect and dissolve the fix hindering action by the bleach accelerator.

It is also preferred that an automatic processor being suitably used for processing the color photographic materials of this invention has a conveying means for light-sensitive materials as described in JP-A-60-191257 JP-A-60-191258 and JP-A-60-191259, such a conveying means can remarkably reduce the amount of processing solution carried over from a bath to the succeeding bath as disclosed in JP-A-60-191257, to thereby inhibit the deterioration of the properties of the processing solution. Such as effect is particularly effective for reducing the processing time at each step or for reducing the replenishing rate of the processing solution.

It is general that the thus desilvered silver halide color photographic materials of this invention are subjected to washing and/or stabilization. The amount of water being used for washing can be selected in a wide range depending on the characteristics (e.g., the kind of couplers, etc.) and the use of the color photographic material, the temperature of wash water, the number (stage number) of washing tanks, the replenishing system (e.g., countercurrent flow system or co-current flow system), and other various factors. Of these factors, the relation between the number of washing tanks and the amount of water in a multistage countercurrent flow system can be obtained according to the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May, 1955).

According to the multistage countercurrent flow system described in the above reference, the amount of washing water can be greatly reduced but bacteria would grow due to the increase of the retension time of water in the tanks and floating masses of bacterial would stick to the color photographic materials. In processing of the color photographic materials of this invention, for dissolving the aforesaid problem, the method of reducing calcium and magnesium ion concentrations described in JP-A-62-288838 can be used effectively. Also, it is effective to use isothiazolone compounds or thiabendazoles described in JP-A-57-8542, chlorine series fungicides such as chlorinated sodium isocyanurate, etc., benzotriazole, and other fungicides described in Hiroshi Horiguchi, Bookin Boobaizai no Kagaku (Chemistry of Fungicides), edited by Eisei Gijutsu Gakkai, published bu Koogyo Kijutsu Kai, 1982, and Bookin Boobai Zai Jitan (Handbood of Bactericides and Fungicides), edited by Nippon Bookin Boobai Gakkai.

The washing water in the processing of the color photographic materials of this invention has a pH value of from 4 to 9, and preferably from 5 to 8. The temperature of washing water and the washing time can be selected in broad ranges depending on the characteristics and the use of the color photographic material but in general they are selected in the ranges of from 15 °C to 45 °C in temperature and from 10 minutes to 20 seconds in washing time, and preferably from 25 °C to 40 °C in temperature and from 5 minutes to 30 seconds in washing time.

The color photographic material of this invention may be directly processed with a stabilizer in place of the aforesaid washing step. For such a stabilization, any of the known techniques described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used.

As the case may be, a stabilization process is further applied after applying the aforesaid washing step. For example, a stabilizing bath containing a dye stabilizer and a surface active agent is used as a final bath for color photographic materials for in camera use. Examples of the dye stabilizer are aldehydes such as formalin, glutaraldehyde, etc., N-methylol compounds, hexamethylenetetramine, and aldehyde-sulfurous acid addition products.

The stabilizing bath may also contain various chelating agents or bactericides.

The overflow accompanying the replenishment of wash water and/or the stabilizing solution can be reused in other steps such as desilvering steps, etc.

In processing using an automatic processor, if the processing solution is concentrated due to evaporation, it is preferred to supply water for compensating the concentration.

The silver halide color photographic material of this invention may contain a color developing agent for simplifying and quickening processing. Such a color developing agent is preferably used in the form of a precursor. Examples of such a precursor are indoaniline compounds described in U.S. Patent 3,342,597, Schiff's base type compounds described in U.S. Patent 3,342,599, Research Dusclosure, No. 14850 and ibid., no. 15159, aldol compounds described in ibid., No. 13924, metal complexes described in U.S. Patent 3,719,492, and urethane compounds described in JP-A-53-135628.

The silver halide color photographic materials of this invention may contain, if necessary, various 1-

phenylpyrazolidaones for the purpose of accelerating color development. Typical examples of such compounds are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

In this invention, the various processing solutions are used at temperature of from 10° C to 50° C. The standard temperature range is normally from 33° C to 38° C. However, a higher temperature may be employed for accelerating processing to reduce the processing time. On the other hand, a lower temperature may be employed for improving the image quality and stabilizing the processing solutions.

The silver halide color photographic material of this invention can be also applied to a heat-developable light-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 following examples are intended to illustrate the present invention but not to limit it in any way.

Example 1

A multilayer color photographic material having the layers of the compositions shown below on an undercoated cellulose triacetate film support was prepared as Sample 101.

Compositions of Layers

The numerals are the coated amounts shown by a g/m^2 unit as converted silver amount for a silver halide emulsion and colloid silver, by a g/m^2 unit for couplers, aditives, and gelatin, and a mol number per mol of silver halide in the same layer for a sensitizing dye.

Layer 1 Antihalation Layer

Black colloidal silver	0.20 (as Ag)
Gelatin	2.20
UV - 1	0.11
UV - 2	0.20
Cpd - 1	4.0×10^{-2}
Cpd - 2	1.9×10^{-2}

Solv - 1	0.30
Solv - 3	1.2×10^{-2}

Layer 2 Interlayer

Fine Grain Silver Iodobromide (AgI 1.0 mol%, sphere-corresponding diameter 0.07 μm	0.15 (as Ag)
Gelatin	1.00
ExC - 4	6.0×10^{-2}
Cpd - 3	2.0×10^{-2}

Layer 3 1st Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 5.0 mol%, surface high AgI type, sphere-corresponding diameter 0.9 μm, variation coeff. 21%, tabular grain, aspect ratio 7.5)	0.42 (as Ag)
Silver Iodobromide Emulsion (AgI 4.0 mol%, inside high AgI type, sphere-corresponding diameter 0.4 μm, variation coeff. of sphere-corresponding diameters 18%, tetradecahedral grains)	0.40
Gelatin	1.90
ExS - 1	4.5×10^{-4}
ExS - 2	1.5×10^{-4}
ExS - 3	4.0×10^{-5}
ExC - 1	0.65
ExC - 3	1.0×10^{-2}
ExC - 4	2.3×10^{-2}
Solv - 1	0.32

Layer 4 2nd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 8.5 mol%, inside high AgI type, sphere-corresponding diameter 1.0 μm, variation coeff. of sphere-corresponding diameters 25%, tabular grains, aspect ratio 3.0)	0.85 (as Ag)
Gelatin	1.91
ExS - 1	3.0×10^{-4}
ExS - 2	1.0×10^{-4}
ExS - 3	3.0×10^{-5}
ExC - 1	0.13
ExC - 3	6.2×10^{-2}
ExC - 4	4.0×10^{-2}
Solv - 1	0.10

<u>Layer 5</u> 3rd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 11.3 mol%, inside high AgI type, sphere-corresponding diameter 1.4 μm, variation coeff. of sphere-corresponding diameters 28%, tabular grains, aspect ratio 6.0)	1.50 (as Ag)
Gelatin	1.20
ExS - 1	2.0×10^{-4}
ExS - 2	6.0×10^{-5}
ExS - 3	2.0×10^{-5}
ExC - 2	8.5×10^{-2}
ExC - 5	7.3×10^{-2}
Solv - 1	0.12
Solv - 2	0.12

<u>Layer 6</u> Interlayer

Gelatin	1.15
Cpd - 4	8.0×10^{-2}
Solv - 1	8.0×10^{-2}

Layer 7 1st Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 15.0 mol%, inside high AgI type, sphere-corresponding diameter 0.9 μm, variation coeff. of sphere-corresponding diameters, tabular grains, aspect ratio 7.0)	0.28 (as Ag)
Silver Iodobromide Emulsion (AgI 4.0 mol%, inside high AgI type, sphere-corresponding diameter 0.4 μm, variation coeff. of sphere-corresponding diameters 18%, octadecahedral grains)	0.16 (as Ag)
Gelatin	1.35
ExS - 4	5.0×10^{-4}
ExS - 5	2.0×10^{-4}
ExS - 6	1.0×10^{-4}
ExM - 1	0.55
ExM - 2	0.05
ExM - 5	3.5×10^{-2}
Solv - 1	0.30
Solv - 3	3.0×10^{-2}

Layer 8 2nd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 8.5 mol%, inside high AgI type, sphere-corresponding diameter 1.0 μm, variation coeff. of sphere-corresponding diameters, tabular grains, aspect ratio 3.0)	0.57 (as Ag)

Gelatin	0.50
ExS - 4	3.5×10^{-4}
ExS - 5	1.4×10^{-4}
ExS - 6	7.0×10^{-5}
ExM - 1	0.14
ExM - 2	5.1×10^{-3}
ExM - 3	3.5×10^{-2}
Solv - 1	0.20
Solv - 3	1.0×10^{-2}

Layer 9 Interlayer

Gelatin	0.45
Solv - 1	2.0×10^{-2}

Layer 10 3rd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 11.3 mol%, inside high AgI type, sphere-corresponding diameter 1.4 μm, variation coeff. of sphere-corresponding diameters 28%, tabular grains, aspect ratio 6.0)	1.30 (as Ag)
Gelatin	1.10
ExS - 4	2.0×10^{-4}
ExS - 5	8.0×10^{-5}
ExS - 6	8.0×10^{-5}
ExM - 4	4.5×10^{-2}
ExM - 6	1.0×10^{-2}
ExC - 2	4.5×10^{-2}
Solv - 1	0.20

Layer 11 Yellow Filter Layer

Gelatin	0.50
Cpd - 6	5.2×10^{-2}
Solv - 1	0.12

Layer 12 Interlayer

Gelatin	0.45
Cpd - 3	0.10

Layer 13 1st Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 12 mol%, inside high AgI type, sphere-corresponding diameter 0.55 μm, variation coeff. of sphere-corresponding diameters 25%, tabular grains, aspect ratio 7.0)	0.20 (as Ag)
Gelatin	1.00
ExS - 7	3.0×10^{-4}
ExY - 1	0.60
ExY - 2	2.3×10^{-2}
Solv - 1	0.15

Layer 14 2nd Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 19.0 mol%, inside high AgI type, sphere-corresponding diameter 1.0 μm, variation coeff. of sphere-corresponding diameters 16%, Octahedral grains)	0.19 (as Ag)
Gelatin	0.35
ExS - 7	2.0×10^{-4}
ExY - 1	0.22
Solv - 1	7.0×10^{-2}

Layer 15 Interlayer

Fine Grain Silver Iodobromide (AgI 2 mol%, homogeneous AgI type, sphere-corresponding diameter 0.13 μm)	0.20 (as Ag)
Gelatin	0.36

Layer 16 3rd Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 14.0 mol%, inside high AgI type, sphere-corresponding diameter 1.0 μm, variavariation coeff. of sphere-corresponding diameters 16%, Octahedral grains, aspect ratio 5.0)	1.55 (as Ag)
Gelatin	1.00
ExS - 8	1.5×10^{-4}
ExY - 1	0.21
Solv - 1	7.0×10^{-2}

Layer 17 1st Protective Layer

Gelatin	1.80
UV - 1	0.13
UV - 2	0.21
Solv - 1	1.0×10^{-2}
Solv - 2	1.0×10^{-2}

Layer 18 2nd Protective Layer

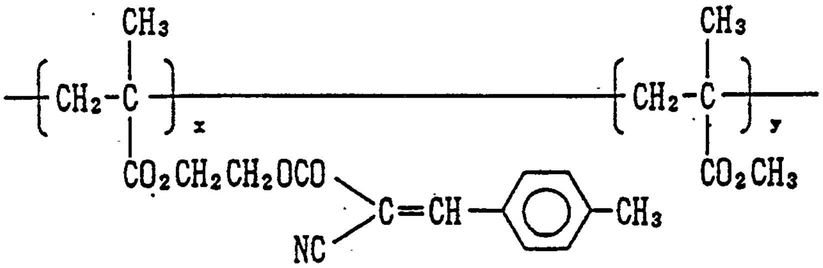
Fine Grain Silver Iodobromide (sphere-corresponding diameter 0.07 μm)	0.36 (as Ag)
Gelatin	0.70
B - 1 (diameter 1.5 μm)	2.0×10^{-2}
B - 2 (diameter 1.5 μm)	0.15

B - 3	3.0×10^{-2}
W - 1	2.0×10^{-2}
H - 1	0.35
Cpd - 7	1.00

To the sample were added 1.2-benzizothiazolon-3-one (in a mean amount of 200 ppm to gelatin), n-butyl-p-hydroxy benzoate (in a mean amount of about 1.000 ppm to gelatin), and 2-phenoxy ethanol (in a mean amount of about 10,000 ppm to gelatin). Furthermore, the sample contained B - 4,B - 5, W - 2, W - 3, F - 1, F - 2, F - 3, F - 4, F - 5, F - 6, F - 7, F - 8, F - 9, F - 10, F - 11, F - 12, F - 13, an iron salt, a lead salt, a gold salt, a platinum salt, an iridium salt, and a rhodium salt.

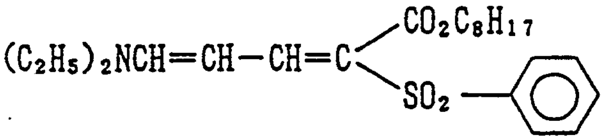
The compounds used for the sample are as follows.

