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71 Applicant: **FUJI PHOTO FILM CO., LTD.**  
**210 Nakanuma Minamiashigara-shi**  
**Kanagawa-ken, 250-01(JP)**

72 Inventor: **Yasuhiro, Shimada Fuji Photo Film**  
**Co., Ltd.**  
**No. 210 Nakanuma**  
**Minami Ashigara-shi Kanagawa-ken(JP)**  
Inventor: **Selji, Ichijima Fuji Photo Film Co.,**  
**Ltd.**  
**No. 210 Nakanuma**  
**Minami Ashigara-shi Kanagawa-ken(JP)**  
Inventor: **Yoshio, Ishii Fuji Photo Film Co.,**  
**Ltd.**  
**No. 210 Nakanuma**  
**Minami Ashigara-shi Kanagawa-ken(JP)**

74 Representative: **Hansen, Bernd, Dr.rer.nat. et**  
**al**  
**Hoffmann, Eitle & Partner Patentanwälte**  
**Arabellastrasse 4 Postfach 81 04 20**  
**D-8000 München 81(DE)**

54 **Silver halide color photographic material.**

57 There is provided a silver halide color photographic material which contains a novel DIR coupler. The silver halide color photographic material has the effects of a dye produced by coupling with the oxidized product of a color developing agent being sufficiently fast, of not contaminating a development processing solution, and providing a highly sensitive color photographic image excellent in sharpness and color reproduction.

**EP 0 336 411 A2**

## SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a color photographic material excellent in sharpness and color reproduction quality.

BACKGROUND OF THE INVENTION

Hitherto, many studies have been made to improve the sharpness and the color reproduction quality of color photographic materials. One of the techniques is the development of couplers capable of releasing a development retarder (called DIR couplers). For example, DIR couplers described, for example, in U.S. Patent Nos. 3,227,554, 3,701,783, 3,615,506, and 3,617,291, and JP-A ("JP-A" means unexamined published Japanese patent application) No. 82423/1987 are known. In these couplers, the development retarder released at the time of color development diffuses from the photographic material into the processing solution and accumulates in the processing solution, which brings about a problem that the processing solution exhibits a development-retarding effect. To obviate this problem, such DIR couplers are required that can be decomposed into a substantially photographically noninfluential compound after flowing into the color-development processing solution. Examples of such DIR couplers are described, for example, in U.S. Patent No. 4,477,563. These couplers were couplers that indeed did not contaminate a color-developing solution and were suitable for a process wherein the color-development processing solution was continuously used repeatedly. In particular, malondianilide couplers, described in U.S. Patent No. 4,477,563 mentioned above, have been used as DIR couplers because their coupling activity is high. However, their use is accompanied by the defect that the color image obtained from a malondianilide coupler is weakly resistant to humidity and heat. Particularly, if the amount of the DIR coupler to be added is increased, the color image obtained from the DIR coupler is required to be fast enough to retain the image density.

BRIEF SUMMARY OF THE INVENTION

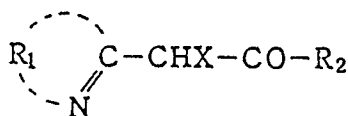
Therefore, the object of the present invention is to provide a highly sensitive color photographic material excellent in sharpness and color reproduction quality which contains a novel DIR coupler, whose dye produced by coupling with the oxidized product of a color-developing agent is sufficiently fast, and which will not contaminate development processing solutions.

Other and further objects, features, and advantages of the invention will appear more fully from the following description.

DETAILED DESCRIPTION OF THE INVENTION

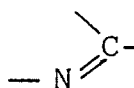
The above objects have been attained by a silver halide color photographic material wherein a compound represented by the formula (I) given below is contained in at least one hydrophilic colloid layer formed on a support.

Formula (I)



wherein  $R_1$  represents a group of non-metallic atoms required to form a heterocyclic group together with the

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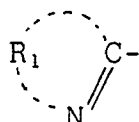


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residue,  $R_2$  represents an organic residue, and  $X$  represents a group of such a nature that when the compound reacts with the oxidized product of an aromatic primary amine developing agent,  $X$  splits off to act as a development retarder or a development retarder precursor that will be decomposed into a substantially photographically noninfluential compound after flowing into the color-developing solution.

Couplers represented by formula (I) used in the present invention will now be described further in detail. In formula (I), the heterocyclic group represented by

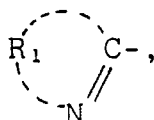
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contains at least one nitrogen atom, with all the remaining atoms forming the ring being carbon atoms, several (for example one or two) of which may be replaced with hetero atoms, such as nitrogen atoms, oxygen atoms, or sulfur atoms. The thus formed basic heterocyclic group is preferably a 5- to 7-membered group. The heterocyclic group may have substituents or other condensed ring. These condensed rings may

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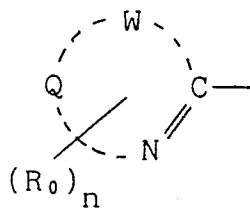
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preferable ones are group represented by formula (IIa), (IIb), (IIc), (IIId):

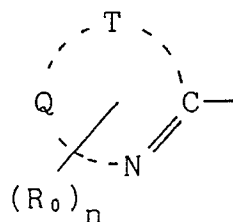
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Formula (IIa)

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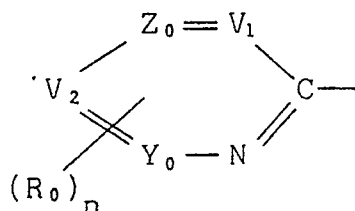
Formula (IIb)



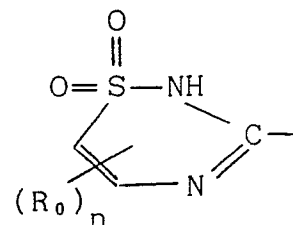
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Formula (IIc)

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Formula (IIId)



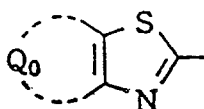
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wherein  $W$  represents  $N$ ,  $O$ , or  $S$ ;  $Q$  represents a group of nonmetallic atoms which form a 5- to 7-membered ring together with  $W$  and  $-N=C$ ;  $R_0$  represents a substituent;  $n$  is an integer of 0 to 2;  $T$  represents a carbonyl group or a sulfonyl group,  $T$ ,  $Q$ , and  $-N=C$  together form a 5- to 7-membered ring;

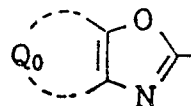
at least one of  $Y_0$  and  $Z_0$  represents N, otherwise being C;  $V_1$  and  $V_2$  each represent N or C; and when n is 2, two  $R_0$ 's each may be the same or different, including either to form a ring together or not to form a ring. The substituent represented by  $R_0$  can be mentioned include, for example, a halogen atom, an acyloxy group, a sulfonyloxy group, an alkyl group, a nitro group, a cyano group, an acylamino group, and sulfonamido group. When two of  $R_0$ 's together combine to form a ring, which represents a substituted or unsubstituted benzene ring or a substituted or unsubstituted heterocyclic group.

Further, particularly preferable rings are rings represented by formula (III), (IV), (V), (VI), (VII), and (VIII):

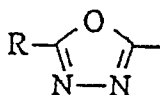
Formula (III)



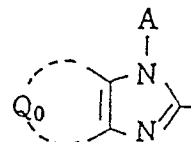
Formula (IV)



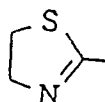
Formula (V)



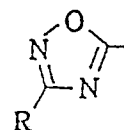
Formula (VI)



Formula (VII)

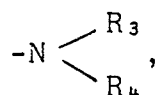


Formula (VIII)



wherein  $Q_0$  represents an substituted or unsubstituted 1,2-condensed benzene ring, A represents a hydrogen atom, a monovalent group e.g., {alkyl, alkoxyalkyl (e.g., methoxyethyl and propoxyethyl) or halogenoalkyl (e.g., chloroethyl and bromopropyl) having preferably 1 to 20 carbon atoms, aralkyl (e.g., benzyl and phenethyl) having preferably 7 to 20 carbon atoms; or an aryl (e.g., phenyl, and a substituted phenyl, such as tosyl and chlorophenyl) having preferably 6 to 20 carbon atoms}, and R represents a hydrogen atom, or a substituent, such as an alkyl group having preferably 1 to 20 carbon atoms (e.g., methyl, ethyl, and dodecyl), an aryl group having preferably 6 to 20 carbon atoms (e.g., phenyl and o-methylphenyl), a halogen atom (e.g., chlorine and fluorine), an alkoxy group having preferably 1 to 20 carbon atoms (e.g., methoxy and ethoxy), an acylamino group having preferably 2 to 20 carbon atoms (e.g., benzamido and pivalylamido), or an alkylthio group having preferably 1 to 20 carbon atoms (e.g., methylthio and dodecylthio).

$R_2$  in formula (I) represents an organic residue, which herein stands for a straight-chain or branched, or chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group (preferably having 1 to 30 carbon atoms, e.g., methyl, propyl, t-butyl, trifluoromethyl, tridecyl, 3-(2,4-di-t-amyloxy)propyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonyl, cyclopentyl and benzyl), an aryl group (preferably having 6 to 30 carbon atoms, e.g., phenyl, 4-t-butylphenyl and 4-tetradecanamidophenyl), a heterocyclic group (preferably a 5- to 7-membered ring, e.g., 2-furyl, 2-thienyl, 2-pyrimidyl, and 2-benzothiazolyl), an alkoxy group (preferably having 1 to 30 carbon atoms, e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecyloxyethoxy, and 2-methanesulfonylethoxy), an aryloxy group (preferably having 6 to 30 carbon atoms, e.g., phenoxy, 2-methylphenoxy, and 4-t-butylphenoxy), a heterocyclic oxy group (preferably a 5- to 7-membered ring, e.g., 2-benzimidazolyl, or a group



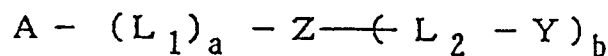
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in which  $R_3$  and  $R_4$  each represent an aliphatic group, an aromatic group, a hydrogen atom, or a heterocyclic group. The aliphatic group represented by  $R_3$  and  $R_4$  may be straight-chain or branched, or chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group preferably having 1 to 30 carbon atoms, such as methyl, propyl, isoamyl, trifluoromethyl, 3-(2,4-di-*t*-amylphenoxy)propyl, 2-dodecyloxyethyl, 3-phenoxypropyl, and benzyl. The aromatic group represented by  $R_3$  and  $R_4$  includes a substituted or unsubstituted phenyl group, whose substituent includes a halogen atom (e.g., fluorine, chlorine and bromine), a straight-chain or branched, or chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group (e.g., methyl, propyl, *t*-butyl, trifluoromethyl, tridecyl, 3-(2,4-di-*t*-amylphenoxy)propyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonylethyl, cyclopentyl, and benzyl), an aryl group (e.g., phenyl, 4-*t*-butylphenyl, and 4-tetradecaneamidophenyl), a heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pyrimidyl, and 2-benzothiazolyl), a cyano group, an alkoxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecyloxyethoxy, and 2-methanesulfonylethoxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, and 4-*t*-butylphenoxy), a heterocyclic oxy group (e.g., 2-benzimidazolyl), an acyloxy group (e.g., acetoxy and hexadecanoyloxy), a carbamoyloxy group (e.g., *N*-ethylcarbamoyloxy), a silyloxy group (e.g., trimethylsilyloxy), a sulfonyloxy group (e.g., dodecylsulfonyloxy), an acylamino group (e.g., acetamido, benzamido, tetradecaneamido,  $\alpha$ -(2,4-di-*t*-amylphenoxy)butylamido, 2,4-di-*t*-amylphenoxyacetamido,  $\alpha$ -{4-(4-hydroxyphenylsulfonyl)phenoxy}decaneamido, and isopentadecaneamido), an anilino group (e.g., phenylamino, 2-chloroanilino, 2-chloro-5-tetradecaneamidoanilino, 2-chloro-5-dodecyloxycarbonylanilino, *N*-acetylanilino, and 2-chloro-5-{ $\alpha$ -(2-*t*-butyl-4-hydroxyphenoxy)dodecaneamido} anilino), a ureido group (e.g., phenylureido, methylureido, and *N,N*-dibutylureido), an imido group (e.g., *N*-succinimido, 3-benzylhydantoinyl, and 4-(2-ethylhexanoylamino)phthalimido), a sulfamoylamino group (e.g., *N,N*-dipropylsulfamoylamino and *N*-methyl-*N*-decylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, and 3-(4-*t*-butylphenoxy)propylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-*t*-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, and 4-tetradecaneamidophenylthio), a heterocyclic thio group (e.g., 2-benzothiazolylthio), an alkoxycarbonylamino group (e.g., methoxycarbonylamino and tetradecyloxycarbonylamino), an aryloxycarbonylamino group (e.g., phenoxy carbonylamino and 2,4-di-*tert*-butylphenoxy carbonylamino), a sulfonamido group (e.g., methanesulfonamido, hexadecane-sulfonamido, benzenesulfonamido, *p*-toluenesulfonamido, octadecanesulfonamido, and 2-methoxy-5-*t*-butylbenzenesulfonamido), a carbamoyl group (e.g., *N*-ethylcarbamoyl, *N,N*-dibutylcarbamoyl, *N*-(2-dodecyloxyethyl)carbamoyl, *N*-methyl-*N*-dodecylcarbamoyl, and *N*-{3-2,4-di-*tert*-amylphenoxy}propyl}carbamoyl), an acyl group (e.g., acetyl, (2,4-di-*tert*-amylphenoxy)acetyl, and benzoyl), a sulfamoyl group (e.g., *N*-ethylsulfamoyl, *N,N*-dipropylsulfamoyl, *N*-(2-dodecyloxyethyl)sulfamoyl, *N*-ethyl-*N*-dodecylsulfamoyl, and *N,N*-diethylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, and toluenesulfonyl), a sulfinyl group (e.g., octanesulfinyl, dodecylsulfinyl, and phenylsulfinyl), an alkoxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl, dodecylcarbonyl, and octadecylcarbonyl), and an aryloxycarbonyl group (e.g., phenyloxycarbonyl and 3-pentadecyloxycarbonyl).