UV-1

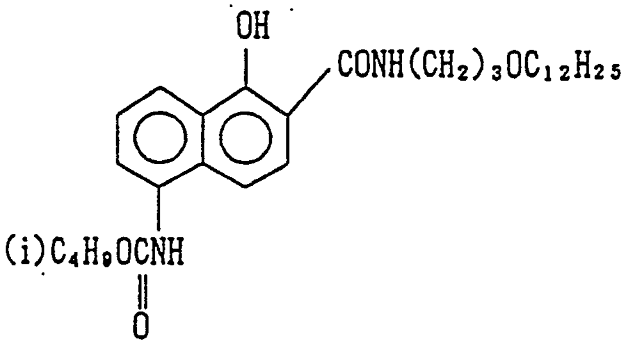


x/y=7/3 (weight ratio)

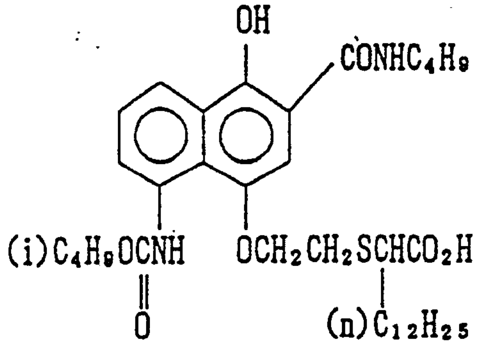
UV-2



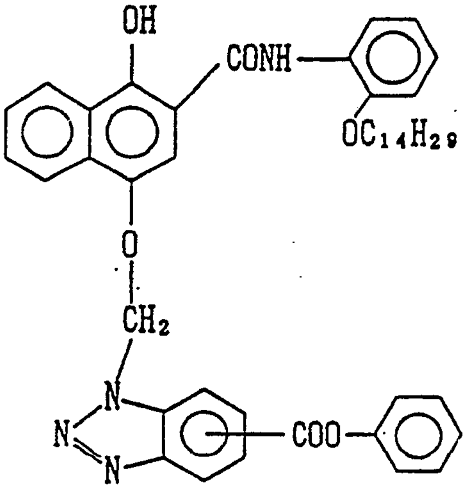
ExC-1



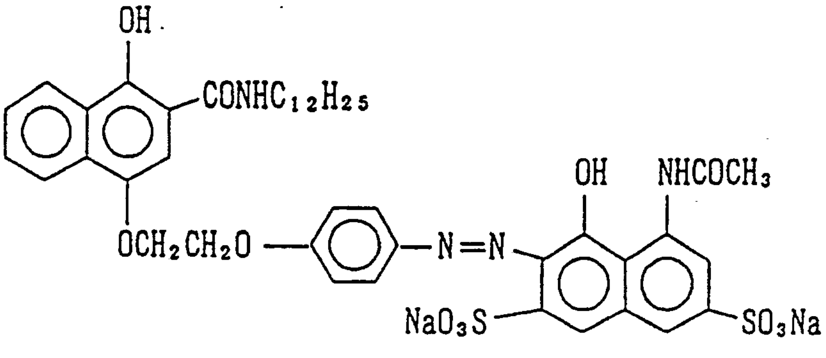
ExC-2



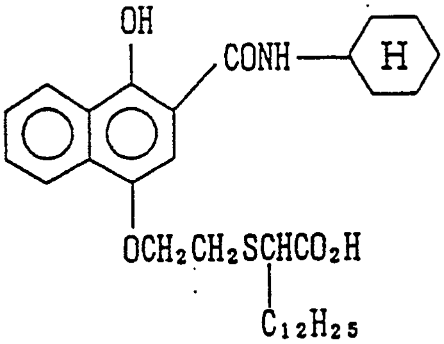
ExC-3



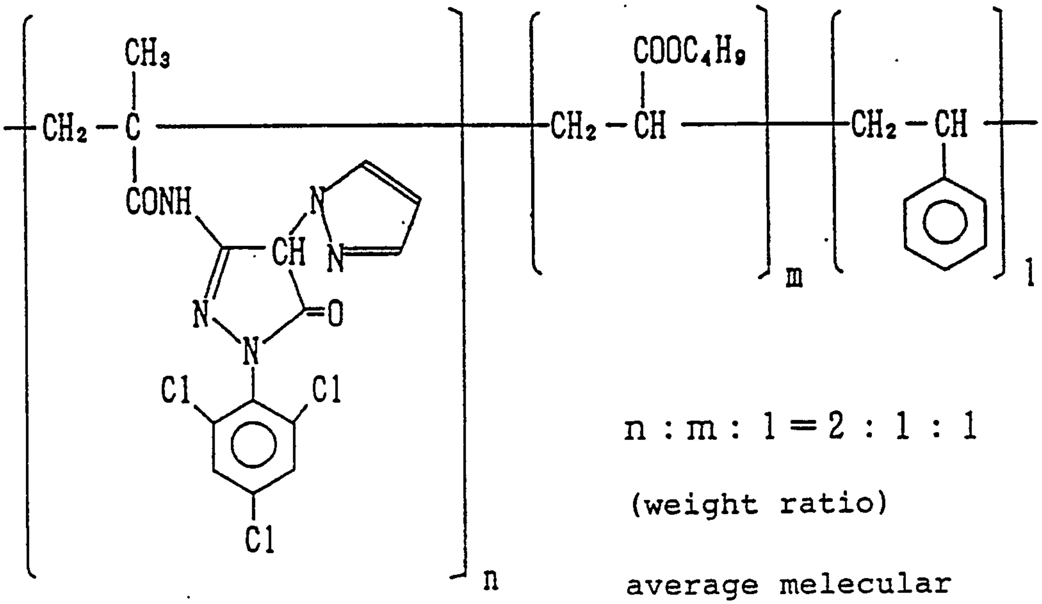
ExC-4



ExC-5



ExM-1

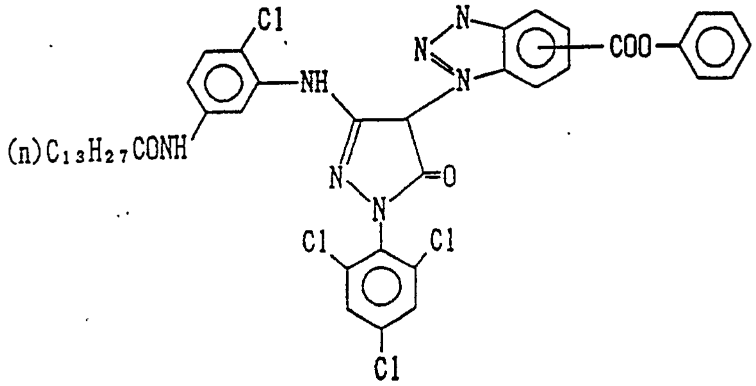


n : m : l = 2 : 1 : 1

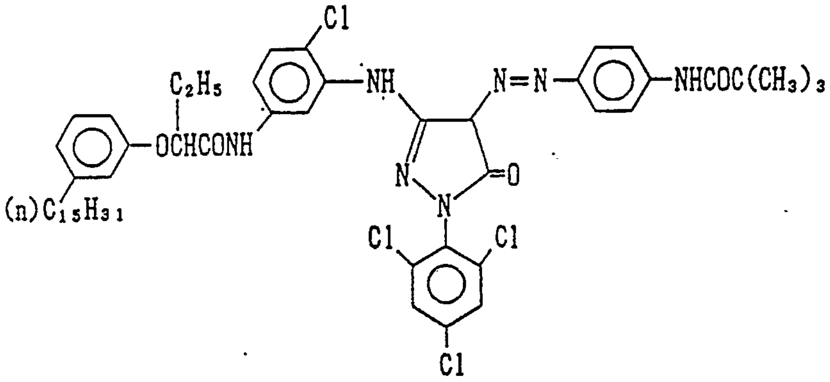
(weight ratio)

average melecular weight: 20,000

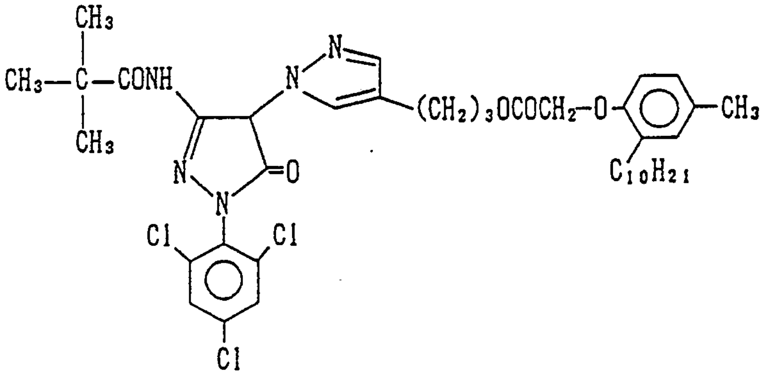
ExM-2 (Comparison Compound-1)



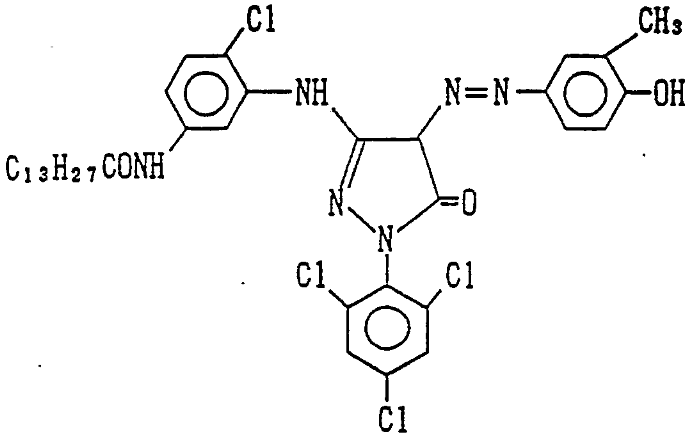
ExM-3



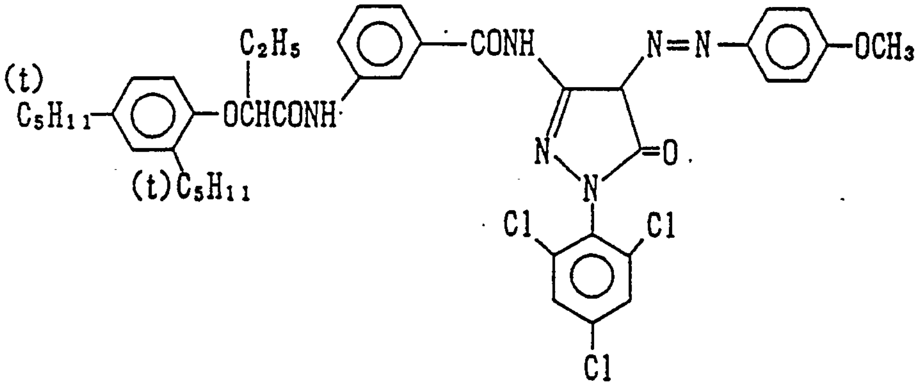
ExM-4



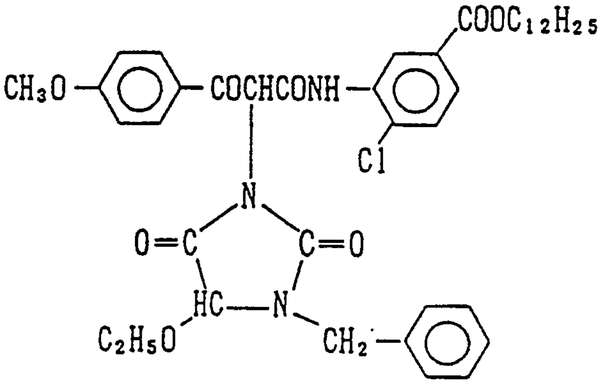
ExM－5



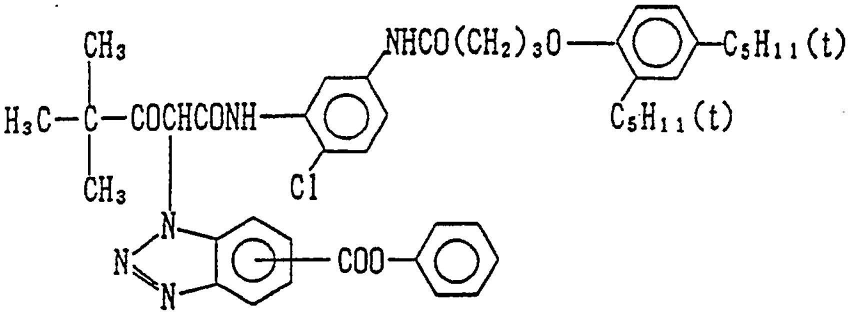
ExM－6



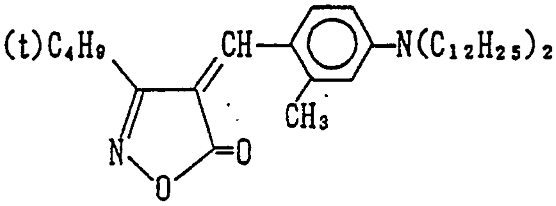
ExY－1



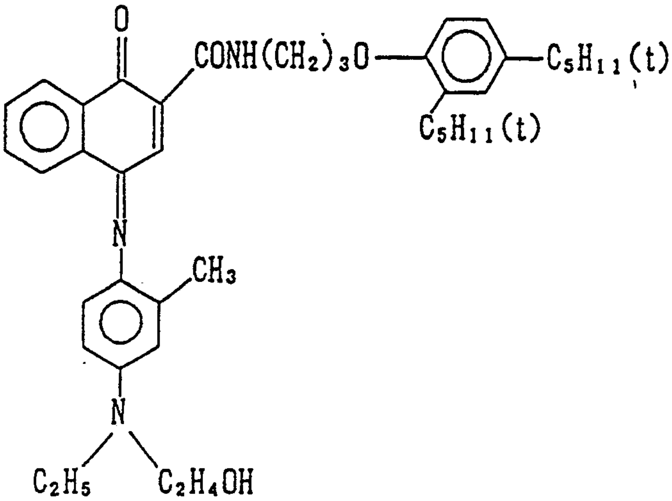
ExY-2



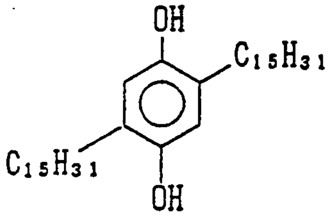
Cpd-1



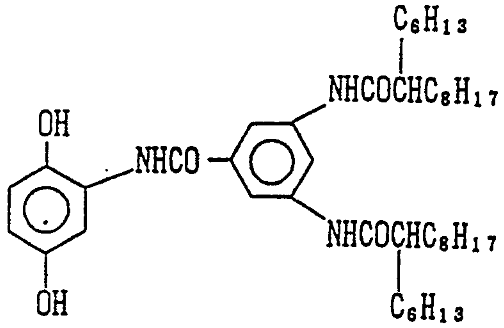
Cpd-2



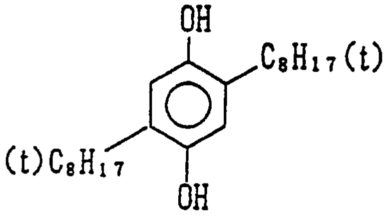
Cpd－3



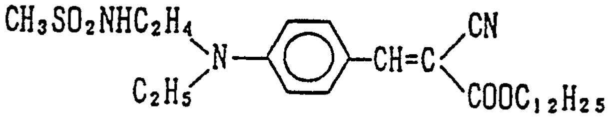
Cpd－4



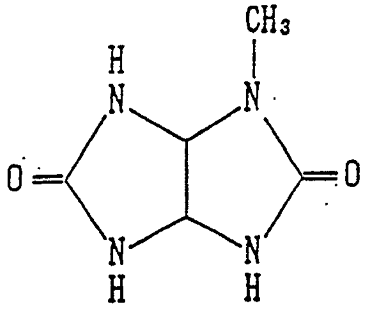
Cpd－5



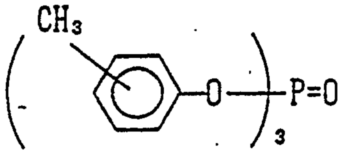
Cpd－6



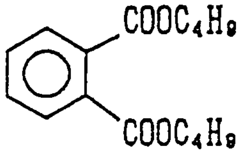
Cpd−7



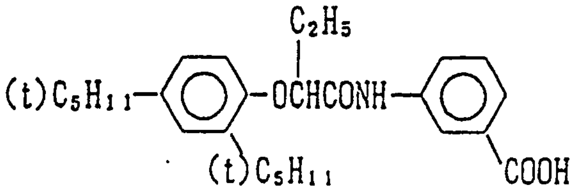
Solv−1



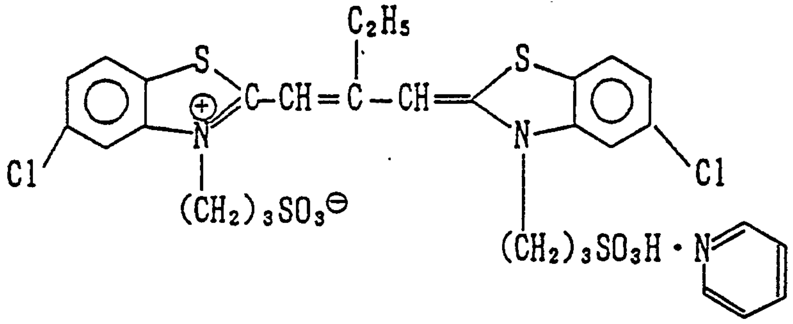
Solv−2



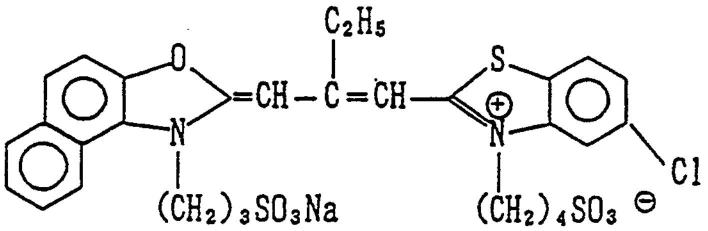
Solv−3



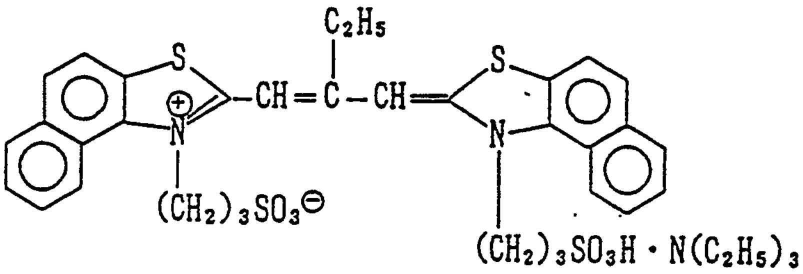
ExS-1



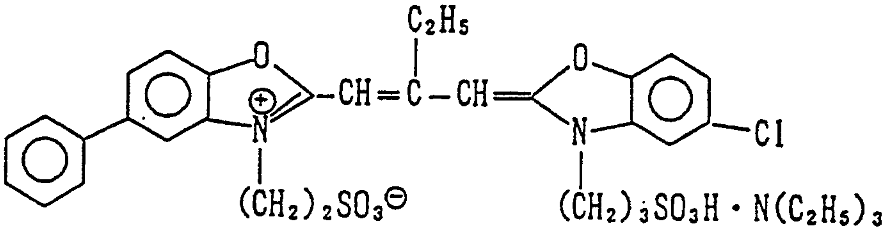
ExS-2



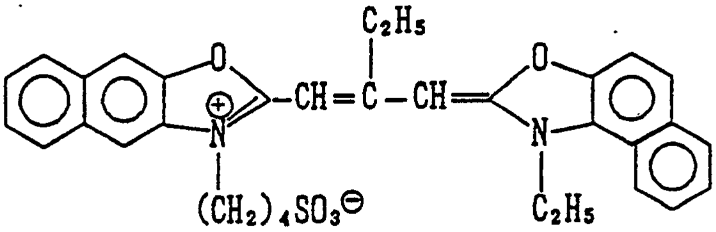
ExS-3



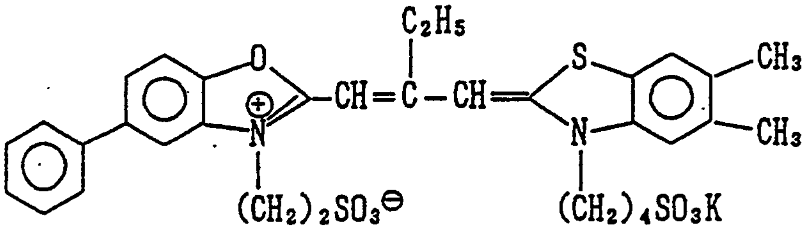
ExS-4



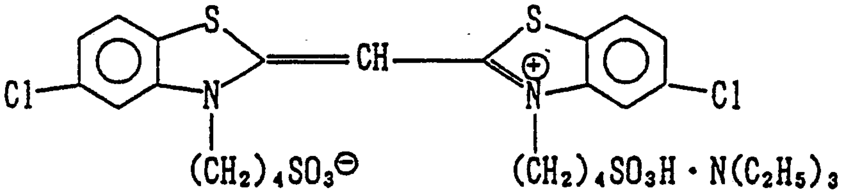
ExS－5



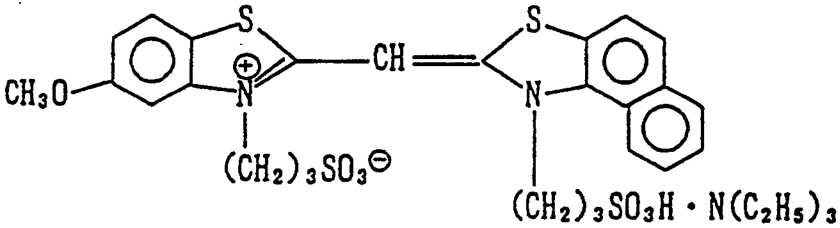
ExS－6



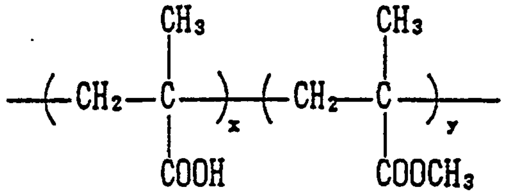
ExS－7



ExS－8



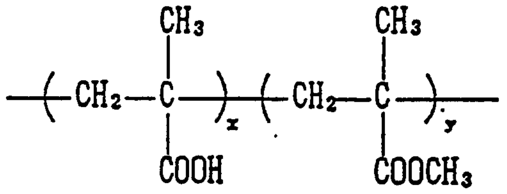
B－1



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}}\right)_x\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}\right)_y\!-$$

x/y=10/90

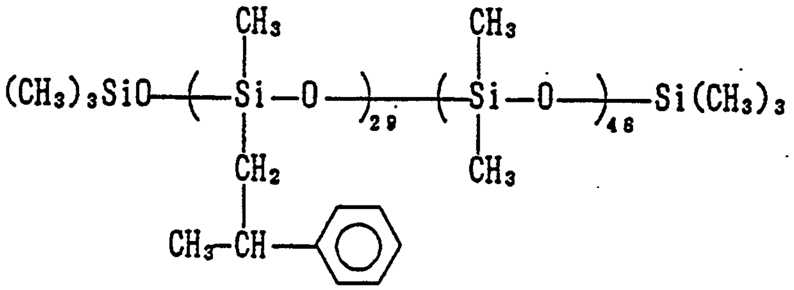
B－2



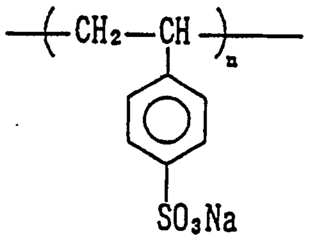
$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}}\right)_x\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}\right)_y\!-$$