The heterocyclic group represented by  $R_3$  and  $R_4$  is preferably a 5- to 6-membered ring whose hetero atom is, for example, nitrogen, oxygen, or sulfur, and which preferably contains 1 to 25 carbon atoms and may have a substituent (e.g., an alkyl, such as methyl, isopropyl, and octyl; alkoxy, such as methoxy, isopropoxy and, octoxy; and an alkoxycarbonyl, such as methoxycarbonyl, ethoxycarbonyl, and octoxycarbonyl).

In formula (I), preferably X is represented by formula (IX) in which X is linked to a coupler residue A:

Formula (IX)



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wherein A represents a coupler component excluding X in formula (I), Z represents a basic part of a compound that exhibits a development-retarding effect and is linked to the coupling position of the coupler

directly (when  $a = 0$ ), or through a linking group  $L_1$  (when  $a = 1$ ), Y is linked to Z through a linking group  $L_2$ , and represents a substituent that will cause the development-retarding effect of Z to be exhibited, the linking group represented by  $L_2$  includes a chemical bond that will be severed in the developing solution,  $a$  is 0 or 1,  $b$  is 1 or 2, and when  $b$  is 2,  $-L_2-Y$ 's may be the same or different.

5 The compound represented by formula (IX) will release  $^{\ominus}Z-(L_2-Y)_b$  or  $^{\ominus}L_1-Z-(L_2-Y)_b$  after it is coupled with the oxidized product of a color-developing agent.  $L_1$  in the  $^{\ominus}L_1-Z-(L_2-Y)_b$  will immediately split off, and  $^{\ominus}Z-(L_2-Y)_b$  is formed. The  $^{\ominus}Z-(L_2-Y)_b$  diffuses in the photosensitive layer while exhibiting a development-retarding effect, and part of it flows into the color-development processing solution. The  $^{\ominus}Z-(L_2-Y)$  that has  
 10 flowed into the processing solution decomposes quickly at the chemical bond part in  $L_2$ , that is, the linkage between Z and Y is cleaved, leaving in the developing solution a compound wherein a water-soluble group is attached to Z and whose developing-retarding property is low. Hence the development-retarding effect substantially disappears.

As a result, a compound having a development-retarding effect will not accumulate in the processing solution. Accordingly not only has it become possible to repeatedly reuse the processing solution, it has  
 15 also become possible to allow an adequate amount of a DIR coupler to be contained in a photographic material.

As the basic part of the development retarder represented by Z can be mentioned a divalent nitrogen-containing heterocyclic group or nitrogen-containing heterocyclic thio group, such as a tetrazolylthio group, a benzthiazolylthio group, a benzimidazolylthio group, a thiadiazolylthio group, an oxadiazolylthio group, a  
 20 triazolylthio group, and an imidazolylthio group. Examples are shown below in the formulae connecting with  $A-(L_1)_a$ - group and  $-(L_2-Y)_b$  group.

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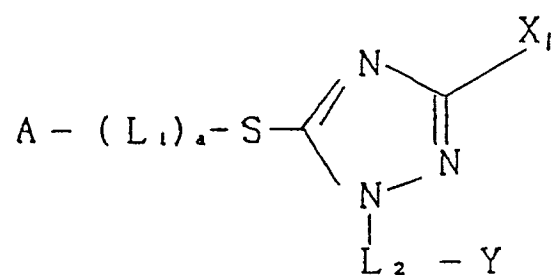
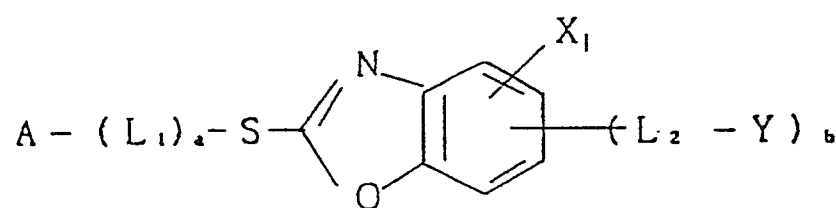
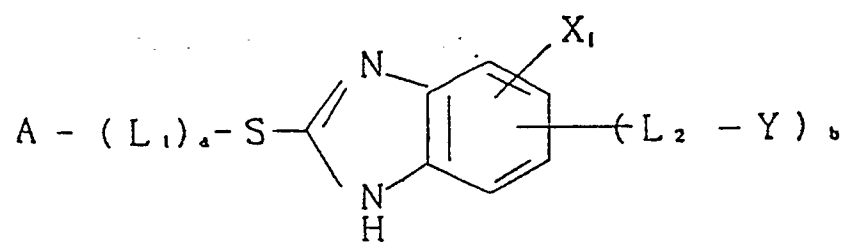
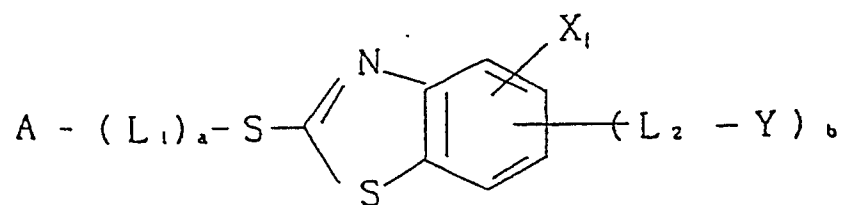
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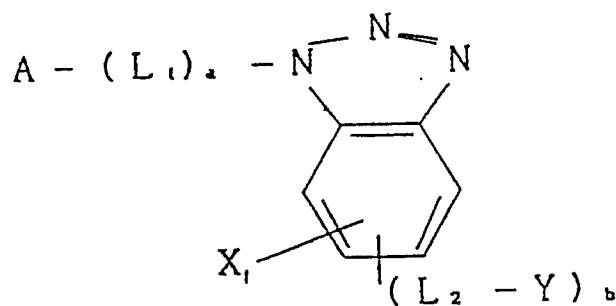
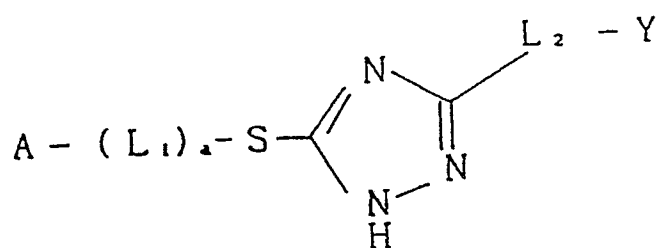
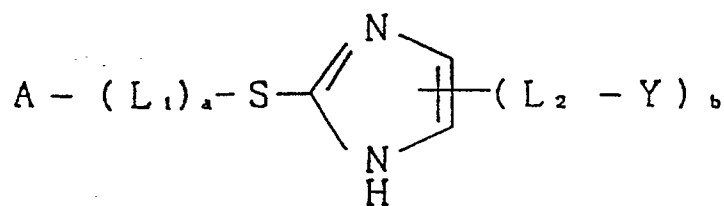
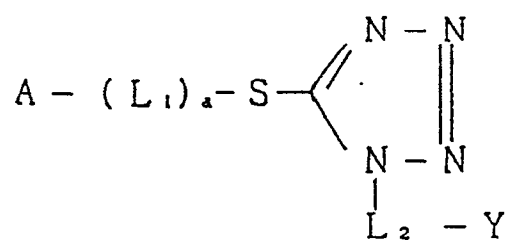
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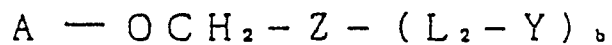




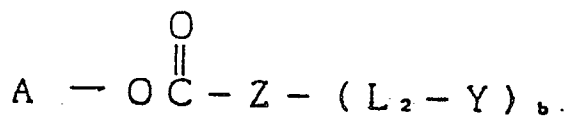
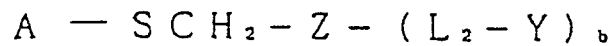
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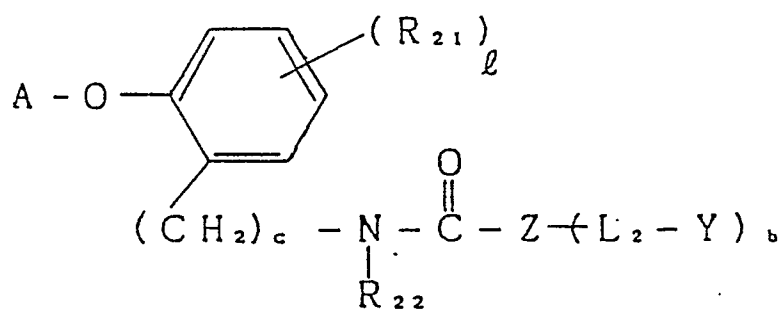
As the linking group represented by L in formula (IX) can be mentioned, for example, the following,



(linking group described in  
U.S. Patent No. 4,146,396)

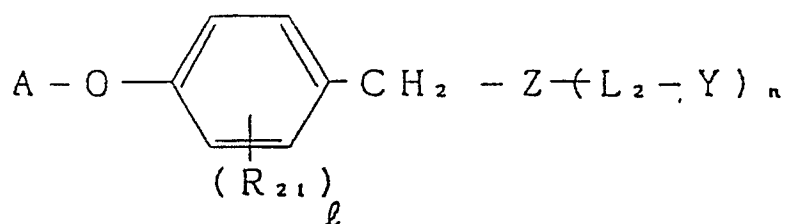
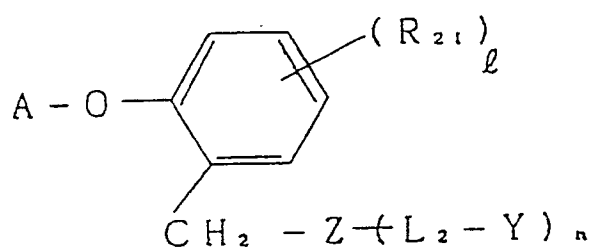
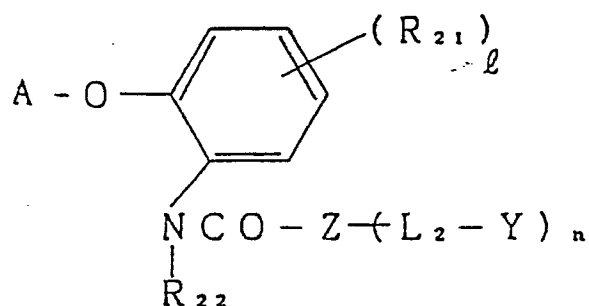


(linking group described in West  
German Patent Application (OLS)  
No. 2,626,315)



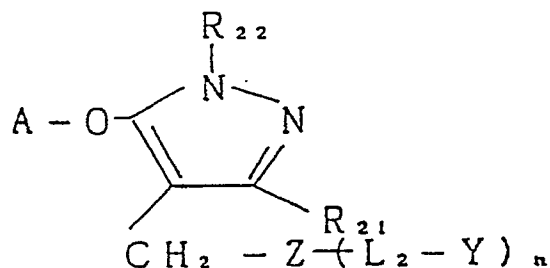
(linking group described in West  
German Patent Application (OLS)  
No. 2,855,697, wherein c represents  
an integer of 0 to 2)

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wherein  $\text{R}_{21}$  represents a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an aralkyl group, an alkoxy group, an alkoxy carbonyl group, an anilino group, an acylamino group, a ureido group, a cyano group, a nitro group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, an aryl group, a carboxy group, a sulfo group, a cycloalkyl group, an alkanesulfonyl group, an arylsulfonyl group, or an acyl group;  $\text{R}_{22}$  represents a hydrogen atom, an alkyl group, an alkenyl group, an aralkyl group, a cycloalkyl group, or an aryl group;  $n$  and  $l$  each is 1 or 2, and when  $l$  is 2,  $\text{R}_{21}$  and  $\text{R}_{21}$  may bond together to form a condensed ring.

In these DIR couplers (when  $a = 1$  in formula (IX)), the split-off group that has been released after the reaction with the oxidized product of a developing agent immediately decomposes to release the development retarder ( $\text{H}-\text{Z}-(\text{L}_2-\text{Y})_n$ ). As a result, the effect of the DIR couplers is the same as that of a DIR coupler without a group represented by  $\text{L}_1$  (when  $a = 0$  in formula (IX)).

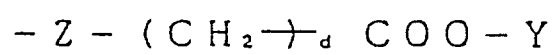
The linking group represented by  $\text{L}_2$  in formula (IX) includes a chemical bond that will cleave in a developing solution.

Examples of such a chemical bond include those listed in the following Table. Since those may be cleaved by a nucleophilic reagent, such as a hydroxy ion or hydroxylamine, the effect of the present invention can be obtained.

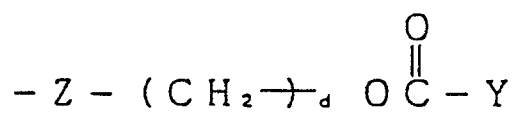
Chemical Bond included in $\text{L}_2$	Cleavage Reaction of the Bond (Reaction with $\text{OH}^-$ )
$-\text{COO}-$	$-\text{COOH}- + \text{HO}-$
$-\overset{\text{H}}{\text{N}}\text{COO}-$	$-\text{NH}_2 + \text{HO}-$
$-\text{SO}_2\text{O}-$	$-\text{SO}_2\text{H} + \text{HO}-$
$-\text{OCH}_2\text{CH}_2\text{SO}_2-$	$-\text{OH} + \text{CH}_2=\text{CHSO}_2-$
$-\text{O}\overset{\text{O}}{\parallel}\text{CO}-$	$-\text{OH} + \text{HO}-$
$-\text{NH}\overset{\text{O}}{\parallel}\overset{\text{O}}{\parallel}\text{CO}-$	$-\text{NH}_2 + \text{HO}-$

The divalent linking group shown in the above Table is attached to  $\text{Z}$ , directly or through an alkylene group and/or a phenylene group, and to  $\text{Y}$  directly. If the divalent linking group is attached to  $\text{Z}$  through an alkylene group or a phenylene group, the divalent group may contain, for example, an ether linkage, an amido linkage, a carbonyl group, a thioether bond, a sulfone group, a sulfonamido linkage, and a urea bond.