x/y=40/60

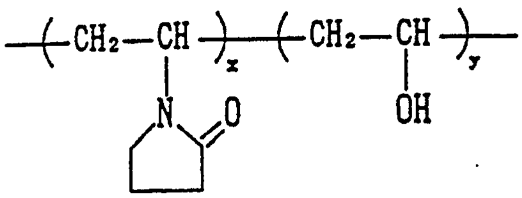
B－3



B－4

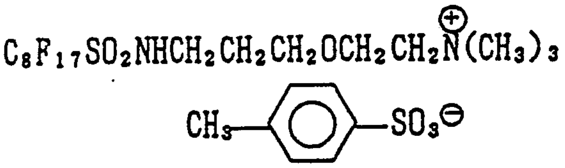


B－5

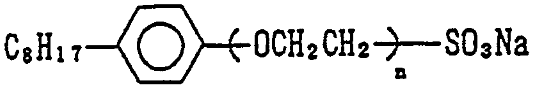


x/y=70/30

W－1

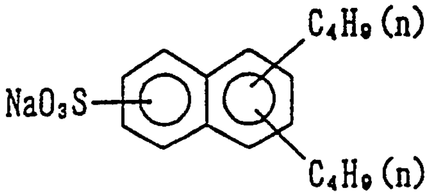


W－2

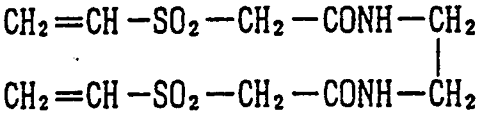


n =2 ～ 4

W－3

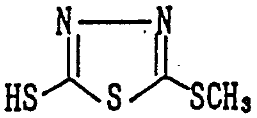


H－1

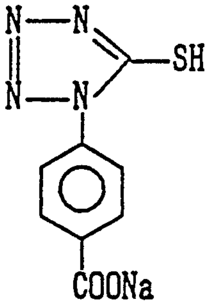


$$\begin{array}{l} CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

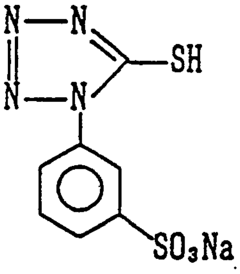
F − 1



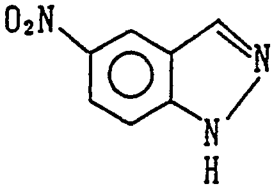
F − 2



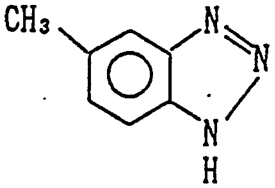
F − 3



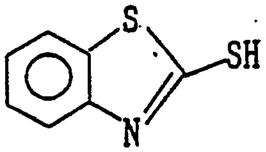
F − 4



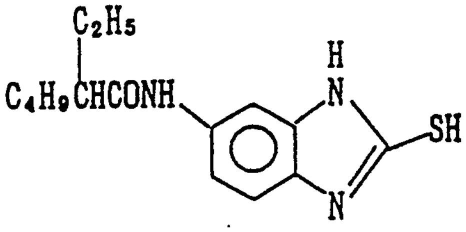
F − 5



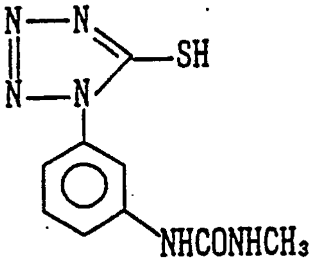
F－6



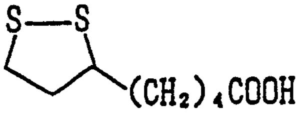
F－7



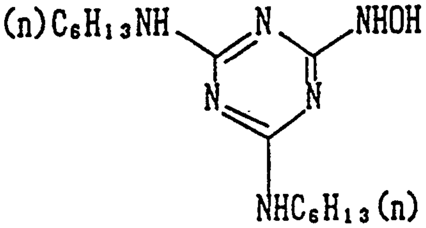
F－8



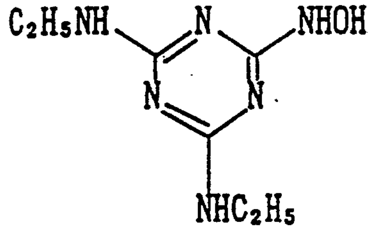
F－9



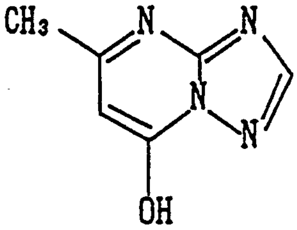
F－10



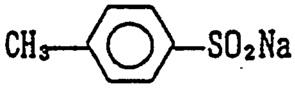
F-11



F-12



F-13

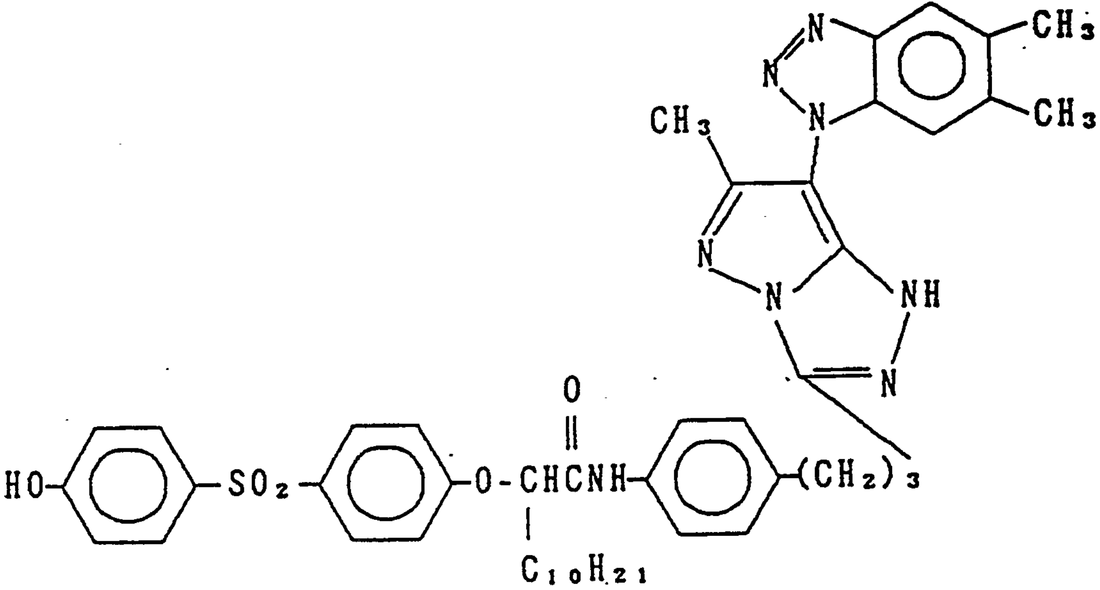


Preparation of Samples 102 to 112

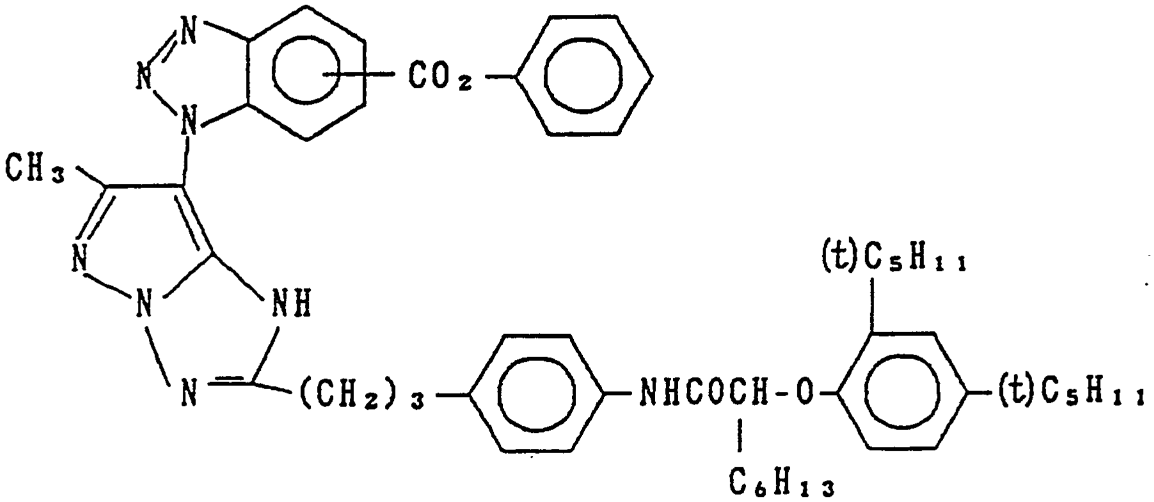
By following the same procedure as the case of preparing Sample 101 except that Coupler ExM - 2 in Layer 7 and Layer 8 of Sample 101 was changed as shown in Table 1 below, Samples 102 to 112 were prepared.

When each of Samples 101 to 112 was wedge exposed to white light with a 3-color separation filter and processed by the processing steps shown below, the sensitivity and the gradation of all the samples were almost same about a magenta color density. Also, the sharpness of the magenta color images was evaluated using a conventional MTF value on each sample.

Comparison Compounds 2 (the coupler described in JP-A-61-28947):



Comparison Compound 3 (the coupler described in JP-A-61-28947):



Comparison Compound 4 (the coupler described in JP-A-62-81638):

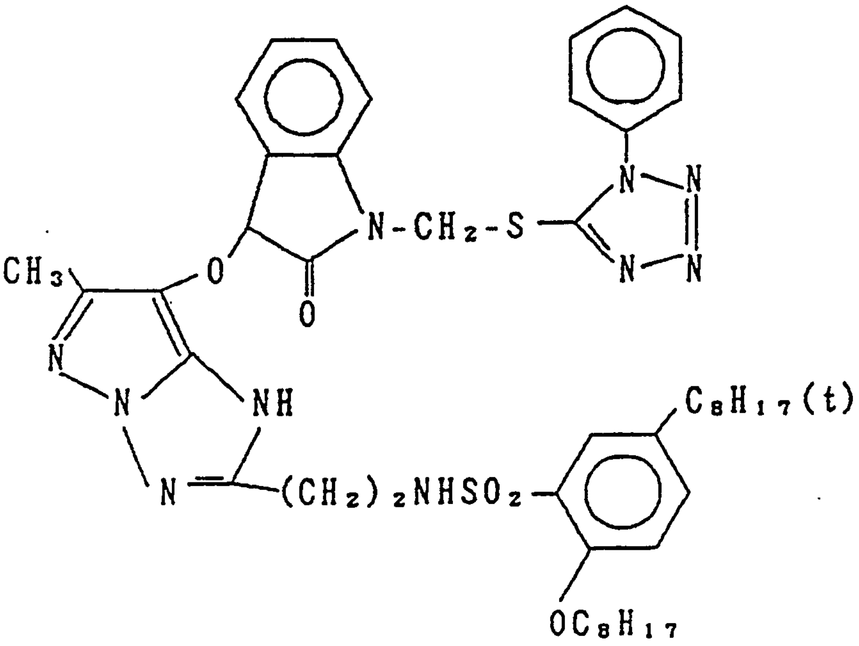


Table 1

Sample No.	Compounds uses in place of E x M-2		MTF Value (25 cycle/mm)	
	Compound	Amount*	Before Storing	After Storing
101 (Comparative Example)	ExM-2 (Comparison Compound 1)	1.0	0.53	0.41
102 (")	Comparison Compound 2	1.2	0.55	0.55
103 (")	Comparison Compound 3	1.1	0.56	0.55
104 (")	Comparison Compound 4	0.9	0.59	0.54
105 (Present Invention)	(1)	0.85	0.64	0.64
106 (")	(4)	1.0	0.61	0.60
107 (")	(5)	0.8	0.60	0.61
108 (")	(9)	0.95	0.63	0.61
109 (")	(10)	0.85	0.61	0.61
110 (")	(13)	0.80	0.63	0.62
111 (")	(14)	0.85	0.61	0.60
112 (")	(25)	0.95	0.61	0.60

* mol ratio when the addition amount of ExM-2 is 1.0

After exposing each sample as described above, the sample was processed by the steps shown below using an automatic processore (until the replenished amount of the processing solution became thrice the volume oft he mother liquid tank).

Processing Steps

Step	Processing Time	Processing Temp.	Replening Amount*	Tank Volume
Color Development	3 min. and 15 sec.	38°C	45 ml	10 liters
Bleach	60 sec.	38°C	20 ml	4 "
Blix	3 min. and 15 sec.	38°C	30 ml	8 "
Wash (1)	40 sec.	35°C	(**)	2 "
Wash (2)	60 sec	35°C	30 ml	4 "
Stabilization	40 sec.	38°C	20 Ml	4 "
Drying	1 min. and 15 sec.	55°C		

(*): The replenishing amount is per sample having 35 mm in width and 1 meter in length.

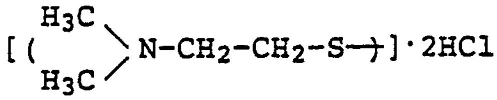
(**): Countercurrent flow system from (2) to (1).

Then, the compositions of the processing solutions used for the aforesaid steps are shown below.

Color Developer	Mother Liquid(g)	Replenisher (g)
Diethylenetriaminepenta Acetic Acid	1.0	1.1

1-Hydroxyethylidene-1,1-diphosphonic Acid	3.0	3.2
Sodium Sulfite	4.0	4.4
Potassium Carbonate	30.0	37.0
Potassium Bromide	1.4	0.7
Potassium Iodide	1.5 mg	-
Hydroxylamine Sulfate	2.4	2.8
4-[N-Ethyl-N-β-hydroxyethylamino]-2-methylaniline Sulfate	4.5	5.5
Water to make	1.0 liter	1.0 liter
pH	10.05	10.10

<u>Bleach Solution</u> The replenisher was same as the mother liquid. (unit g)

Ethylenediaminetetraacetic Acid Ferric Ammonium Dihydrate	120.0
Ethylenediaminetetraacetic Acid Di-sodium Salt	10.0
Ammonium Bromide	100.0
Ammonium Nitrate	10.0
Bleach Accelerator shown by  $[(\mathrm{(H_3C)_2N-CH_2-CH_2-S}-)]\cdot 2\mathrm{HCl}$	0.005 mol
Aqueous Ammonia (27%)	15.0 ml
Water to make	1.0 liter
pH	6.3

<u>Blix Solution</u> The replenisher was same as the mother liquid. (unit g)

Ethylenediaminetetraacetic Acid Ferric Ammonium Dihydrate	50.0
Ethylenediaminetetraacetic Acid Di-Sodium Salt	5.0
Sodium Sulfite	12.0
Aqueous solution (70%) of Ammonium Thiosulfate	240.0 ml
Aqueous ammonia (27%)	6.0 ml
Water to make	1.0 liter
pH	7.2

Wash Water The replenisher was same as the mother liquid.

City water was passed through a mixed bed system column packed with an H-type strong acid cation exchange resin (Amberlite IR-120B, trade name, made by Rohm and Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400, trade name, made by the same company) to reduce the calcium and magnesium ion concentrations below 3 mg/liter and then 20 mg/liter of sodium dichloroisocyanurate and 0.1 g g/liter of sodium sulfate were added to the water. The pH of the wash water was in the range of from 6.5 to 7.5.

Stabilization Solution The replenisher was sale as the mother liquid. (unit g)

Formalin (37%)	2.0 ml
Polyoxyethylene-p-mononomyl Phenyl Ether (mean polymerization degree 10)	0.3
Ethylenediaminetetraacetic Acid Di-Sodium Salt	0.05
Water to make	1.0 liter
pH	0.5-8.0

About each sample thus obtained, the MTF values of 25 magenta color image lines per mm was measured. Furthermore, for the purpose of testing the storage stability of each film, after storing each of Samples 101 to 112 for 3 days under the condition of 45° C and 80%, each sample was exposed and developed by the same manners as described above and then the MTF value was similarly measured.

The results obtained are shown in Table 1 above.

From the results of Table 1, it can be seen that the use of the DIR coupler for use in this invention gives a higher sharpness of the magenta color images than the case of using the comparison compounds and also the reduction of the MTF value with the passage of time is less in the former case. That is, it can be seen that the DIR couplers for use, in this invention give a lage effect of improving the sharpness and shows good heat stability as compared with conventionally known magenta coloring DIR couplers.

Example 2

A multilayer color photographic material having layers of the compositions shown below on an undercoated triacetyl cellulose film support was prepared as Sample 201.

Compositions of Layers

The numerals shown below were the coating amount shown by a g/m^2 unit as silver converted for a silver halide emulsion and colloidal silver, the coating amount shown by a g/m^2 unit for couplers, additives, and gelatin, and the coating amount shown by mol number per mol of silver halide in the same layer for sensitizing dyes. In addition, the marks showing additive are as follows.

UV: Ultraviolet absorbent, Solv: High-boiling organic solvent, ExF: Dye, ExS: Sensitizing dye, ExC: Cyan coupler, ExM: Magenta coupler, ExY: yellow coupler, Cpd: Additive.

Layer 1 Antihalation Layer

Black colloidal silver	0.15
Gelatin	2.33
ExM - 6	0.11
UV - 1	3.0×10^{-2}
UV - 2	6.0×10^{-2}
UV - 3	7.0×10^{-2}

Solv - 1	0.16
Solv - 2	0.10
ExF - 1	1.0 x 10^{-2}
ExF - 2	4.0 x 10^{-2}
ExF - 3	5.0 x 10^{-3}
Cpd - 6	1.0 x 10^{-3}

<u>Layer 2</u> Low-Sensitive Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 4.0 mol%, homogeneous AgI type, sphere-corresponding diameter 0.4 μm, variation coeff. of sphere-corresponding diameter, tabular grains, aspect ratio 3.0)	0.35 (as Ag)
Silver Iodobromide Emulsion (AgI 6.0 mol%, inside high AgI type of core/shell ratio of 1/2, sphere-corresponding diameter 0.45 μm, variation coeff. of sphere-corresponding diameters 23%, tabular grains, aspect ratio 2.0)	0.18 (as Ag)
Gelatin	0.77
ExS - 1	2.4 x 10^{-4}
ExS - 2	1.4 x 10^{-4}
ExS - 5	2.3 x 10^{-4}
ExS - 7	2.3 x 10^{-6}
ExC - 1	0.17
ExC - 2	4.0 x 10^{-2}
ExC - 3	8.0 x 10^{-2}

<u>Layer 3</u> Intermediate-Sensitive Red-Sensitive Layer

Silver Iodobromide Emulsion (AgI 6.0

mol%, inside high AgI type of core/shell ratio of 1/2, sphere-corresponding diameter 0.65 μm, variation coeff. of sphere-corresponding diameters 23%, tabular grains, aspect ratio 2.0)	0.80 (as Ag)
Gelatin	1.46
ExS - 1	2.4×10^{-4}
ExS - 2	1.4×10^{-4}
ExS - 5	2.4×10^{-4}
ExS - 7	4.3×10^{-6}
ExC - 1	0.38
ExC - 2	2.0×10^{-2}
ExC - 3	0.12
ExC - 7	3.0×10^{-2}
UV - 2	5.7×10^{-2}
UV - 3	5.7×10^{-2}

<u>Layer 4</u> High-Sensitive Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 9.3 mol%,multilayer structure grains of core-shell ratio of 3:4:2, AgI contents 24, 0, and 6 mol% from the inside, sphere-corresponding diameter 0.65 μm, variation coeff. of sphere-corresponding diameters 23%, tabular grains, aspect ratio 2.5)	1.49 (as Ag)
Gelatin	1.38
ExS - 1	2.0×10^{-4}
ExS - 2	1.1×10^{-4}
ExS - 5	1.9×10^{-4}
ExC - 7	1.4×10^{-5}

ExC - 1	8.0×10^{-2}
ExC - 4	9.0×10^{-2}
Solv - 1	0.20
Solv - 2	0.53

Layer 5 Interlayer

Gelatin	0.62
Cpd - 1	0.13
Polyethylene Acrylate Latex	8.0×10^{-2}
Solv - 1	8.0×10^{-2}

Layer 6 Low-Sensitive Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 4.0 mol%, homogeneous AgI type, sphere-corresponding diameter 0.33 μm, variation coeff. of sphere-corresponding diameters 37%, tabular grains, aspect ratio 2.0)	0.19 (as Ag)
Gelatin	0.44
ExS - 3	1.5×10^{-4}
ExS - 4	4.4×10^{-4}
ExS - 5	9.2×10^{-5}
ExM - 5	0.19
ExM - 7	3.0×10^{-2}
Solv - 1	0.13
Solv - 4	1.0×10^{-2}

Layer 7 Intermediate-Sensitive Green-Sensitive Layer

Silver Iodobromide Emulsion (AgI 8.0

mol%, homogenous AgI type, sphere-corresponding diameter 0.55 μm, variation coeff. of sphere-corresponding diameters 15%, tabular grains, aspect ratio 4.0)	0.24 (as Ag)
Gelatin	0.54
ExS - 3	2.1×10^{-4}
ExS - 4	6.3×10^{-4}
ExS - 5	1.3×10^{-4}
ExM - 5	0.17
ExM - 7	4.0×10^{-2}
ExY - 8	3.0×10^{-2}
Solv - 1	0.13
Solv - 4	1.0×10^{-2}

<u>Layer 8</u> High-Sensitive Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 10.0 mol%, multilayer structure grains of core-shell ratio of 3 : 4 : 2, AgI contents 24, 0, and 3 mol% from the inside, sphere-corresponding diameter 0.75 μm, variation coeff. of sphere-corresponding diameters 23%, tabular grains, aspect ratio 1.6)	0.49 (as Ag)
Gelatin	0.61
ExS - 4	4.3×10^{-4}
ExS - 5	8.6×10^{-5}
ExS - 8	2.8×10^{-5}
ExM - 5	9.0×10^{-2}
ExM - 6	3.0×10^{-2}
ExY - 8	3.0×10^{-2}

ExC - 1	1.0×10^{-2}
ExC - 4	1.0×10^{-2}
Solv - 1	0.23
Solv - 2	5.0×10^{-2}
Solv - 4	1.0×10^{-2}
Cpd - 8	1.0×10^{-2}

Layer 9 Interlayer

Gelatin	0.56
Cpd - 1	4.0×10^{-2}
Polyethylene Acrylate Latex	5.0×10^{-2}
Solv - 1	3.0×10^{-2}
UV - 4	3.0×10^{-2}
UV - 5	4.0×10^{-2}

Layer 10 Doner Layer Giving Double Layer Effect to Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 9.5 mol%, inside high AgI type of core/shell ratio of 1/2, sphere-corresponding diameter 0.65 μm, variation coeff. of sphere-corresponding diameters, tabular grains, aspect ratio 2.0)	0.67 (as Ag)
Silver Iodobromide Emulsion (AgI 4.0 mol%, homogeneous AgI type, sphere-corresponding diameter 0.4 μm, variation coeff. of sphere-corresponding diameters, tabular grains, aspect ratio 3.0)	0.20 (as Ag)
Gelatin	0.87
ExS - 3	6.7×10^{-4}
ExM - 10	0.18
Solv - 1	0.30

Solv - 6	3.0×10^{-2}

Layer 11 Yellow Filter Layer

Yellow Colloidal Silver	9.0×10^{-2}
Gelatin	0.84
Cpd - 2	0.13
Solv - 1	0.13
Cpd - 1	8.0×10^{-2}
Cpd - 6	2.0×10^{-3}
H - 1	0.25

Layer 12 Low-Sensitive Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 4.5 mol%, homogeneous AgI type, sphere-corresponding diameter 0.7 μm, variation coeff. of sphere-corresponding diameters 15%, tabular grains, aspect ratio 7.0)	0.50 (as Ag)
Silver Iodobromide Emulsion (AgI 3.0 mol%, homogeneous AgI type, sphere-corresponding diameter 0.3 μm, variation coeff. of sphere-corresponding diameters 30%, tabular grains, aspect ratio 7.0)	0.30 (as Ag)
Gelatin	2.18
ExS - 6	9.0×10^{-4}
ExC - 1	0.14
ExY - 9	0.17
ExY - 11	1.09
Solv - 1	0.54

Layer 13 Interlayer

Gelatin	0.40
ExY - 12	0.19
Solv - 1	0.19

Layer 14 High-Sensitive Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI 10.0 mol%, inside high AgI type, sphere-corresponding diameter 1.0 μm, variation coeff. of sphere-corresponding diameters 25%, Multilayer twin tabular grains, aspect ratio 2.0)	0.40 (as Ag)
Gelatin	0.49
ExS - 6	2.6 x 10^{-4}
ExY - 9	1.0 x 10^{-2}
ExY - 11	0.20
ExC - 1	1.0 x 10^{-2}
Solv - 1	9.0 x 10^{-2}

Layer 15 1st Protective Layer

Fine Grain Silver Indobromide Emulsion (AgI 2.0 mol%, homogeneous AgI type, shere-corresponding diameter 0.07 μm)	0.12 (as Ag)
Gelatin	1.63
UV - 4	0.11
UV - 5	0.18
Solv - 5	2.0 x 10^{-2}
Cpd - 5	0.10
Polyethylene Acrylate Latex	9.0 x 10^{-2}

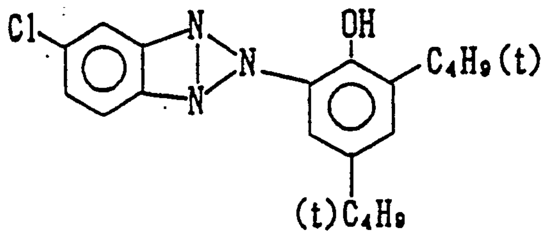
Layer 16 2nd Protective Layer

Fine Grain Silver Indobromide Emulsion (AgI 2.0 mol%, homogeneous AgI type, shere-corresponding diameter 0.07 μm)	0.36 (as Ag)
Gelatin	0.85
B - 1 (diameter 1.5 μm)	8.0×10^{-2}
B - 2 (diameter 1.5 μm)	8.0×10^{-2}
B - 3	2.0×10^{-2}
W - 4	2.0×10^{-2}
H - 1	0.18

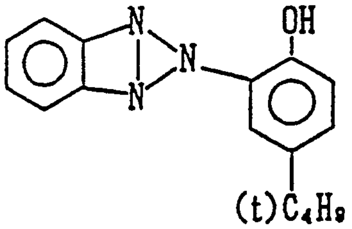
To the sample thus prepared were added 1,2-benzisothiazolon-3-one (in a mean amount of 200 ppm to gelatin), n-butyl-p-hydroxy benzoate (in a mean amount of about 1,000 ppm to gelatin), and 2-phenoxy ethanol (in a mean amount of about 1,000 ppm to gelatin), and 2-phenoxy ethanol (in a mean amount of about 10,000 ppm to gelatin). Furthermore, the sample contained B - 4, B - 5, F - 1, F - 2, F - 3, F - 4, F - 5, F - 6, F - 7, F - 8, F - 9, F - 10, F - 11, F - 12, F - 13, and also an iron salt, a lead salt, a gold salt, a platinum salt, an iridium salt, and a rhodium salt.

The compounds used for the sample are as follows.

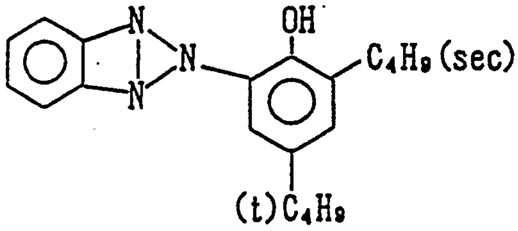
UV－1



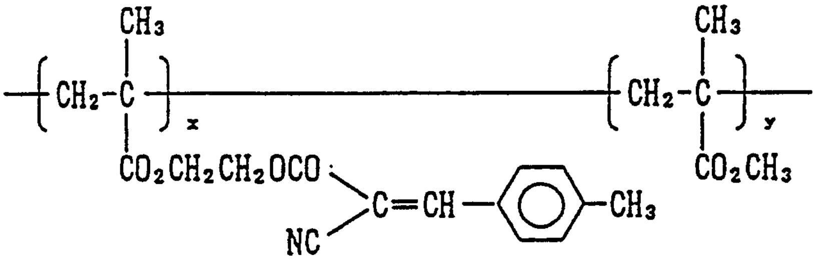
UV－2



UV－3

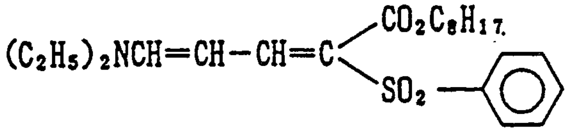


UV－4



x : y＝70 : 30 (wt%)