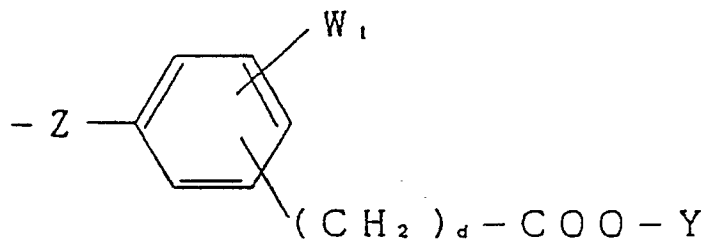
As examples of the linking group represented by  $\text{L}_2$ , the following are preferable. The substitution position of  $\text{Z}$  and the substitution position of  $\text{Y}$  are also shown.



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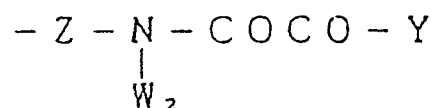
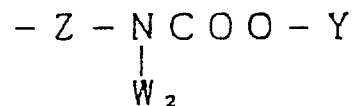
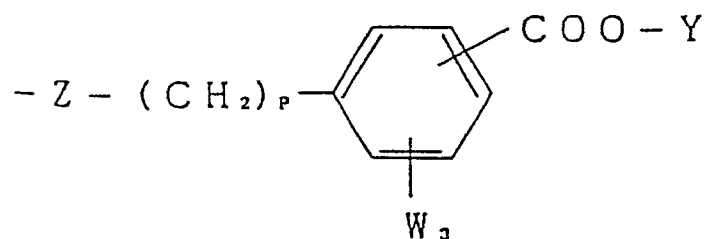
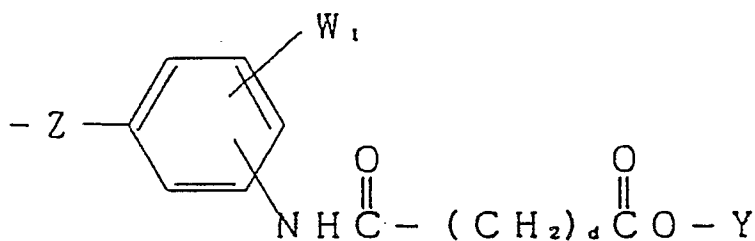
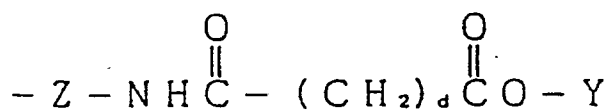
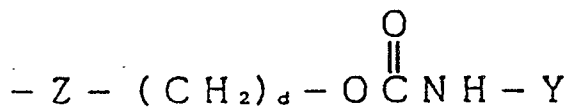
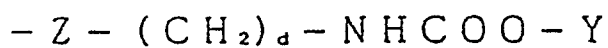
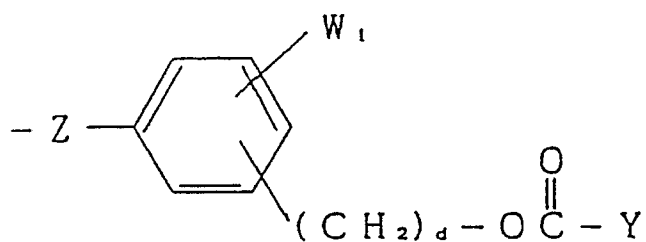
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wherein d is an integer of 0 to 10, preferably 0 to 5, W<sub>1</sub> represents a hydrogen atom, a halogen atom, an alkyl group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, an alkaneamido group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, an alkoxy carbonyl group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, an aryloxy carbonyl group, an alkanesulfonamido group having 1 to 10 carbon atoms, preferably 1 to 5

carbon atoms, an aryl group, a carbamoyl group, an N-alkylcarbamoyl group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, a nitro group, a cyano group, an arylsulfonamido group, a sulfamoyl group, or an imido group,  $W_2$  represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an aryl group, or an alkenyl group,  $W_3$  represents a hydrogen atom, a halogen atom, a nitro group, or an alkoxy group or alkyl group having 1 to 6 carbon atoms, and  $p$  is an integer of 0 to 6.

The alkyl group or alkenyl group represented by  $X_1$  and  $Y$  more particularly represents a straight-chain, branched or cyclic alkyl group or alkenyl group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, which preferably has a substituent, such as a halogen atom, a nitro group, an alkoxy group having 1 to 4 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an alkanesulfonyl group having 1 to 4 carbon atoms, an arylsulfonyl group having 6 to 10 carbon atoms, an alkaneamido group having 1 to 5 carbon atoms, an anilino group, a benzamido group, an alkyl-substituted carbamoyl group having 1 to 6 carbon atoms, a carbamoyl group, an aryl-substituted carbamoyl group having 6 to 10 carbon atoms, an alkylsulfonamido group having 1 to 4 carbon atoms, an arylsulfonamido group having 6 to 10 carbon atoms, a phthalimido group, a succinimido group, an imidazolyl group, a 1,2,4-triazolyl group, a pyrazolyl group, a benzotriazolyl group, a furyl group, a benzthiazolyl group, an alkylamino group having 1 to 4 carbon atoms, an alkanoyl group having 1 to 4 carbon atoms, a benzoyl group, an alkanoyloxy group having 1 to 4 carbon atoms, a benzoyloxy group, a perfluoroalkyl group having 1 to 4 carbon atoms, a cyano group, a tetrazolyl group, a hydroxyl group, a carboxyl group, a mercapto group, a sulfo group, an amino group, an alkylsulfamoyl group having 1 to 4 carbon atoms, an arylsulfamoyl group having 6 to 10 carbon atoms, a morpholino group, an aryl group having 6 to 10 carbon atoms, a pyrrolidinyl group, a ureido group, a urethane group, an alkoxy-substituted carbonyl group having 1 to 6 carbon atoms, an aryloxy-substituted carbonyl group having 6 to 10 carbon atoms, an imidazolydiny group, or an alkylideneamino group having 1 to 6 carbon atoms.

The alkaneamido group or alkeneamido group represented by  $X_1$  more particularly represents a straight-chain, branched or cyclic alkaneamido group or alkeneamido group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, which may have a substituent, such as those mentioned for the above alkyl group and alkenyl group.

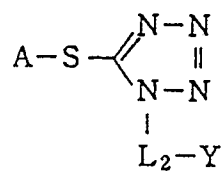
The alkoxy group represented by  $X_1$  more particularly represents a straight-chain, branched, or cyclic alkoxy group having 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, which may have a substituent, such as those mentioned for the above alkyl group and alkenyl group.

The aryl group represented by  $Y$  preferably represents a phenyl group or a naphthyl group whose substituent is selected, for example, from such substituents as those mentioned for the above alkyl group or alkenyl group, and an alkyl group having 1 to 4 carbon atoms.

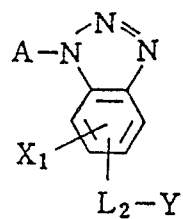
The heterocyclic group represented by  $Y$  is preferably a 5- to 7-membered heterocyclic group, such as a diazolyl group (e.g., 2-imidazolyl and 4-pyrazolyl), a triazolyl group (e.g., 1,2,4-triazol-3-yl), a thiazolyl group (e.g., 2-benzothiazolyl), an oxazolyl group (e.g., 1,3-oxazol-2-yl), a pyrrolyl group, a pyridyl group, a diazonyl group (e.g., 1,4-diazin-2-yl), a triazinyl group (e.g., 1,2,4-triazin-5-yl), a furyl group, a diazolinyl group (e.g., imidazolin-2-yl), a pyrrolinyl group, and a thienyl group.

Of the couplers represented by formula (IX), useful ones are those represented by the following formulae (X), (XI), (XII), (XIII), (XIV), (XV), and (XVI). These couplers are preferable because their split development retarders are high in development-retarding effect.

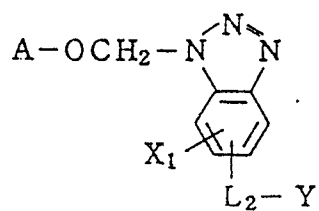
Formula (X)



Formula (XI)



Formula (XII)

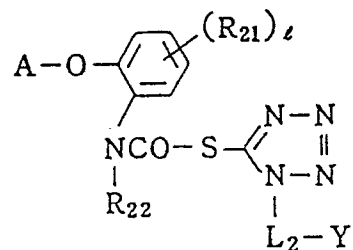




Formula (XIII)

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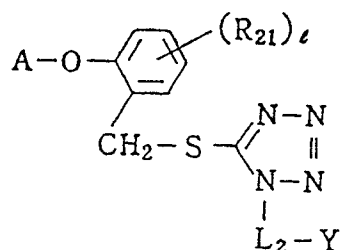


Formula (XIV)

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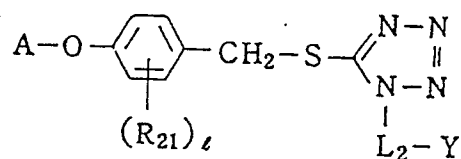
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Formula (XV)

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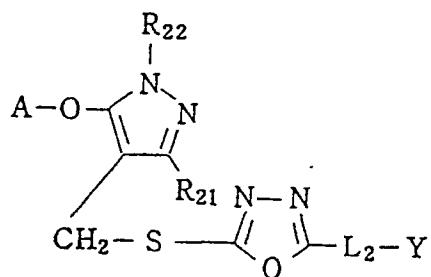
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Formula (XVI)

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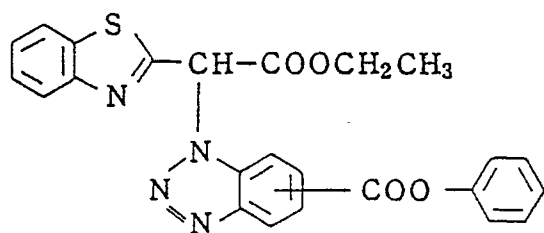


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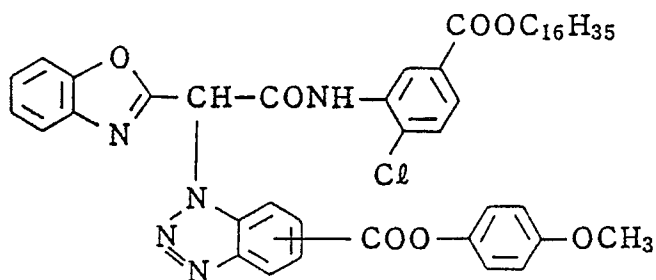
A,  $L_2$ , and Y in formulae (X) to (XVI) have the same meanings as those described for formula (IX).  
As examples of couplers that are used in the present invention, the following compounds can be mentioned, but the present invention is not limited to them.

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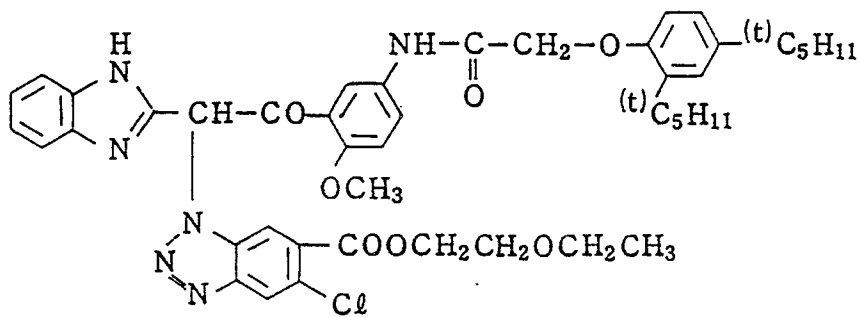
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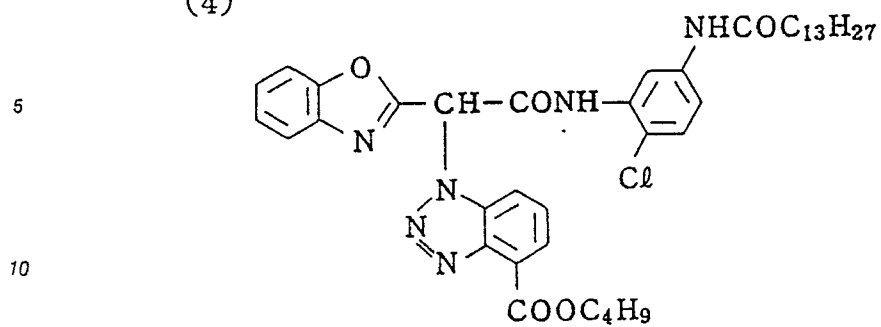
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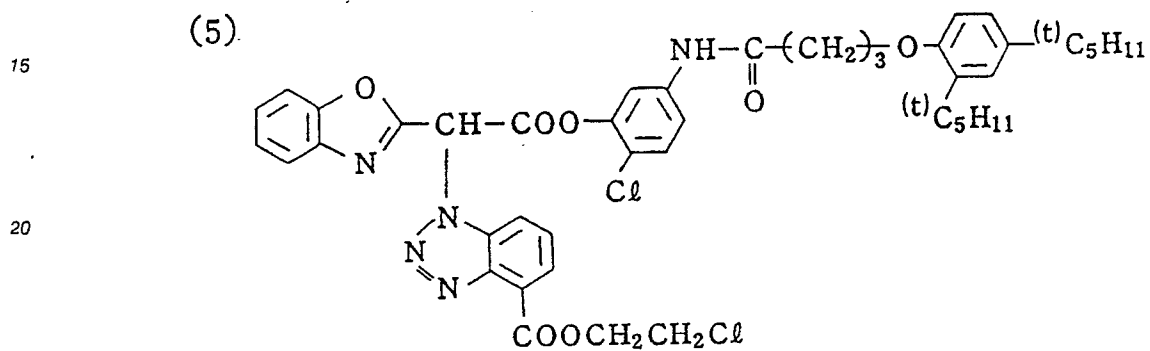
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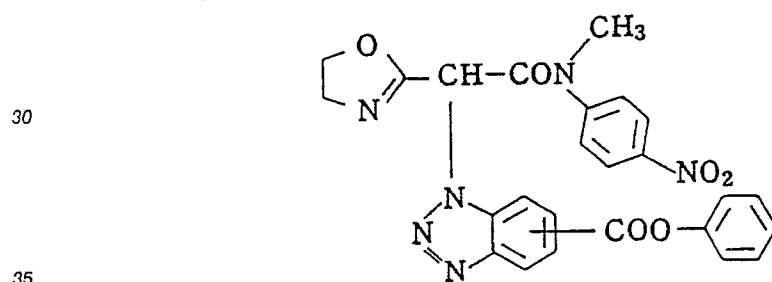
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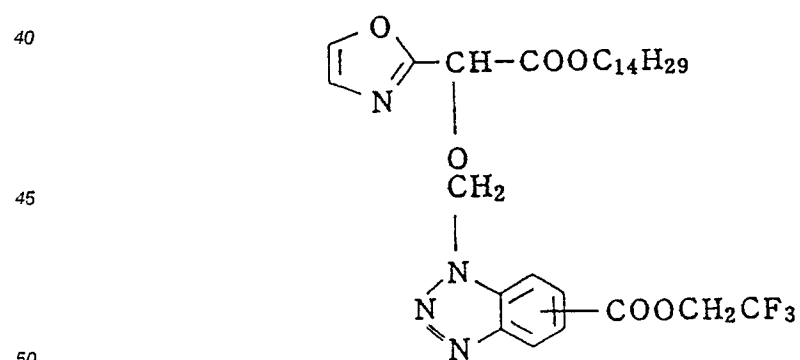
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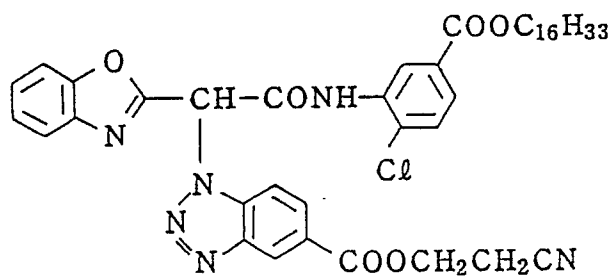