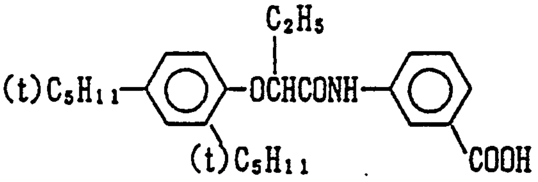
UV-5



Solv-1 Tricresyl phosphate

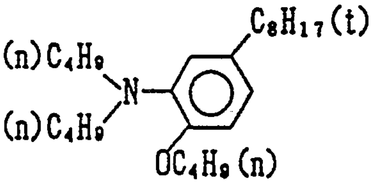
Solv-2 Butyl phthalate

Solv-4

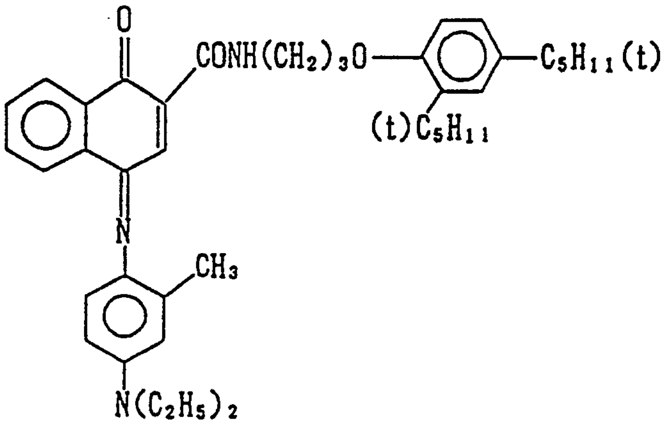


Solv-5 Trihexyl phosphate

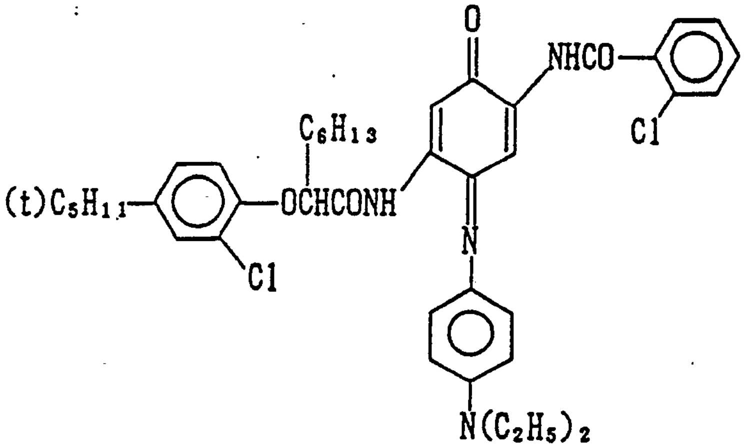
Solv-6



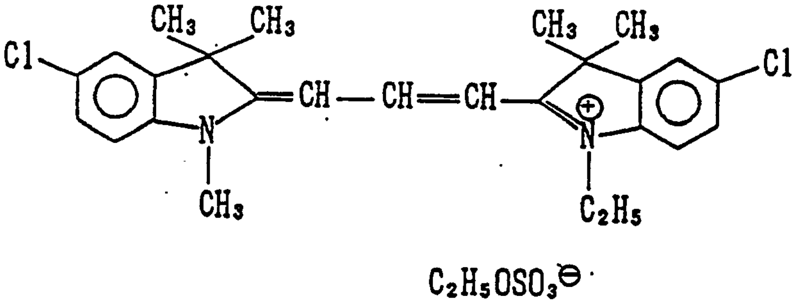
ExF-1



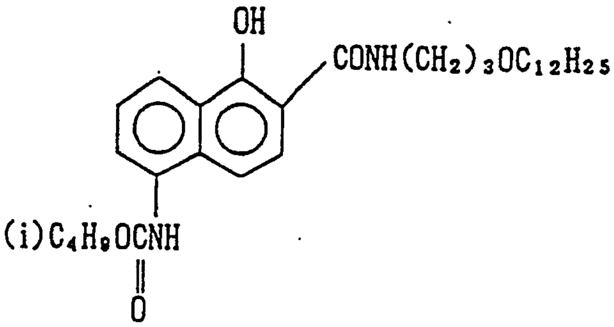
ExF−2



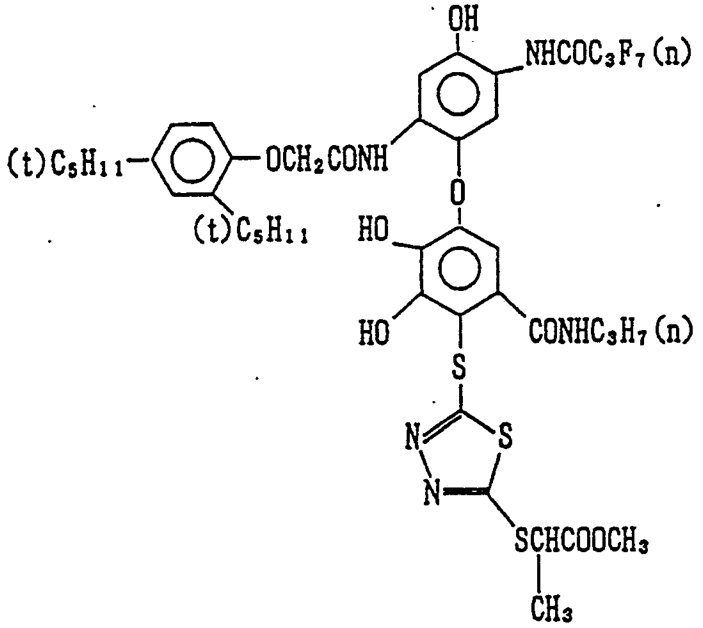
ExF−3



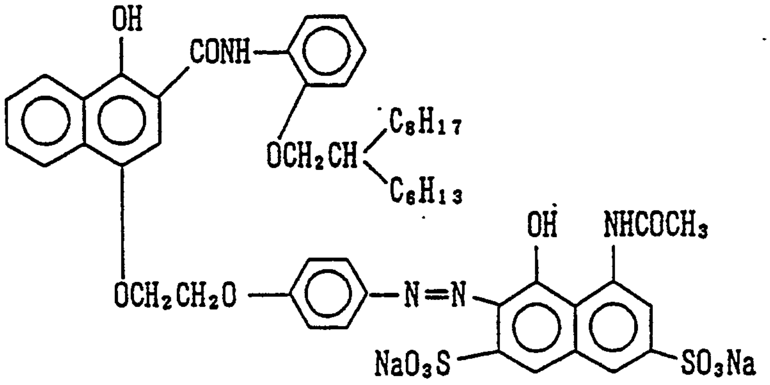
ExC−1



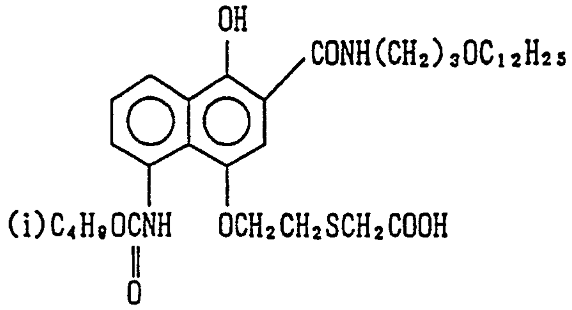
ExC－2



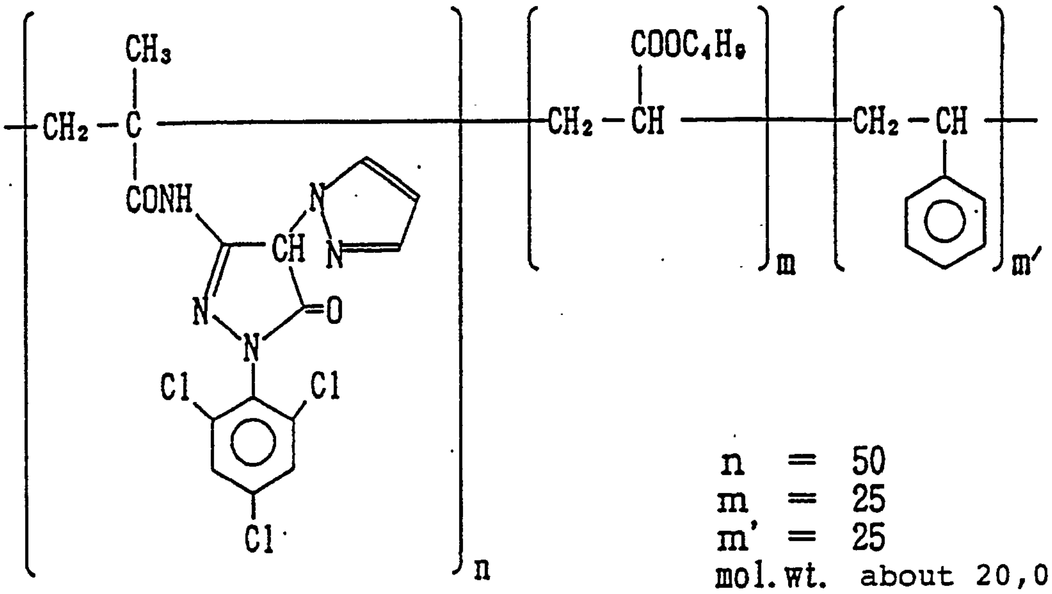
ExC－3



ExC－4

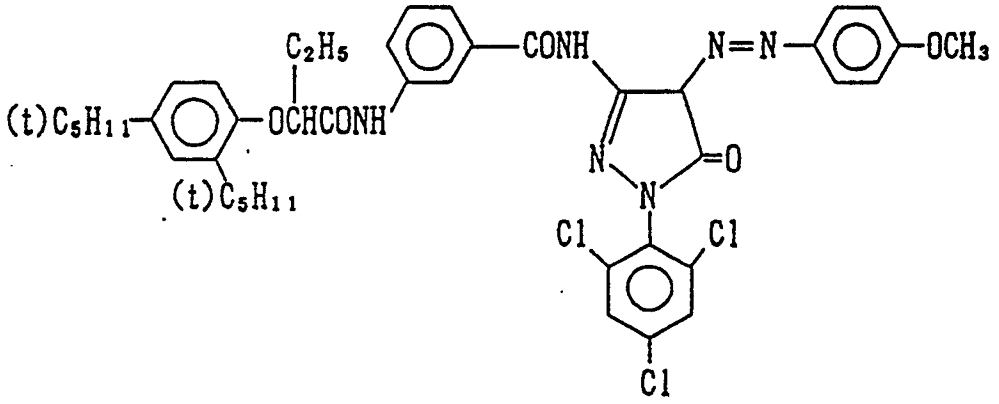


ExM-5

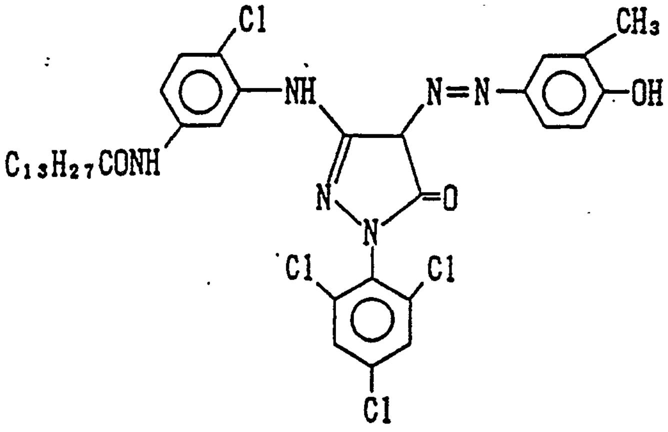


n = 50
m = 25
m' = 25
mol. wt. about 20,000

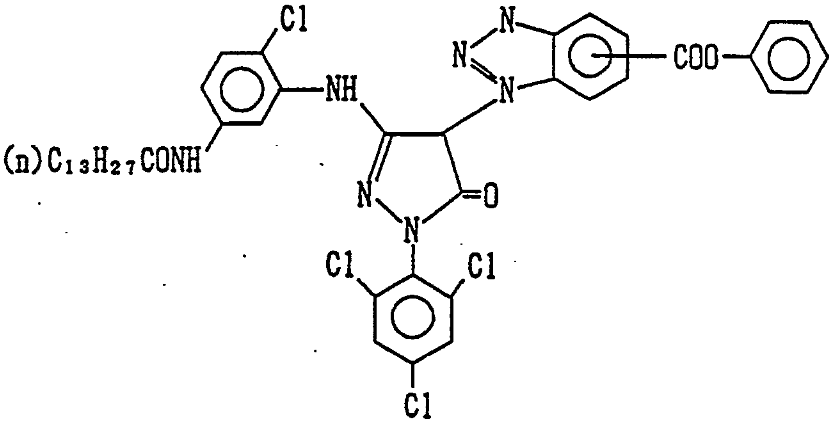
ExM-6



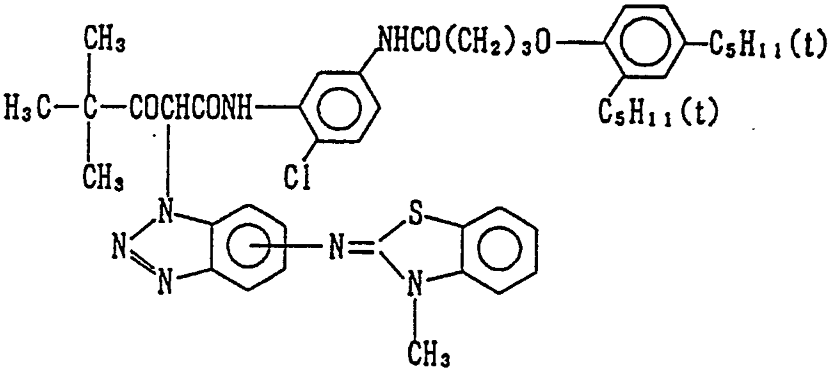
ExM-7



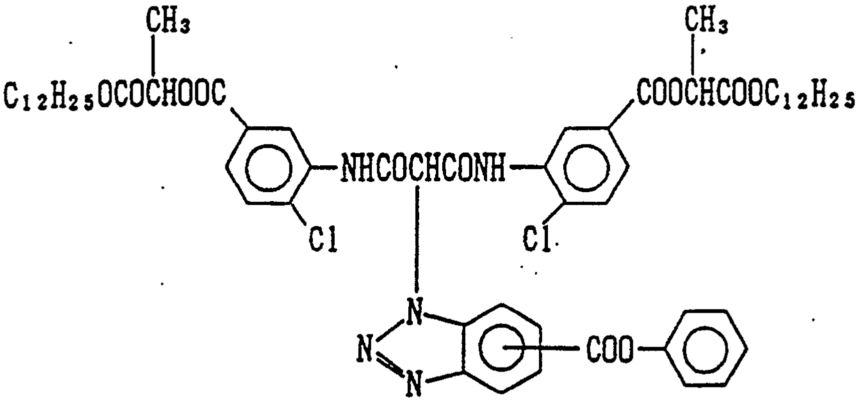
ExM-10 (Comparison Compound -1)



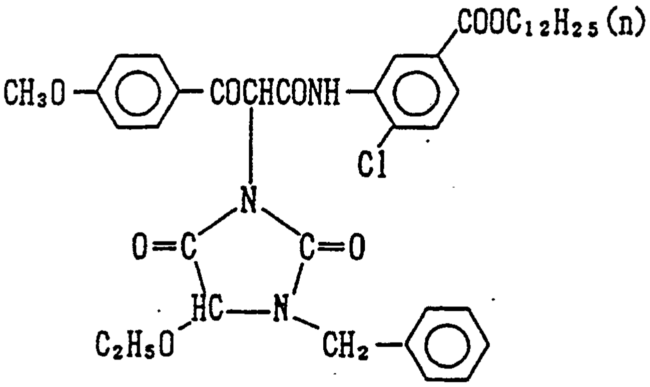
ExY-8



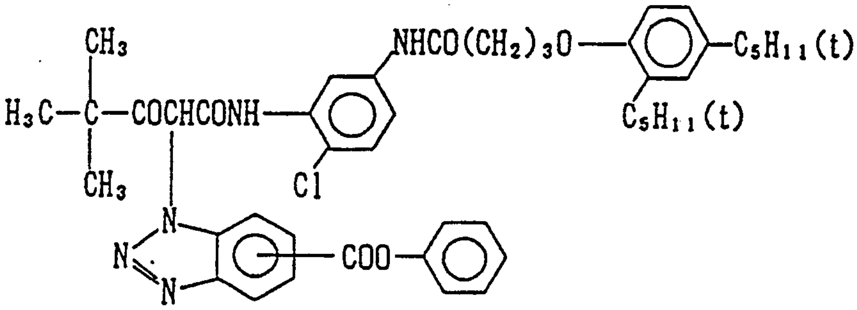
ExY-9



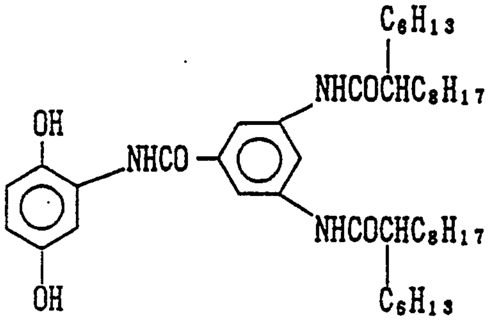
ExY-11



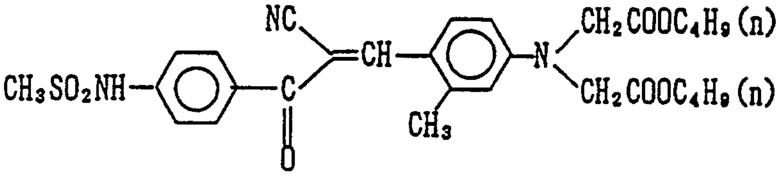
ExY-12



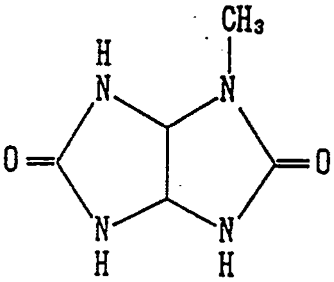
Cpd-1



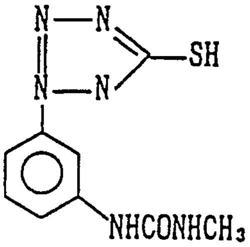
Cpd-2



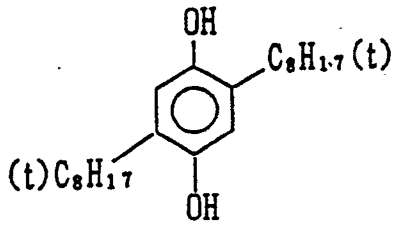
Cpd-5



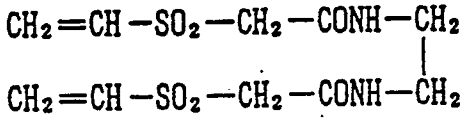
Cpd-6



Cpd-8

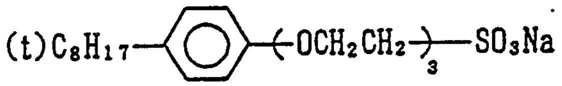


H-1

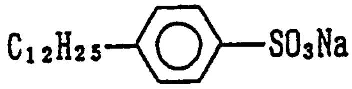


$$\begin{array}{l} CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \\ \hspace{20em}| \\ CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