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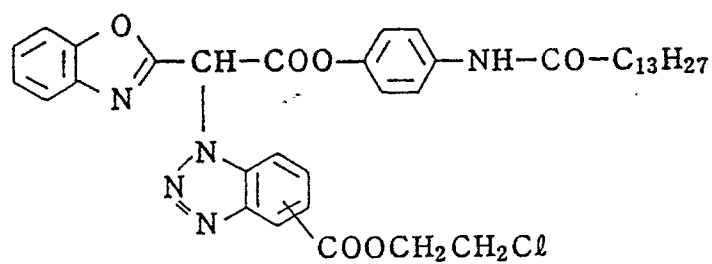




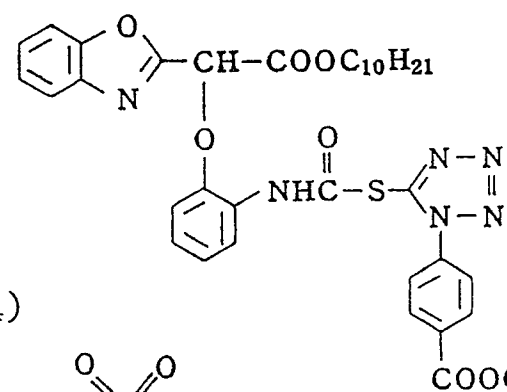
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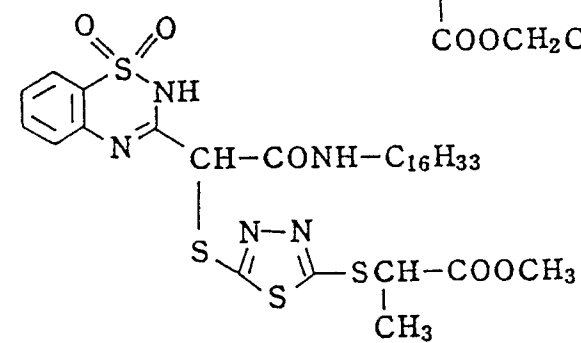
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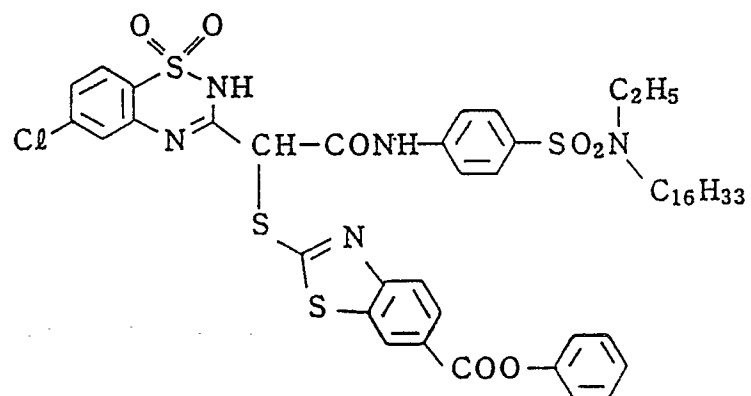
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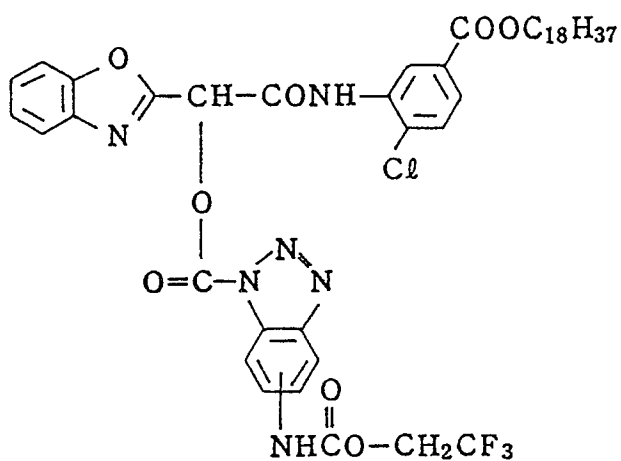
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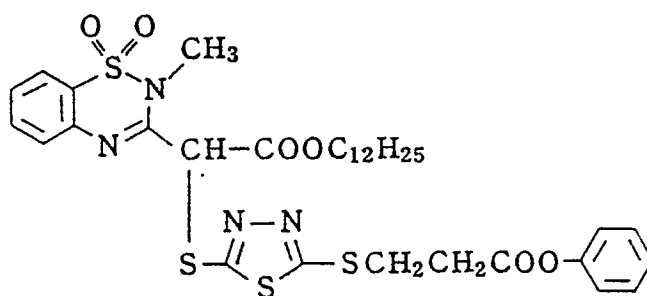
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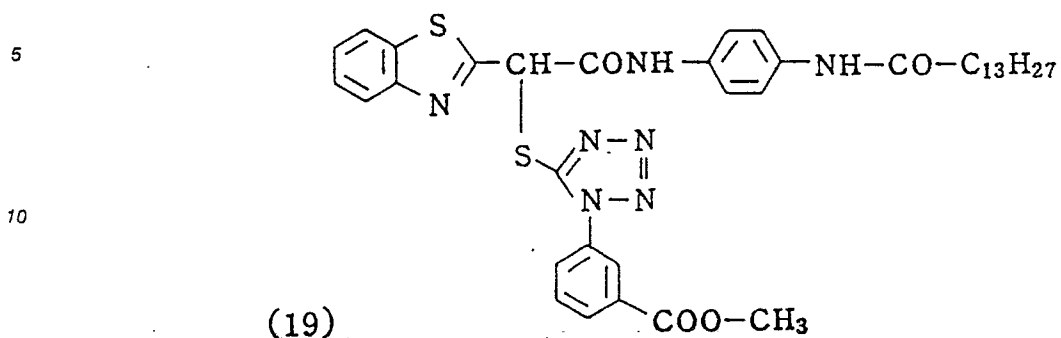
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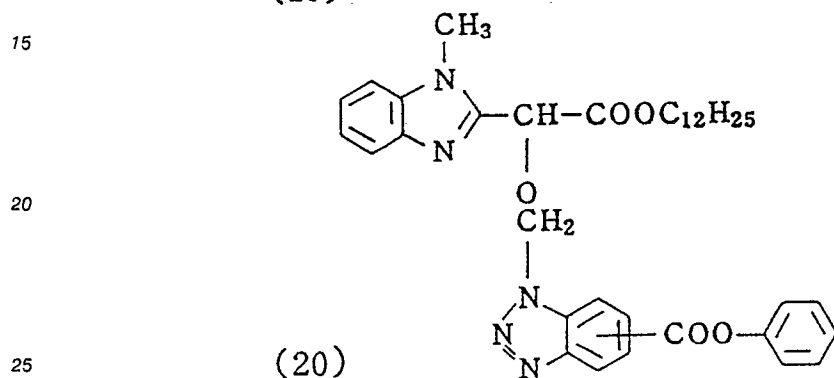
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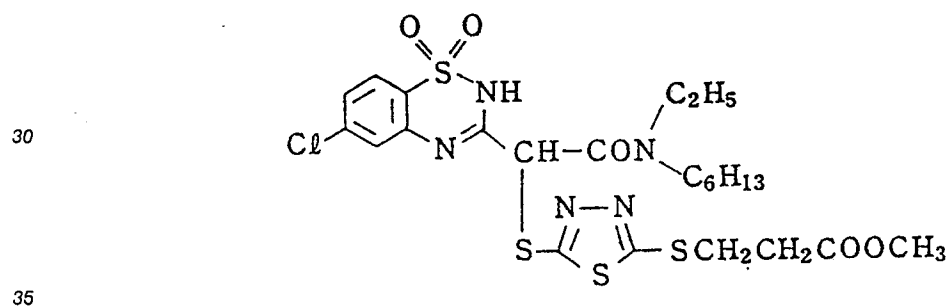
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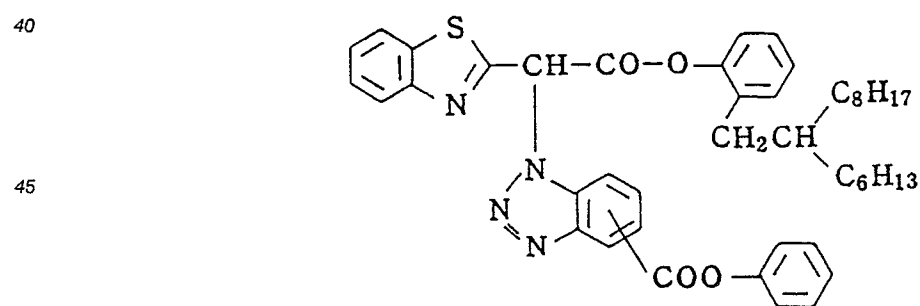
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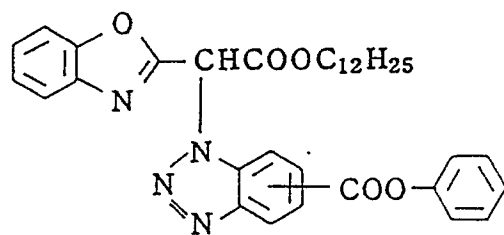
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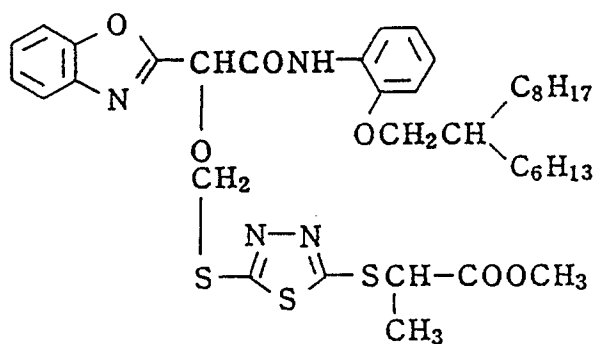
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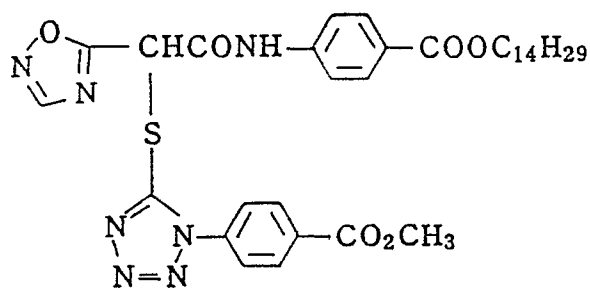
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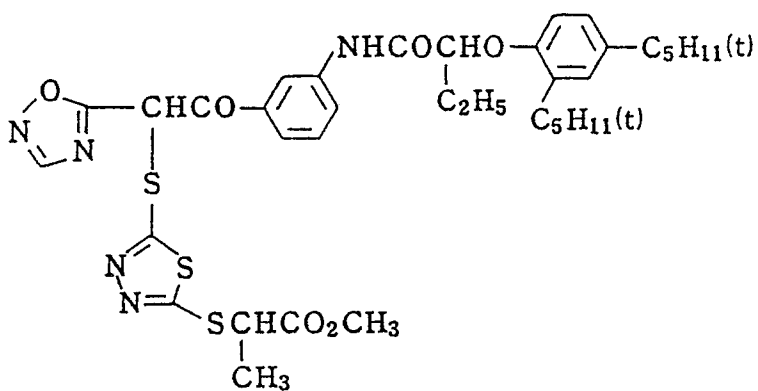
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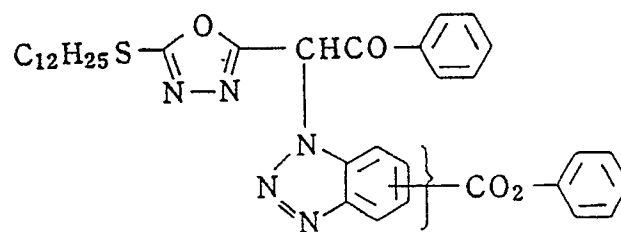




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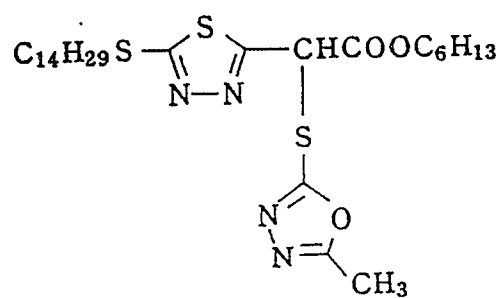


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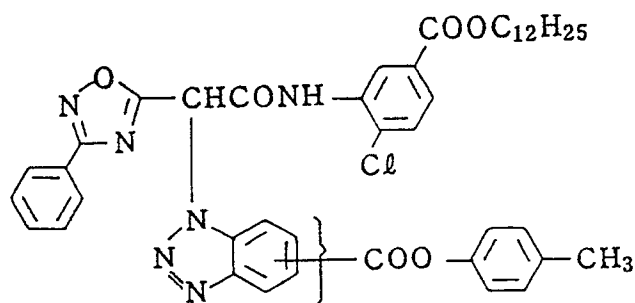
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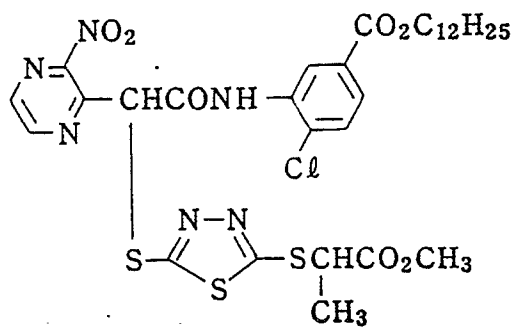
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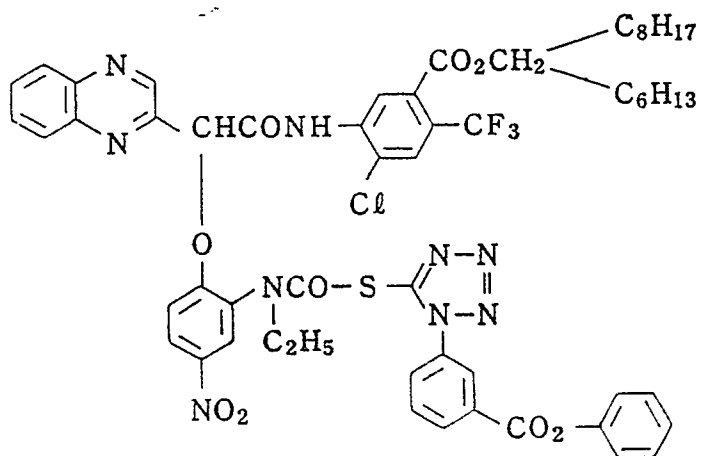
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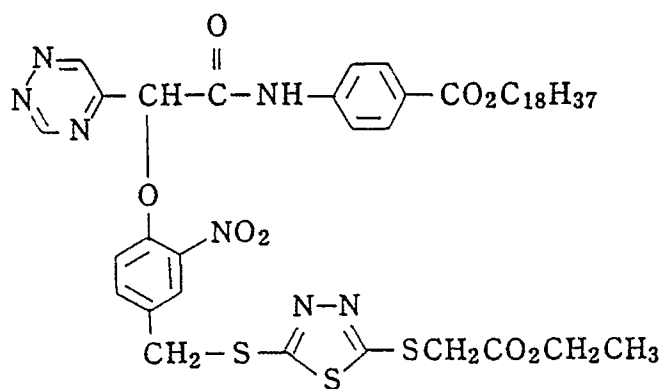
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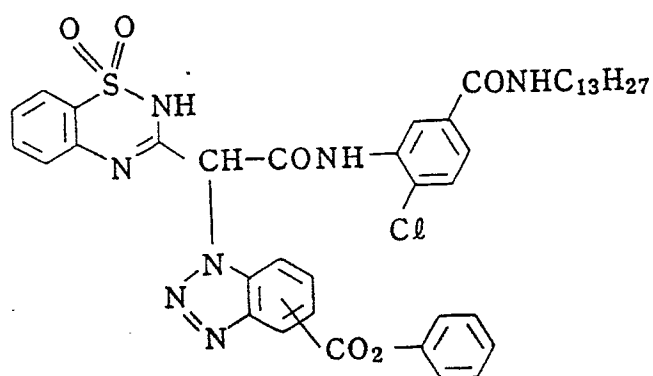


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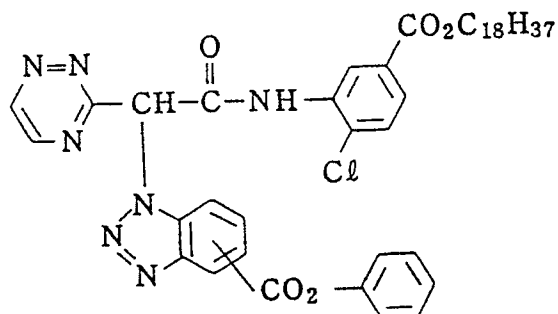


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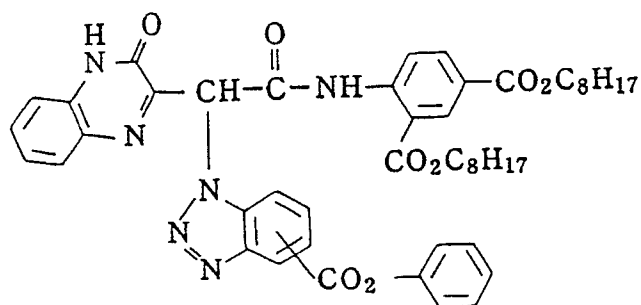


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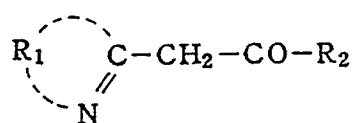
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These compounds can be synthesized easily, for example, by a method wherein after the active methylene of a compound represented by formula (XX):

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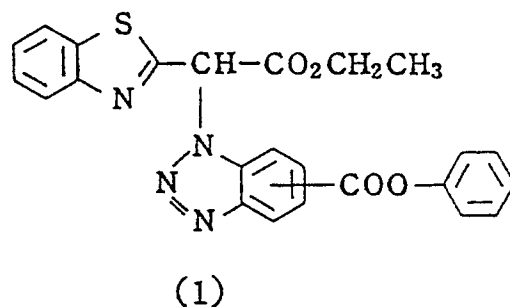
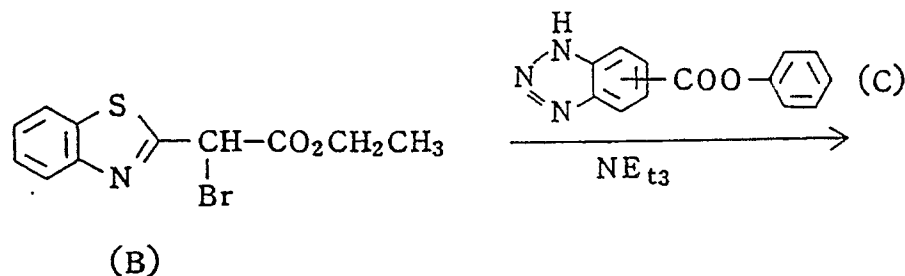
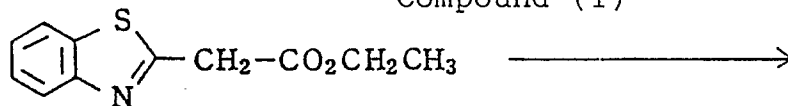
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wherein  $R_1$  and  $R_2$  have the same meanings as those for formula (I), is halogenated in a general manner, XH, wherein X has the same meaning as that in formula (I), is reacted in the presence of a base. In the case of a compound of formula (I) wherein X is attached through a sulfur atom, the compound can be synthesized by reacting sulfonyl chloride,  $\text{XCl}$ , which is obtained by interaction of XH with chlorine gas or

Typical Synthesis Examples of compounds of the present invention are given below.

Other compounds can also be produced in the same way as in the following Synthesis Examples.

### Synthesis Example 1 : Synthesis of Exemplified Compound (1)



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3.0 g of compound (A) was dissolved in 30.0 ml of chloroform, and 2.2 g of bromine was added dropwise thereto over 10 min. while being cooled with ice. After the reaction, an aqueous saturated sodium carbonate solution was added thereto, the layers were separated, and the procedure was repeated three times. After neutralizing, the chloroform layer was dried with magnesium sulfate. After the magnesium sulfate was filtered off, the filtrate was added dropwise to a solution of 3.3 g of compound (C) and 1.4 g of triethylamine in 20 ml of dimethylformamide. After the reaction, 100 ml of hexane and 100 ml of an aqueous 10 % hydrochloric acid solution were added thereto to effect extraction. After neutralizing, the organic layer was distilled off under reduced pressure, and 50 ml of isopropyl alcohol was added to the residue to carry out recrystallization. After drying, the desired exemplified compound (1) was obtained in an

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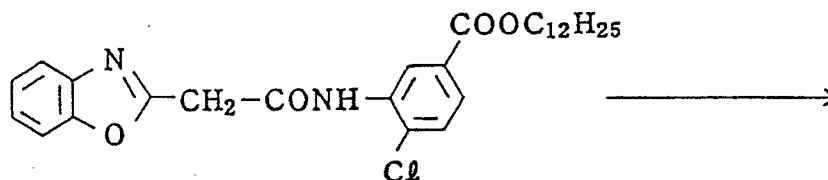
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amount of 3.4 g (yield: 65.0 %).

Synthesis Example 2 : Synthesis of Exemplified Compound (10)

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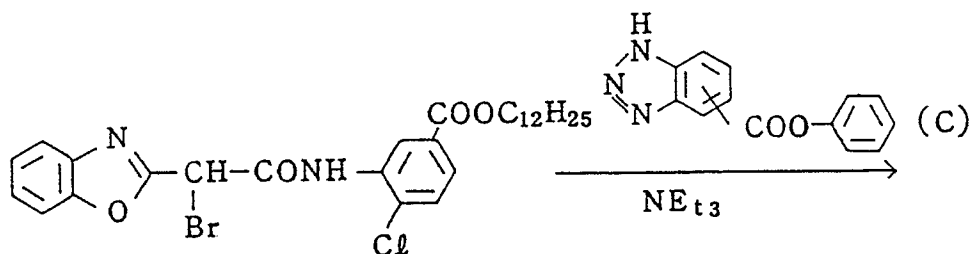


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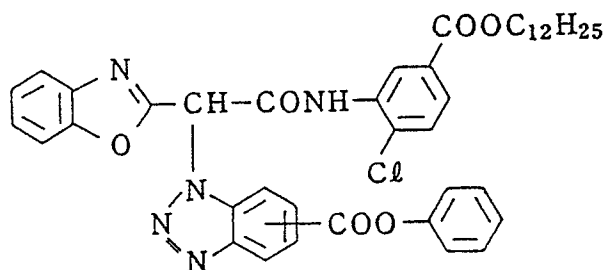


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(10)

10.0 g of compound (D) was dissolved in 100.0 ml of chloroform, and 3.2 g of bromine was added dropwise thereto over 10 min. while being cooled with ice. After the reaction, an aqueous saturated sodium carbonate solution was added thereto, the layers were separated, and the procedure was repeated three times. After neutralizing, the chloroform layer was dried with magnesium sulfate. After the drying, the magnesium sulfate was filtered off, the filtrate was added dropwise to a solution of 4.8 g of compound (C) and 2.0 g of triethylamine in 100 ml of dimethylformamide. After the reaction, 500 ml of hexane and 100 ml of an aqueous 10 % hydrochloric acid solution were added thereto to effect extraction. After neutralizing, the organic layer was distilled off under reduced pressure, and 100 ml of ethanol was added to the residue to carry out recrystallization, thereby obtaining the desired exemplified compound (10) in an amount of 9.1 g (yield: 62.0 %).

Although the amount of the compound represented by formula (I) of the present invention to be added varies depending on the structure of the compound or the application of the compound, the amount preferably is  $1 \times 10^{-7}$  to 0.5 mol, more preferably  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol, per mol of silver present in the same layer or in the adjacent layer.

5 The compound represented by formula (I) of the present invention may be used alone or in combination with a known coupler in a certain layer. If the compound represented by formula (I) of the present invention is used in combination with another color image-forming coupler, the molar ratio of the present compound to the other color image-forming coupler is from 0.1/99.9 to 90/10, preferably from 1/99 to 50/50.

The photographic material of the present invention may be one having, on a support, at least one silver  
10 halide emulsion layer of at least a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, and there is no limit to the number and order of the silver halide emulsion layers and the nonsensitive layers. As a typical example can be mentioned a silver halide photographic material having on the support at least one photosensitive layer consisting of several silver halide emulsion layers, whose color sensitivities are substantially the same and whose photographic sensitivities are different, the photosensitive layer being  
15 a unit photosensitive layer having a color sensitivity to any one of blue light, green light, and red light, and in the case of a multilayer silver halide color photographic material, the unit photosensitive layers are arranged in such a manner that there are, on the support, a red-sensitive layer, a green-sensitive layer, and then a blue-sensitive layer, in the order stated. However, the order may be reversed according to the purpose, or the same color-sensitive layers may have a different color-sensitive layer between them.

20 Nonsensitive layers, such as various intermediate layers, may be placed between said silver halide photosensitive layers, or on the top or bottom layer of said silver halide photosensitive layers.

Such intermediate layers may contain couplers, DIR compounds, etc., as described in JP-A Nos. 43748/1986, 113438/1984, 113440/1984, 20037/1986, and 20038/1986, and also color-mix inhibitors as used usually.

25 As each of the silver halide emulsion layers constituting respective unit photosensitive layers, preferably use can be made of a two-layer constitution consisting of a high-speed emulsion layer and a slow-speed emulsion layer, as described in West German Patent No. 1,121,470 or British Patent No. 923,045. Generally it is preferable that the emulsion layers are arranged in such an order that the sensitivities lower successively toward the support, and it also is possible to provide a nonsensitive layer between the halogen  
30 emulsion layers. As described in JP-A No. 112751/1982, 200350/1987, 206541/1987, and 206543/1987, it is possible to provide a slow-speed emulsion layer away from the support and a high-speed emulsion layer near the support.

As a specific example can be mentioned an arrangement of a slow-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)/slow-speed green-sensitive layer  
35 (GL)/high-speed red-sensitive layer (RH)/slow-speed red-sensitive layer (RL), with the slow-speed blue-sensitive layer (BL) being furthest from the support, an arrangement of BH/BL GL/GH/RH/RL with the BH being furthest from the base, or an arrangement of BH/BL GH/GL/RL RH with the BH being furthest from the support.

As described in JP-B ("JP-B" means examined Japanese patent publication) No. 34932/1980, an  
40 arrangement of a blue-sensitive layer/GH/RH/GL/RL with the blue-sensitive layer being furthest from the support is also possible. As described in JP-A Nos. 25738/1981 and 63936/1987, an arrangement of a blue-sensitive layer GL/RL GH/RH with the blue sensitive layer being furthest from the support is also possible.