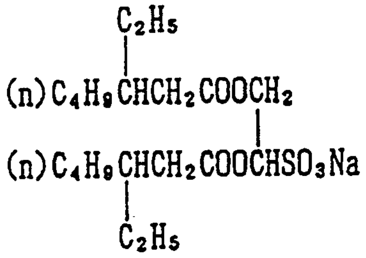
W-1



W-2



W-3

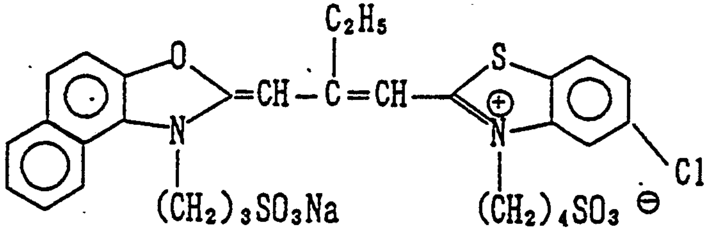


$$\begin{array}{l} \qquad\quad C_2H_5 \\ \qquad\quad | \\ (n)C_4H_9CHCH_2COOCH_2 \\ \qquad\qquad\qquad\quad | \\ (n)C_4H_9CHCH_2COOCHSO_3Na \\ \qquad\quad | \\ \qquad\quad C_2H_5 \end{array}$$

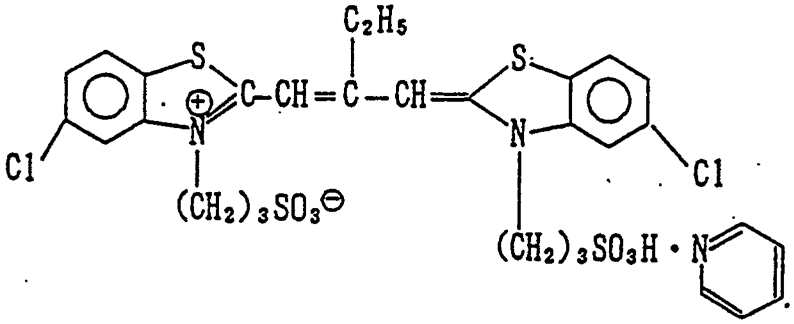
W-4

$C_8F_{17}SO_2N(C_3H_7)CH_2COOK$

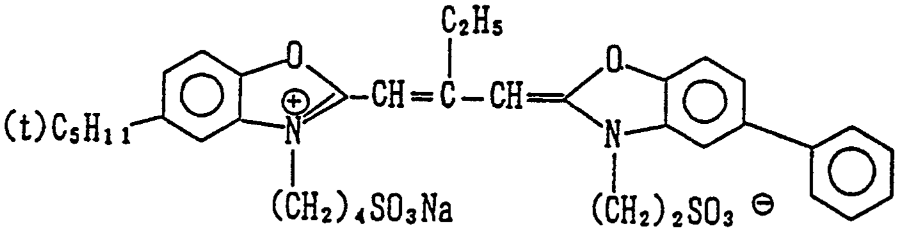
ExS－1



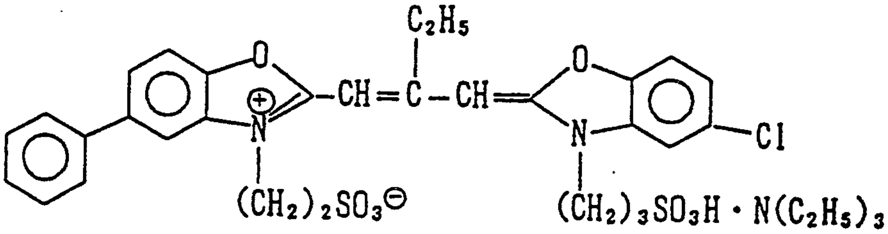
ExS－2



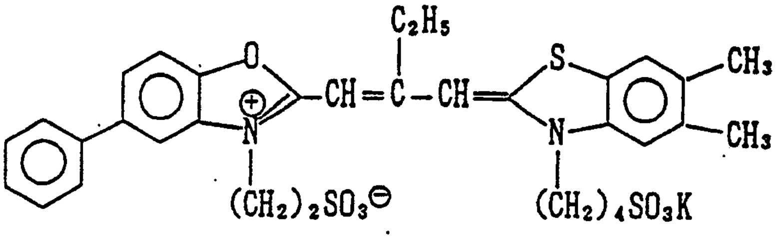
ExS－3



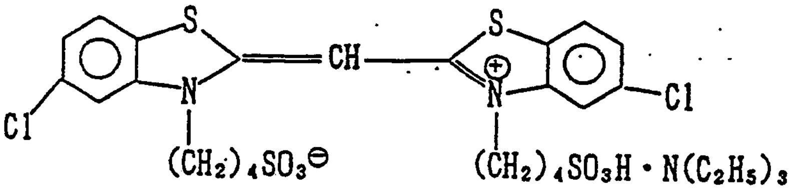
ExS－4



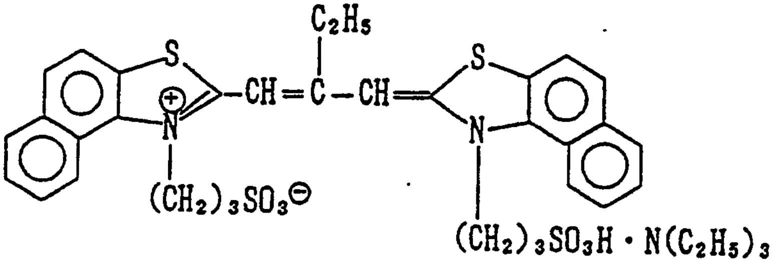
ExS-5



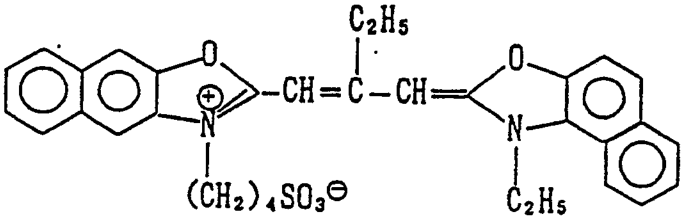
ExS-6



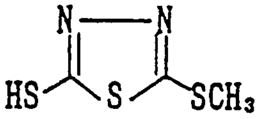
ExS-7



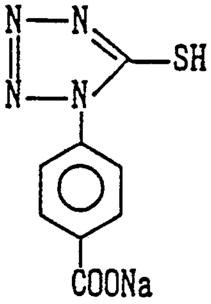
ExS-8



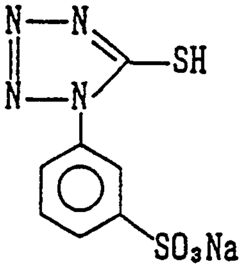
F－1



F－2



F－3



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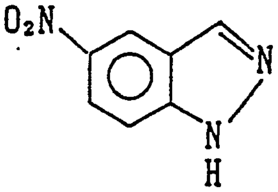
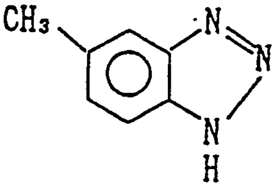
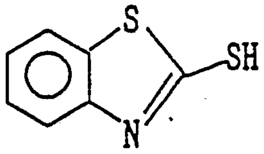


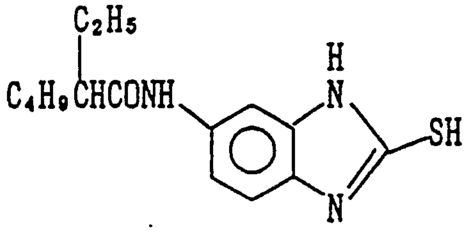
F－5



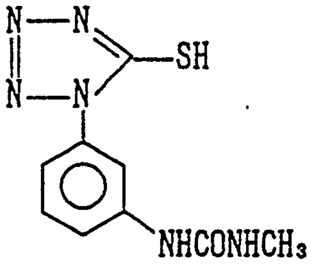
F－6



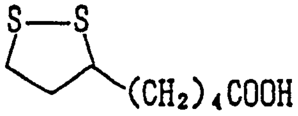
F－7



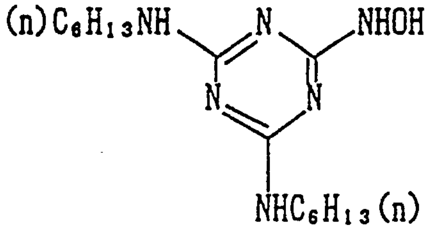
F－8



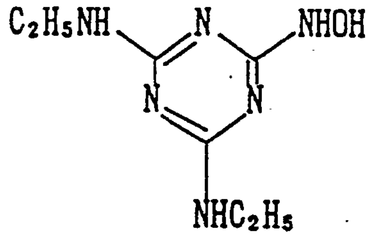
F－9



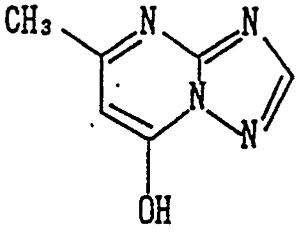
F－10



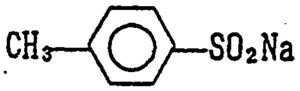
F－1 1



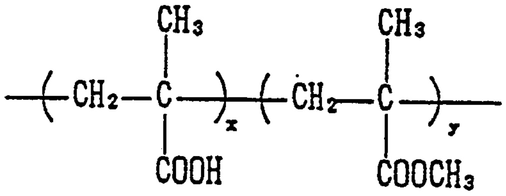
F－1 2



F－1 3



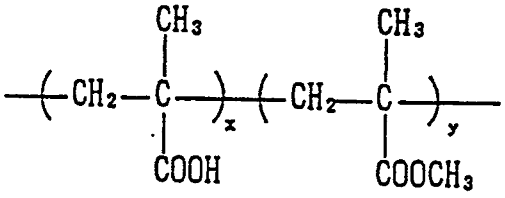
B－1



$$-\left(CH_2-\underset{COOH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_x\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_y-$$

x/y=10/90

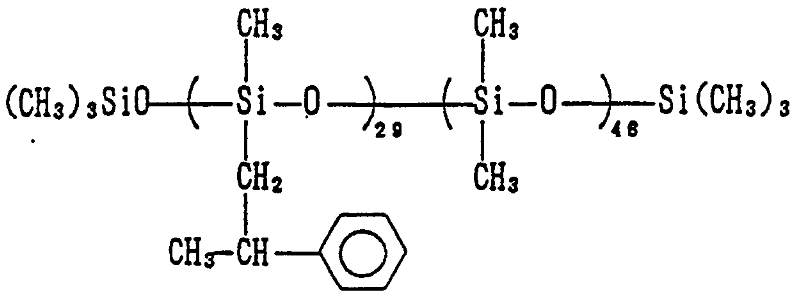
B－2



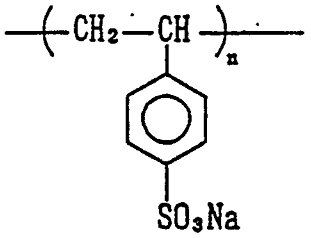
$$-\left(CH_2-\underset{COOH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_x\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_y-$$

x/y=40/60

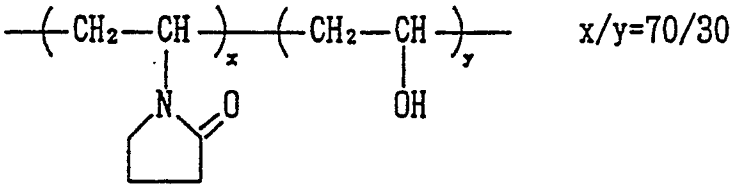
B - 3



B - 4



B - 5

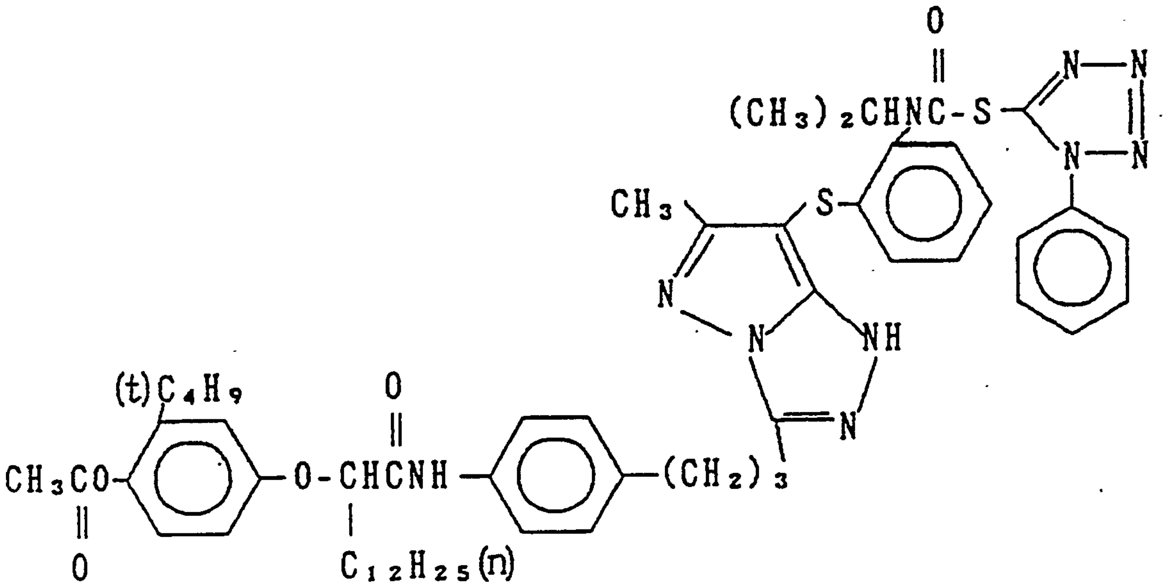


Preparation of Samples 202 to 214

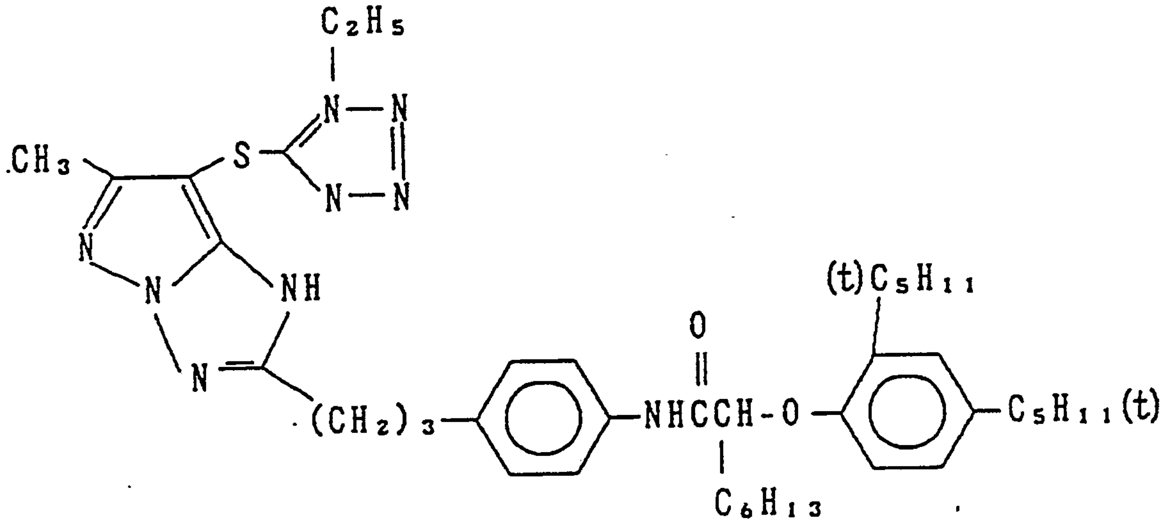
By following the same procedure as the case of preparing Sample 201 except that Coupler ExM - 10 in Layer 10 of Sample 201 was changed as shown in Table 2, Samples 202 to 214 were prepared.