Further, as described in JP-B No. 15495/1979, an arrangement of three layers having different sensitivities on a support with the sensitivities being lowered toward the support, that is, an arrangement  
45 including, on the support, a silver halide emulsion layer highest in sensitivity as an upper layer, a silver halide emulsion layer as an intermediate layer lower in sensitivity than that of the upper layer, and a silver halide emulsion layer as a lower layer lower in sensitivity than that of the intermediate layer, in the stated order, can be mentioned. In the case of such an arrangement of three layers having different sensitivities, an arrangement of a medium-speed emulsion layer/high-speed emulsion layer/slow-speed emulsion layer in  
50 the same color-sensitive layer with the medium-speed emulsion layer being furthest from the support is possible, as described in JP-A No. 202464/1984.

As stated above, various layer constitutions and arrangements may be chosen in accordance with the purpose of the individual photographic material.

A preferable silver halide contained in the photographic emulsion of the photographic material used in  
55 the present invention is silver bromiodide, silver chloriodide, or silver bromochloriodide containing about up to 30 mol % of silver iodide, with silver bromiodide or silver bromochloriodide containing about 2 mol % to about 25 mol % of silver iodide particularly preferred.

The silver halide grains in the photographic emulsions may have a regular crystal structure such as

cubic, octahedral, or tetradecanahedral, an irregular crystal such as spherical or tabular, a crystal having crystal defects such as twin planes, or a thereof composite crystal structure.

The grain size of the silver halide may be fine grains having a diameter of about 0.2  $\mu\text{m}$  or less, or coarse grains with the diameter of the projected area being down to 10  $\mu\text{m}$ , and a polydisperse emulsion or a monodisperse emulsion can be used.

The silver halide photographic emulsion for use in the present invention can be prepared by the process described, for example, in Research Disclosure (RD) No. 17343 (December, 1987), pp. 22 - 23, "I. Emulsion Preparation and Types"; ibid. No. 18716 (November, 1979), p. 648; P.Giakides, Chimie et Physique Photographique (Paul Montel, 1967); G.F. Duffin, Photographic Emulsion Chemistry (Focal Press, 1966); or V.L. Zelikman, et al., Making and Coating Photographic Emulsion (Focal Press, 1964).

A monodisperse emulsion described, for example, in U.S. Patent Nos. 3,574,628 and 3,655,394, and British Patent No. 1,413,748 is also preferably.

Tabular grains having an aspect ratio of 5 or more can be used in the present invention. Tabular grains may be easily prepared by suitably using the methods described, for example, in Guttoff : Photographic Science and Engineering, Vol. 14, pp. 248 - 257 (1970) : U.S. Patent Nos. 4,434,226, 4,414,310, 4,433,048, and 4,439,520; and British Patent No. 2,112,157.

The crystal structure may be uniform, the outer halogen composition may be different from the inner halogen composition, or the crystal structure may be layered. The halide composition may be joined by the epitaxial joint to a different silver halide composition or a compound other than silver halides, for example, silver rhodanide or lead oxide, is jointed.

Further, a mixture of different crystal structures can be used.

Generally, the emulsion to be used in the present invention may be physically ripened, chemically ripened, and spectrally sensitized. Additives to be used in these steps are described in Research Disclosure Nos. 17643 and 18716, and the involved sections are listed in the Table below.

Known photographic additives that can be used in the present invention are also described in the above-mentioned two Research Disclosures, and the involved sections are listed in the same Table.

Additive		RD 17643	RD 18716
1	Chemical sensitizer	p. 23	p. 648 (right column)
2	Sensitivity-enhancing agents	ditto	ditto
3	Spectral sensitizers, Supersensitizers	pp. 23-24	pp. 648 (right column) -649 (right column)
4	Brightening agents	p. 24	-
5	Antifogging agents and Stabilizers	pp. 24-25	p. 648 (right column)
6	Light absorbers, Filter dyes and UV absorbers	pp. 25-26	pp. 649 (right column) -650 (right column)
7	Stain-preventive agents	p. 25 (right column)	p. 650 (left to right (column))
8	Image-dye stabilizers	p. 25	-
9	Hardeners	p. 26	p. 651 (left column)
10	Binders	p. 26	ditto
11	Plasticizers and Lubricants	p. 27	p. 650 (right column)
12	Coating aids and Surface-active agents	pp. 26-27	ditto
13	Antistatic agents	p. 27	ditto

Further, in order to prevent the deterioration of photographic characteristics due to formaldehyde gas, compounds that can react with formaldehyde to fix it, as described in, for example, U.S. Patent Nos. 4,411,987 and 4,435,503 are added preferably in the photographic material.

Various color couplers may be used in the present invention, and typical examples thereof are described in the patents cited in Research Disclosure (RD) No. 17643, VII-C - G.

As yellow couplers, those described, for example, in U.S. Patent Nos. 3,933,501, 4,022,620, 4,326,024, and 4,401,452, JP-B No. 10793/1983, British Patent Nos. 1,425,020 and 1,476,460, U.S. Patent Nos. 3,973,968, 4,314,023 and 4,511,649, and European Patent No. 249,473A may be used preferably.

As magenta couplers, the 5-pyrazolone type and pyrazoloazole type are preferable, and those described, for example, in U.S. Patent Nos. 4,310,619 and 4,351,897, European Patent No. 73,636, U.S. Patent Nos. 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A No. 33552/1985, Research Disclosure No. 24230 (June 1984), JP-A Nos. 43659/1985, 72238/1986, 35730/1985, 118034/1980, 118034/1980, and 18595/1985, U.S. Patent Nos. 4,500,630, 4,540,654, and 4,556,630 are particularly preferable.

As cyan couplers can be mentioned phenol couplers and naphthol couplers, and those described, for example, in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, European Patent Nos. 121,365A and 249,453A, U.S. Patent Nos. 3,446,622, 4,333,999, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A Nos. 42658/1986 are preferable.

As a colored coupler to rectify the unnecessary absorption of color-forming dyes, those couplers described in paragraph VII-G of Research Disclosure No. 17643, U.S. Patent No. 4,165,670, JP-B No. 39413/1982, U.S. Patent Nos. 4,004,929 and 4,138,258, and British Patent No. 1,146,368 are preferable.

As a coupler which forms a dye having proper diffusibility, those described in U.S. Patent No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570, and West German Patent Application (OLS) No. 3,234,533, are preferable.

Typical examples of a polymerized dye-forming coupler are described in U.S. Patent Nos. 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, and British Patent No. 2,102,173.

A coupler that releases a photographically useful residue can be used favorably in this invention. As a DIR coupler that releases a development retarder, those described in patents cited in paragraph VII-F of the above-mentioned Research Disclosure No. 17643, JP-A Nos. 151944/1982, 145234/1982, and 184248/1985, and U.S. Patent No. 4,248,962 are preferable.

As a coupler which releases, imagewise, a nucleating agent or a development accelerator upon developing, those described in British Patent Nos. 2,097,140 and 2,131,188, and JP-A Nos. 157638/1984 and 170840/1984 are preferable.

Other couplers that can be incorporated in the photographic material of the present invention include competitive couplers described in U.S. Patent No. 4,130,427, multiequivalent couplers described in U.S. Patent Nos. 4,283,472, 4,338,393, and 4,310,618, couplers that release a DIR coupler redox compound or a DIR coupler, as described, for example, in JP-A Nos. 185950/1985 and 24252/1987, couplers that release a dye to regain a color after releasing, as described in European Patent No. 173,302A, couplers that release a bleach-accelerator, as described in RD Nos. 11449 and 24241, and JP-A No. 201247 1066, and couplers that release a ligand, as described in U.S. Patent No. 4,553,477.

Couplers for use in the present invention can be introduced into a photographic material by any one of various known dispersing methods.

Examples of high-boiling organic solvents are described in U.S. Patent No. 2,322,027.

Examples of high boiling organic solvents having a boiling point of 175 °C or higher at the normal pressure include phthalic esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-*t*-amylphenyl)phthalate, bis(2,4-di-*t*-amylphenyl)isophthalate, and bis(1,1-diethylpropyl) phthalate), phosphoric or phosphonic esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, and di-2-ethylhexyl phenyl phosphonate), benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, and 2-ethylhexyl-*p*-hydroxy benzoate), amides (e.g., N,N-diethyldodecanamide, N,N-diethyl laurylamide), and N-tetra-decylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-*tert*-amylphenol), aliphatic carboxylic esters (e.g., bis(2-ethylhexyl)sebacate, dioctylazelaate, glycerol tributyrates, isosteraryl lactate, and trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-*tert*-octyl-aniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropyl-naphthalene). The auxiliary solvents are organic solvents having a boiling point higher than about 30 °C, preferably from about 50 °C to below about 160 °C. Examples of these solvents include ethyl acetate, butyl acetate, ethyl propionate, methylethyl ketone, cyclohexanone, 2-ethoxyethyl acetate, and dimethylformamide.

The steps and effect of the latex dispersion method and the examples of latex for impregnation are disclosed in U.S. Patent No. 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

In the color photographic material of the present invention, it is preferable to add various antiseptics or mildewproofing agent, such as, for example, benzoisothiazolone, *n*-butyl *p*-hydroxybenzoate, phenols, and 2-(4-thiazolyl)benzimidazole, described in JP-A Nos. 257747/1988 and 272248/1987, and Japanese Patent Application No. 238096/1987.



The present invention can be applied to various color photographic materials. Examples may be mentioned include color negative film for general use or movie, color reversal film for slide or television, color paper, color positive film, and color reversal paper.

Suitable bases that can be used in the present invention are described, for example, on p. 28 of the above-mentioned RD No. 17643, and on the right column of p. 627 to the left column of p. 648 in ibid. No. 18716.

The color photographic material according to the present invention can be subjected to development processing as described in pp. 28 - 29 of the above-mentioned RD No. 17643, and on the left to right columns of p. 651 in ibid. No. 18716.

The color-developing solution to be used in the developing process of the photographic material of the present invention is preferably an aqueous alkaline solution whose major component is an aromatic primary amine-type color developing agent. As the color developing agent, aminophenol-type compounds are useful, and p-phenylenediamine-type compounds are preferably used, typical examples thereof being 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, and 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline and their sulfates, and hydrochlorides or p-toluenesulfonates. These compounds may be used in combination according to the purpose.

Generally the color-developing solution contains pH buffers such as carbonates, borates, or phosphates of alkali metals; antifoggants or development retarders, such as mercapto compounds, benzothiazoles, benzimidazoles, iodides or bromides; and if required, preservatives such as hydroxylamines, diethylhydroxylamines, sulfites, hydrazines, phenylsemicarbazides, triethanolamine, catecholsulfonic acids, and triethylenediamines(1,4-diazabicyclo[2,2,2]octane); organic solvents such as ethylene glycol and diethylene glycol; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, and amines; dye-forming couplers; competing couplers; fogging agents such as sodium boron hydride; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; thickening agents; and chelate agents, such as aminopolycarboxylic acids, aminopolyphosphonic acids alkylphosphonic acids, and phosphonocarboxylic acids such as, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminetetraacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethylimidinoacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine, N,N,N',N'-tetramethylenephosphonic acid, and ethylenediamine-di-(o-hydroxyphenylacetic acid), and their salts.

For reversal processing a color development is generally carried out after a black-and-white development. For the black-and-white developing solution, known black-and-white-developing agents such as dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone), and aminophenols (e.g., N-methyl-p-aminophenol) may be used alone or in combination with others.

Generally the color-developing solution has a pH of 9 to 12. Although the replenishing amount of the developing solution varies depending on the color photographic material to be processed, generally the replenishing amount is 3 l or below per m<sup>2</sup> of the photographic material, and the replenishing amount can be lowered to 500 ml or below if the bromide ion concentration of the replenishing solution is lowered. If it is required to lower the replenishing amount, it is preferable that the area of the processing tank in contact with air is minimized to prevent the solution from evaporating or being oxidized by air. The replenishing amount can also be lowered by suppressing the accumulation of bromide ions in the developing solution.

Generally the processing time of color-development is set between 2 and 5 minutes, but the processing time can be shortened by using a processing solution of high temperature and high pH, as well as with a high concentration of color developing agent.

The photographic emulsion layers are generally subjected to a bleaching process after color development.

The bleaching process can be carried out together with the fixing process (bleach-fixing process), or it can be carried out separately from the fixing process. Further, to quicken the process bleach-fixing may be carried out after the bleaching process. In accordance with the purpose, the process may be arbitrarily carried out using a bleach-fixing bath having two successive tanks, or a fixing process may be carried out before the bleach-fixing process, or a bleaching process may be carried out after the bleach-fixing process. As the bleaching agent, use can be made of, for example, compounds of polyvalent metals, such as iron (III), cobalt (III), chromium (VI), and copper (II), peracids, quinones, and nitro compounds. As typical bleaching agents, use can be made of ferricyanides; dichromates; organic complex salts of iron (II) or cobalt (III), such as complex salts of aminopolycarboxylic acids, for example ethylenediaminetetraacetic acid, diethylenetriaminetetraacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycolether diaminetetraacetic acid, citric acid, tartaric acid, and malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Of these, aminopolycarboxylic acid iron (III)

complex salts, including ethylenediaminetetraacetic acid iron (III) complex salts and persulfates are preferable in view of rapid processing and the prevention of environmental pollution. Further, aminopolycarboxylic acid iron (III) complex salts are particularly useful in a bleaching solution as well as a bleach-fix solution. The pH of the bleaching solution or the bleach-fix solution using these aminopolycarboxylic acid iron (III) complex salts is generally 5.5 to 8, but if it is required to quicken the process, the process can be effected at a lower pH.