When each of Samples 201 to 214 was wedge exposed to white light with a 3-color separation filter and processed by the processing steps shown below, the sensitivity and the gradation on the magenta color density were almost same for all the samples. The sharpness and the granularity of the magenta image of each sample were evaluated using the MYF value and RMS value.

Comparison Compound 5 (the coupler described in U.S. Patent 4,248,962):



Comparison Compound 6 (the coupler described in JP-A-61-28947):



Comparison Compound 7 (the coupler described in JP-A-62-86361):

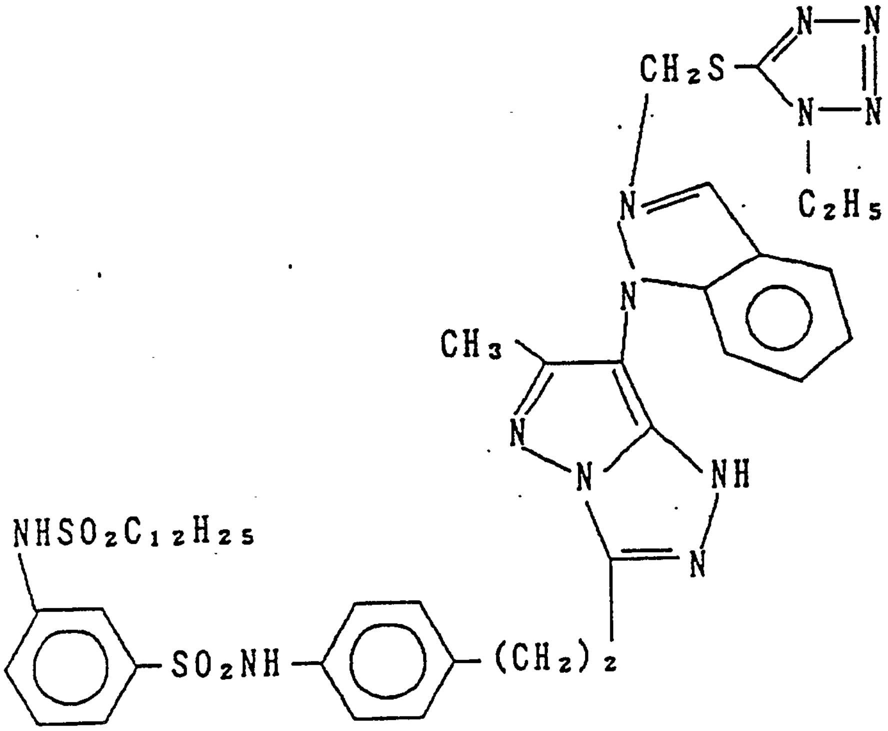

CH₂S
N
N
N
N
C₂H₅
N
N
CH₃
N
N
NH
N
NHSO₂C₁₂H₂₅
SO₂NH
(CH₂)₂

Table 2

Sample No.	Compound uses in place of E x M-10 Compound	Amount*	MTF Value (25 cycle/mm)	RMS Value (x1000) (Density 0.7)	Change of Yellow Density Before & After Storing
201 (Comparative Example)	ExM-10 (Comparison Compound 1)	1.0	0.83	11.5	+0.13
202 (")	Comparison Compound 3	1.1	0.87	11.0	+0.04
203 (")	" 4	0.9	0.90	10.2	+0.08
204 (")	" 5	1.1	0.86	11.2	+0.05
205 (")	" 6	1.2	0.86	11.1	+0.04
206 (")	" 7	1.1	0.88	10.9	+0.05
207 (Present Invention)	(2)	0.8	0.97	9.5	+0.01
208 (")	(6)	0.85	0.94	9.7	+0.02
209 (")	(9)	0.8	0.97	9.5	+0.02

Table 2 (cont'd)

Sample No.	Compound uses in place of E x M-10		MTF Value (25 cycle/mm)	RMS Value (x1000) (Density 0.7)	Change of Yellow Density Before & After Storing
	Compound	Amount*			
210 (Present Invention)	(13)	0.85	0.96	9.6	+0.02
211 (")	(19)	0.8	0.97	9.5	+0.01
212 (")	(26)	0.9	0.95	9.5	+0.02
213 (")	(27)	0.9	0.94	9.8	+0.03
214 (")	(22)	0.85	0.95	9.6	+0.02

* mol ratio when the addition amount of ExM-10 is 1.0

Processing Steps

Step	Processing Time	Processing Temp.
Color Development	3 min. and 15 sec.	38°C
Bleach	6 min. and 30 sec.	38°C
Wash	2 min. and 10 sec.	24°C
Fix	4 min. and 20 sec.	38°C
Wash (1)	65 sec.	24°C
Wash (2)	60 sec.	24°C
Stabilization	65 sec.	38°C
Drying	4 min. 20 sec.	55°C

The compositions of the processing solutions are shown below.

Color Developer	(Unit g)
Diethylenetriaminepentaacetic Acid	1.0
1-Hydroxyethylidene-1,1-diphosphonic Acid	3.0
Sodium Sulfite	4.0
Potassium Carbonate	30.0
Potassium Bromide	1.4
Potassium Iodide	1.5 mg
Hydroxylamine Sulfate	2.4

4-[N-Ethyl-N-β-hydroxyethyl-amino]-2-methylaniline Sulfate	4.5
Water to make	1.0 liter
pH	10.05

Bleach Solution	(unit g)
Ethylenediaminetetraacetic Acid Ferric Ammonium Dihydrate	100.0
Ethylenediaminetetraacetic Acid Di-sodium Salt	10.0
Ammonium Bromide	140.0
Ammonium Nitrate	30.0
Aqueous Ammonia (27%)	6.5 ml
Water to make	1.0 liter
pH	6.0

Fix Solution	(unit g)
Ethylenediaminetetraacetic Acid Di-sodium Salt	0.5
Sodium Sulfite	7.0
Sodium bisulfite	5.0
Aqueous solution (70%) of Ammonium Thiosulfate	170.0 ml
Water to make	1.0 liter
pH	6.7

Stabilization Solution	(unit g)
Formalin (37%)	2.0 ml
Polyoxyethylene-p-mononomyl Phenyl Ether (mean polymerization degree 10)	0.3

Ethylenediaminetetraacetic Acid Di-Sodium Salt	0.05
Water to make	1.0 liter
pH	0.5-8.0

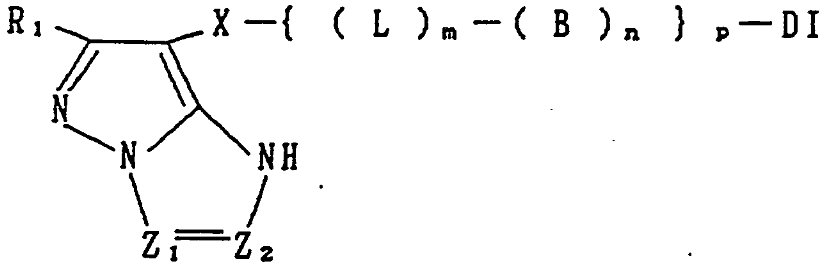
On each of the samples obtained, the MTF value of 25 magenta color image lines per 1 mm and the RMS value at a density of 0.7 were measured. Furthermore, for the purpose of testing the storage stability of each film after processing, after the wedge exposure to white light, the change of the stain density (yellow density) at the fogged portion of the same before and after storing each sample for 14 days at 60° C 70% RH was measured. The results are shown in Table 2 above.

From the results shown in Table 2, it can be seen that the use of the DIR couplers of this invention gives a large effect of improving the sharpness and granularity as compared with the case of using the conventionally known magenta coloring DIR couplers. Also, in the samples using the DIR couplers of this invention, the increase of the yellow density (stain) at the fogged portions in the case of storing the samples for 14 days under the condition of 60° C and 70% RH is less because of the high heat stability of the couplers of this invention.

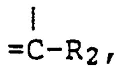
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide color photographic material having at least one silver halide emulsion layer on a support, wherein said emulsion layer contains a development inhibitor-releasing coupler represented by following formula (I);

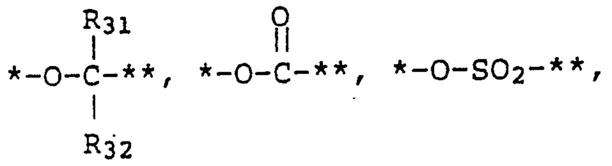


wherein R_1 represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxy group, a nitro group, a carboxy group, an amino group, an alkoxy group, an aryloxy group, an acylamino group, an alkylamino group, an anilino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a sulfonyl group, a phosphinyl group, an aryloxycarbonyl group, an aryl group and when R_1 is a divalent group, the coupler may form a bispcompound at the divalent group; Z_1 and Z_2 each represents a nitrogen atom or $=C\text{-}R_2$ (wherein R_2 has the same meaning as R_1) and when Z_1 and Z_2 are both

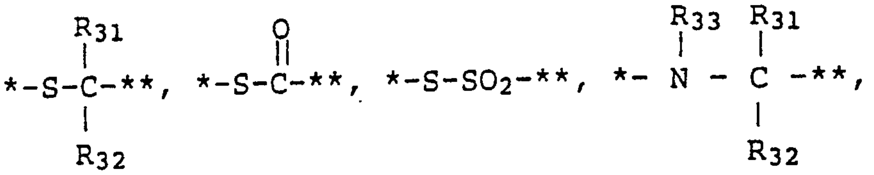


$$\overset{|}{=C}\text{-}R_2,$$

two R_2s may be the same or different; X represents

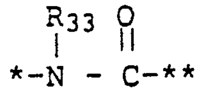


$$*\text{-O-}\underset{R_{32}}{\overset{R_{31}}{C}}\text{-}**,\quad *\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}**,\quad *\text{-O-SO}_2\text{-}**,$$



$$*\text{-S-}\underset{R_{32}}{\overset{R_{31}}{C}}\text{-}**,\quad *\text{-S-}\overset{O}{\overset{\|}{C}}\text{-}**,\quad *\text{-S-SO}_2\text{-}**,\quad *\text{-}\overset{R_{33}}{N}\text{-}\underset{R_{32}}{\overset{R_{31}}{C}}\text{-}**,$$

or



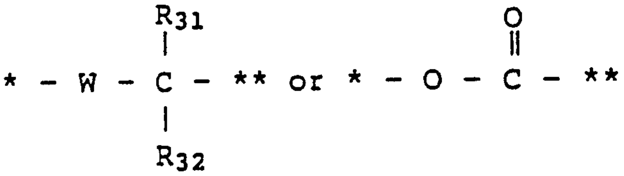
$$*\text{-}\overset{R_{33}}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}**$$

(wherein * represents a group bonding to the left side of X; ** represents a group bonding to the right side of X; R_{31} and R_{32} have the same meaning as R_1; and R_{33} represents an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfonyl group, or a sulfamoyl group); L represents a group of cleaving the bond of the right side [the bond to $(B)_m$] after cleaving the left side of L; B represents a group of cleaving the bond at the right side of B by reacting with the oxidation product of a color developing agent; DI represents a development inhibitor; m and n each represents 0 or 1 with the exclusion that m and n are simultaneously 0; and p represents 1 or 2 and when p is 2, two $[(L)_m\text{-}(B)n]$s maybe the same or different.

2. The silverhalide color photographic material of claim 1, wherein $\text{-X-}\{(L)_m\text{-}(B)n\}_p\text{-DI}$ of the development releasing coupler shown by formula (I) is represented by following formula

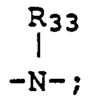
$\text{- }X_1\text{ - }L_1\text{ - DI}$ (VII)

wherein X_1 represents



$$*\text{ - W - }\underset{R_{32}}{\overset{R_{31}}{C}}\text{ - }**\ \text{or}\ *\text{ - O - }\overset{O}{\overset{\|}{C}}\text{ - }**$$

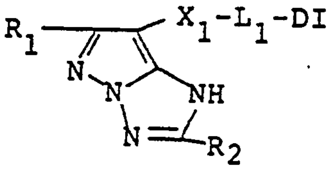
(wherein W represents an oxygen atom, a sulfur atom,
or



$$\overset{R_{33}}{\text{-N-}};$$

L_1 represents a group releasing DI by an electron transfer along a conjugated system; and DI R_{31}, R_{32}, and R_{33} in claim 1).

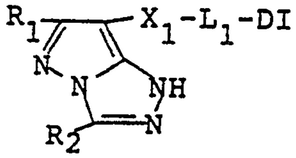
3. A silver halide color photographic material of claim 1, wherein said development inhibitor-releasing coupler is represented by formula (VIII);



(VIII)

wherein X_1 and L_1 represent the same as in claim 2, and R_1 and R_2 represent the same as in claim 1.

4. A silver halide color photographic material of claim 1, wherein said development inhibitor-releasing coupler is represented by formula (IX);



(IX)

wherein X_1 and L_1 represent the same as in claim 2 and R_1 and R_2 represent the same as in claim 1.