In the bleaching solution, the bleach-fix solution, and the baths preceding them a bleach-accelerating solution may be used if necessary. Examples of useful bleach-accelerating agents are compounds having a mercapto group or a disulfide linkage, described in U.S. Patent No. 3,893,858, West German Patent Nos. 1,290,812 and 2,059,988, JP-A Nos. 32736/1978, 57831/1978, 37418/1978, 72623/1978, 95630/1978, 95631/1978, 104322/1978, 124424/1978, 141623/1978, and 28426/1978, and Research Disclosure No. 17129 (July. 1978); thiazolidine derivatives, described in U.S. Patent No. 3,706,561; thiourea derivatives, described in JP-B No. 8506/1970, JP-A Nos. 20832/1977 and 32735/1978, and U.S. Patent No. 3,706,561; iodide salts, described in West German Patent No. 1,127,715 and JP-A No. 16235/1983; polyoxyethylene compounds, described in West German Patent Nos. 966,410 and 2,748,430; polyamine compounds, described in JP-B No. 8836/1970; other compounds, described in JP-A Nos. 42434/1974, 59644/1978, 35727/1979, 26505/1980, and 163940/1983; and bromide ions. Of these, compounds having a mercapto group or a disulfide group are preferable in view of higher acceleration effect, and in particular, compounds described in U.S. Patent No. 3,893,858, West German Patent No. 1,290,812, and JP-A No. 95630/1978 are preferable. Compounds described in U.S. Patent No. 4,552,834 are preferable. These bleach-accelerating agents may be added into the photographic material. When the color photographic materials for photographing are to be bleach-fixed, these bleach-accelerating agents are particularly effective.

As a fixing agent can be mentioned thiosulfates, thiocyanates, thioether-type compounds, thioureas, and large amounts of iodide salts, although thiosulfate is used usually, and in particular ammonium thiosulfate is widely used. As the preservative for bleach-fix solution sulfite salt, bisulfite salt, or carbonyl-bisulfite adduct is preferable.

It is common for the silver halide color photographic material of the present invention to undergo, after a desilvering process such as fixing or bleach-fix, a washing step and/or a stabilizing step. The amount of washing water may be set within a wide range depending on the characteristics (e.g., due to the materials used, such as couplers), the application of the photographic material, the washing temperature, the number of washing tanks (the number of steps), the type of replenishing system, including, for example, the counter-current system and the direct flow system, and other various conditions. Of these, the relationship between the number of water-washing tanks and the amount of washing water in the multi-stage counter-current system can be found according to the method described in Journal of Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May 1955).

According to the multi-stage-counter-current system described in the literature mentioned above, although the amount of washing water can be considerably reduced, bacteria propagate with an increase of retention time of the washing water in the tanks, leading to a problem with the resulting suspend matter adhering to the photographic material. In processing the present color photographic material, as a measure to solve this problem, the method of reducing calcium and magnesium described in JP-A No. 288838/1987 can be used quite effectively. Also chlorine-type bactericides such as sodium chlorinated isocyanurate, cyabendazoles, isothiazolone compounds described in JP-A No. 8542/1982, benzotriazoles, and other bactericides described in Hiroshio Horiguchi "Bokin/bobaizai no Kagaku", in "Biseibutsu no Mekkin, Sakkin, Bobaigijutsu" edited by Eiseigijutsu-kai, and in "Bokin Bibaizai Jiten", edited by Nihon Bokin Bobai-Gakkai, can be used.

The pH of the washing water used in processing the present photographic material is 4 to 9, preferably 5 to 8. The washing water temperature and the washing time to be set may vary depending, for example, on the characteristics and the application of the photographic material, and they are generally selected in the range of 15 to 45 °C for 20 sec. to 10 min., and preferably in the range of 25 to 40 °C for 30 sec. to 5 min. Further, the photographic material of the present invention can be processed directly with a stabilizing solution instead of the above washing. In such a stabilizing process, any of known processes, for example, a multi-step counter-current stabilizing process or its low-replenishing-amount process, described in JP-A Nos. 8543/1982, 14834/1983, and 220345/1985.

In some cases, the above washing process is further followed by a stabilizing process, and as an example thereof can be mentioned a stabilizing bath that is used as a final bath for color photographic materials for photography, which contains formalin and a surface-active agent. In this stabilizing bath, each kind of the chelating agents and bactericides may be added.

The over-flowed solution due to the replenishing of washing solution and/or stabilizing solution may be

reused in other steps, such as a desilvering step.

The silver halide color photographic material of the present invention may contain therein a color-developing agent for the purpose of simplifying and quickening the process. To contain such a color-developing agent, it is preferable to use a precursor for a color-developing agent. For example, indoaniline-type compounds described in U.S. Patent No. 3,342,597, Schiff base-type compounds described in U.S. Patent No. 3,342,599 and Research Disclosure Nos. 14850 and 15159, aldol compounds described in Research Disclosure No. 13924, metal salt complexes described in U.S. Patent No. 3,719,492, and urethane-type compounds described in JP-A No. 135628/1978 can be mentioned.

For the purpose of accelerating the color development, the present silver halide color photographic material may contain, if necessary, various 1-phenyl-3-pyrazolidones. Typical compounds are described in JP-A No. 64339/1981, 144547/1982, and 115438/1983.

The various processing solutions used for the present invention are used at 10 to 50 °C. Although generally a temperature of 33 to 38 °C is standard, a higher temperature can be used to accelerate the process to reduce the processing time, or a lower temperature can be used to improve the image quality or the stability of the processing solutions. Also, to save the silver of the photographic material, a process using hydrogen peroxide intensification or cobalt intensification described in West German Patent No. 2,226,770 and U.S. Patent No. 3,674,499 may be carried out.

The photographic material of the present invention can be applied to the heat development-type photographic material as described in U.S. Patent No. 4,500,626, JP-A Nos. 133449/1985 and 218443/1984, and European Patent No. 210,660A2.

The silver halide color photographic material of the present invention has the effects of a dye produced by coupling with the oxidized product of a color developing agent being sufficiently fast, of not contaminating a development processing solution, and providing a highly sensitive color photographic image excellent in sharpness and color reproduction.

The invention will now be described in further detail with reference to examples, but the invention is not limited to them.

#### Example 1

A multilayer color photosensitive material (Sample 101) consisting of layers of the following composition was prepared on an undercoated triacetate cellulose film support.

#### (Composition of photosensitive layers)

In the following compositions, the coating amount of silver halide and colloidal silver are each indicated in g/m<sup>2</sup> in terms of silver, the coating amount of the coupler, additive, and gelatin are each indicated in g/m<sup>2</sup>, and the coating amount of the sensitizing dye is indicated in mol per mol of silver halide. Symbols showing additives have meanings as shown below, but when having plural effects, one of them is shown as a representative:

UV : ultraviolet absorbent,

Solv : high-boiling organic solvent,

ExS : sensitizing dye,

ExC : cyan coupler,

ExM : magenta coupler,

ExY : yellow coupler,

Cpd : additive,

First layer : Antihalation layer

Black colloidal silver	0.2
Gelatin	1.3
ExM-9	0.06
UV-1	0.03
UV-2	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Second layer : Intermediate layer

Gelatin	1.0
UV-1	0.03
ExC-4	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.1

Third layer : Slow-speed red-sensitive emulsion layer

Silver iodobromide emulsion (Agl : 14 mol%, uniform AgI-type, diameter corresponding to sphere : 0.5  $\mu\text{m}$ , deviation coefficient of diameter : 20 %, tabular grains, diameter/thickness : 3.0) silver 1.2

Silver iodobromide emulsion (Agl : 13 mol%, uniform AgI-type, diameter corresponding to sphere : 0.3  $\mu\text{m}$ , deviation coefficient of diameter : 15 %, cubic grains, diameter/thickness : 1.0) silver 0.6

Gelatin	1.0
ExS-1	$4 \times 10^{-4}$
ExS-2	$5 \times 10^{-5}$
ExC-1	0.05
ExC-2	0.05
ExC-3	0.03
ExC-4	0.12
ExC-5	0.01

Fourth layer : High-speed red-sensitive emulsion layer

Silver iodobromide emulsion (Agl : 16 mol%, inner higher AgI-type of core/shell ratio 1:1, diameter corresponding to sphere : 0.7  $\mu\text{m}$ , deviation coefficient of diameter : 15 %, tabular grains, diameter:thickness : 5) silver 0.7

Gelatin	1.0
ExS-1	$3 \times 10^{-4}$
ExS-2	$2.3 \times 10^{-5}$
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-3	0.05

Fifth layer : Intermediate layer

Gelatin	0.5
Cpd-1	0.1
Solv-1	0.05

Sixth layer : Slow-speed green-sensitive emulsion layer

Silver iodobromide emulsion (Agl : 14 mol%, surface higher AgI-type of core/shell ratio 1:1, diameter corresponding to sphere :  $0.5 \mu\text{m}$ , deviation coefficient of diameter : 15 %, tabular grains, diameter/thickness : 4.0) silver 0.35

Silver iodobromide emulsion (Agl : 3 mol%, uniform AgI-type, diameter corresponding to sphere :  $0.3 \mu\text{m}$ , deviation coefficient of diameter : 25 %, cubic grains, diameter/thickness : 1.0) silver 0.20

Gelatin	1.0
ExS-3	$5 \times 10^{-4}$
ExS-4	$3 \times 10^{-4}$
ExS-5	$1 \times 10^{-4}$
ExM-8	0.4
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Seventh layer : High-speed green-sensitive emulsion layer

Silver iodobromide emulsion (Agl : 14 mol%, inner higher Hgl-type of core/shell ratio 1:3, diameter corresponding to sphere :  $0.7 \mu\text{m}$ , deviation coefficient of diameter : 20 %, tabular grains, diameter/thickness : 5.0) silver 0.8

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Gelatin	0.5
Exs-3	$5 \times 10^{-4}$
ExS-4	$3 \times 10^{-4}$
ExS-5	$1 \times 10^{-4}$
ExM-8	0.1
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03
ExM-14	0.01
Solv-1	0.2
Solv-4	0.01

15 Eighth layer : Intermediate layer

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Gelatin	0.5
Cpd-1	0.05
Solv-1	0.02

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Ninth layer : Doner layer for double layer-effect to red-sensitive layer

Silver iodobromide emulsion (Agl : 12 mol%, inner higher AgI-type of core/shell ratio 2:1, diameter corresponding to sphere : 1.0  $\mu\text{m}$ , deviation coefficient of diameter : 15 %, tabular grains, diameter/thickness : 6.0) silver 0.35

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Silver iodobromide emulsion (Agl : 12 mol%, inner higher AgI-type of core/shell ratio 1:1, diameter corresponding to sphere : 0.4  $\mu\text{m}$ , deviation coefficient of diameter : 20 %, tabular grains, diameter:thickness : 6.0) silver 0.20

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Gelatin	0.5
ExS-3	$8 \times 10^{-4}$
ExY-13	0.11
ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

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Tenth layer : Yellow filter layer

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Yellow colloidal silver	0.05
Gelatin	0.5
Cpd-2	0.13
Solv-1	0.13
Cpd-1	0.10

Eleventh layer : Slow-speed blue-sensitive emulsion layer

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Silver iodobromide emulsion (Agl : 14.5 mol%, uniform AgI-type, diameter corresponding to sphere : 0.7  $\mu\text{m}$ , deviation coefficient of diameter 15 %, tabular grains, diameter/thickness : 7.0) silver 0.3

Silver iodobromide emulsion (Agl : 13 mol%, uniform AgI-type, diameter corresponding to sphere : 0.3  $\mu\text{m}$ ,

deviation coefficient of diameter 25 %, tabular grains, diameter/thickness : 7.0) silver 0.15

5

Gelatin	1.6
ExS-6	$2 \times 10^{-7}$
ExC-16	0.05
ExC-2	0.10
ExC-3	0.02
ExY-13	0.3
ExY-15	1.0
Solv-1	0.20

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Twelfth layer : High-speed blue-sensitive emulsion layer

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Silver iodobromide emulsion (Agl : 10 mol%, inner higher AgI-type, diameter corresponding to sphere : 1.0  $\mu\text{m}$ , deviation coefficient of diameter : 25 %, multiple twinned crystal tabular grains, diameter/thickness : 2.0) silver 0.5

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Gelatin	0.5
ExS-6	$1 \times 10^{-7}$
ExY-15	0.20
ExY-13	0.05
Solv-1	0.10

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Thirteenth layer : First protective layer

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Gelatin	0.8
UV-4	0.1
UV-5	0.15
Solv-1	0.01
Solv-2	0.01

35

Fourteenth layer : Second protective layer

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Fine-grain silver bromide emulsion (Agl : 12 mol%, uniform AgI-type, diameter corresponding to sphere : 0.07  $\mu\text{m}$ ) silver 0.5

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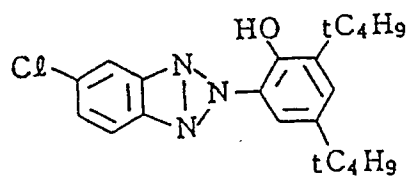
Gelatin	0.45
Poly(methyl methacrylate) particles (particle diameter : 1.5 $\mu\text{m}$ )	0.2
H-1	0.4
Cpd-5	0.5
Cpd-6	0.5

50

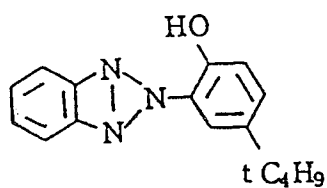
In each layer described above, an emulsion-stabilizer, Cpd-3 (0.04 g/m<sup>2</sup>), and a surface-active agent, Cpd-4 (0.02 g/m<sup>2</sup>), were added as coating aids.

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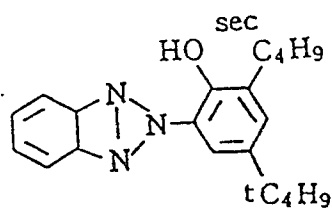
UV-1



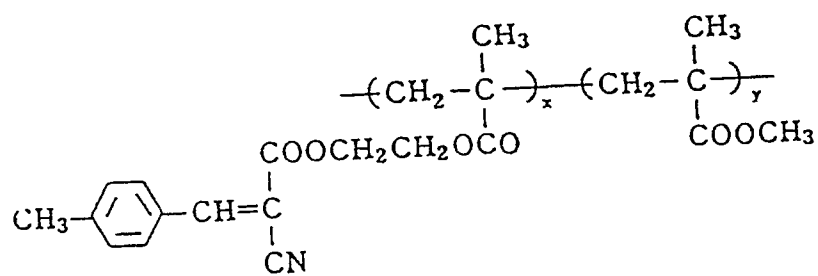
UV-2



UV-3



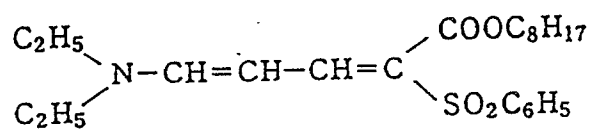
UV-4



(x/y = 7/3 in wt. ratio)



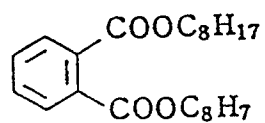
UV-5



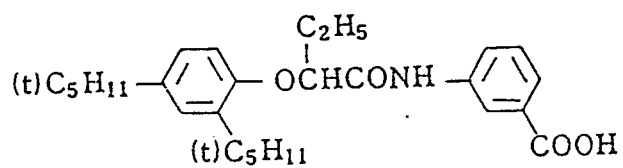
Solv-1 Tricresyl phosphate

Solv-2 Dibutyl phthalate

Solv-3



Solv-4



Cpd-1



Cpd-2



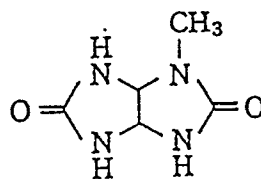
Cpd-3



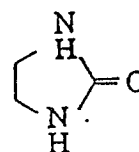
Cpd-4



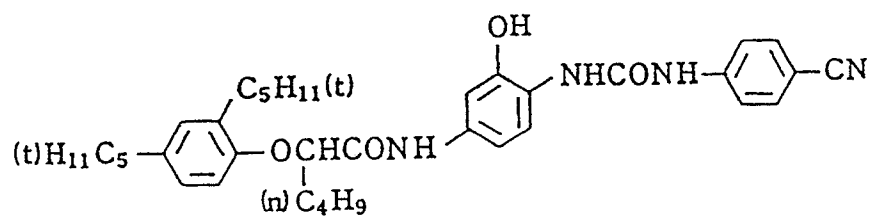
Cpd-5



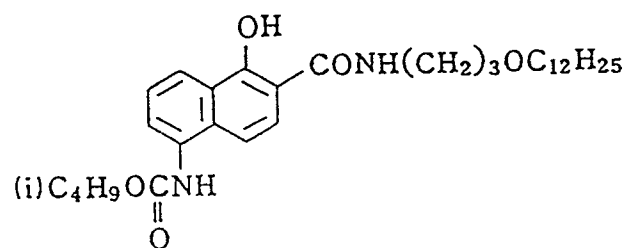
Cpd-6



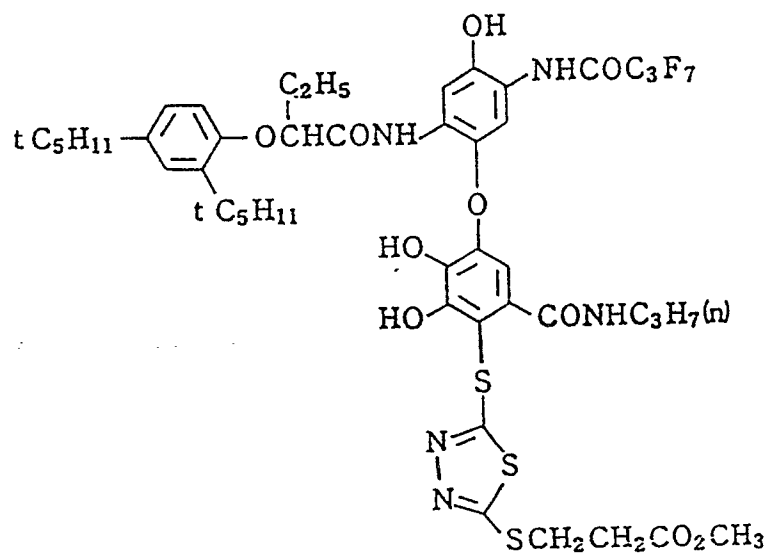
ExC-1



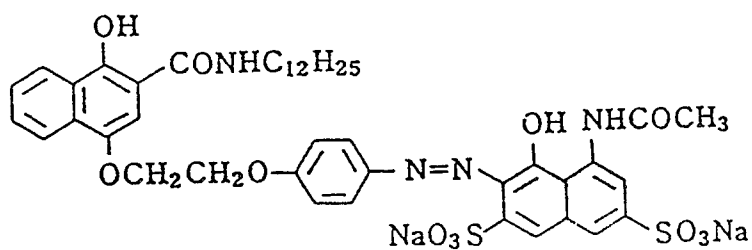
ExC-2



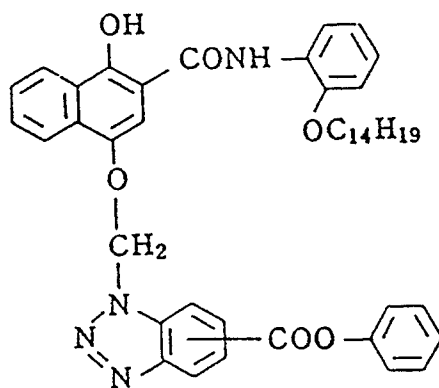
ExC-3



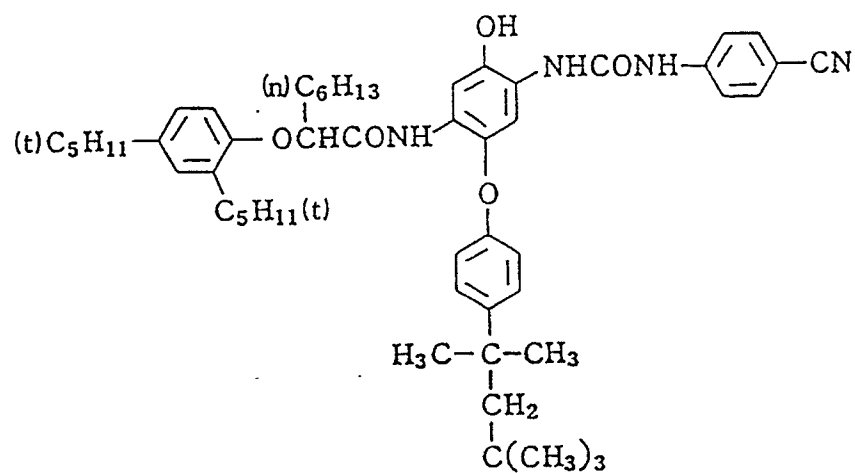
ExC-4



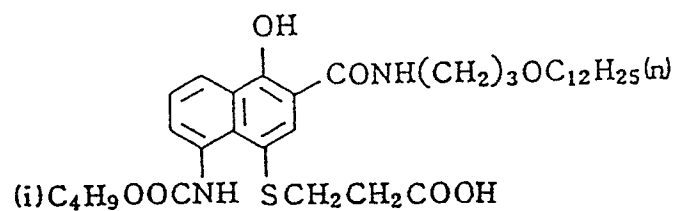
ExC-5



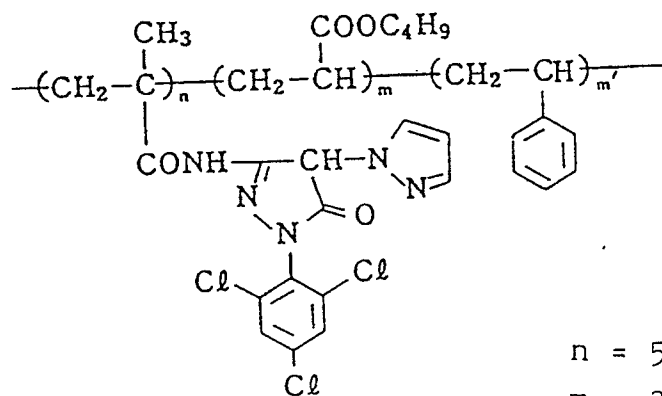
ExC-6



ExC-7



ExM-8



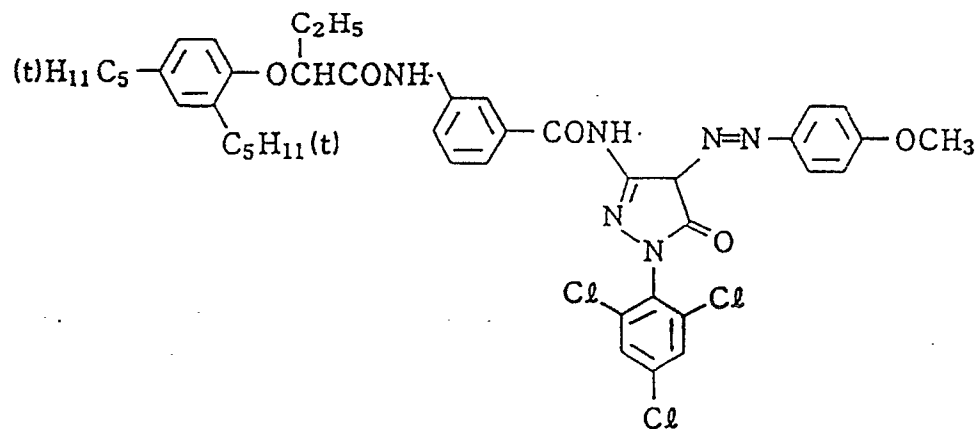
$$n = 50$$

$$m = 25$$

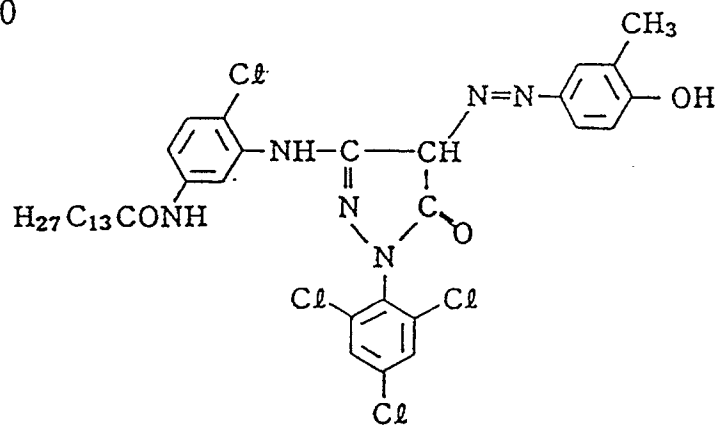
$$m' = 25$$

mol. wt.: about 20,000

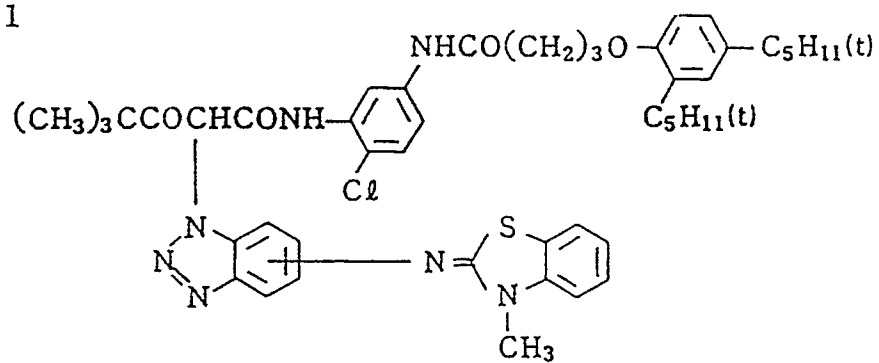
ExM-9



ExM-10



ExY-11

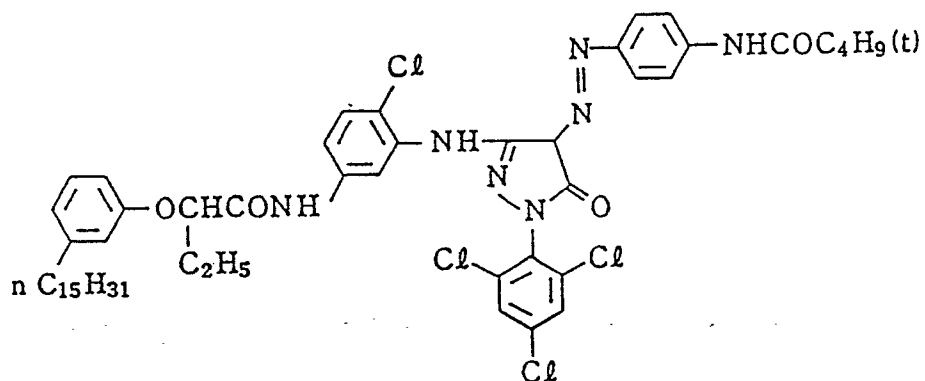


ExM-12

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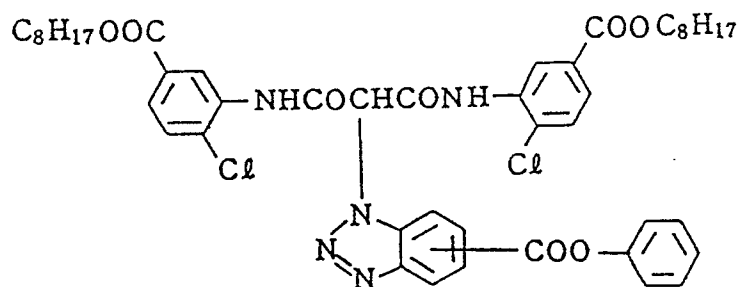


ExY-13 (Coupler described in U.S. Patent No. 4,447,563)

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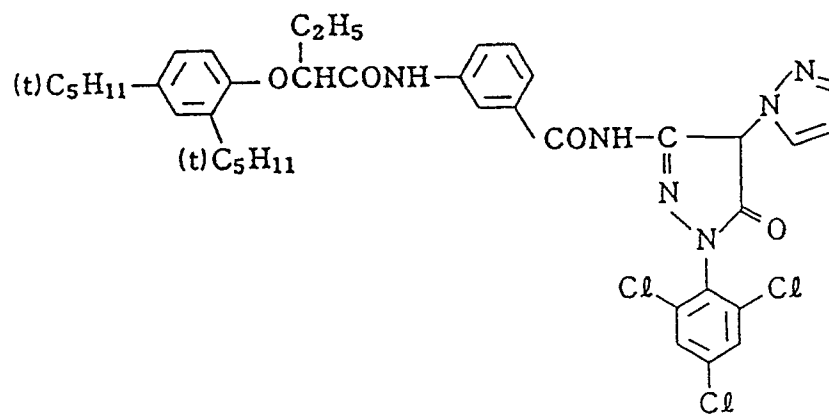
ExM-14

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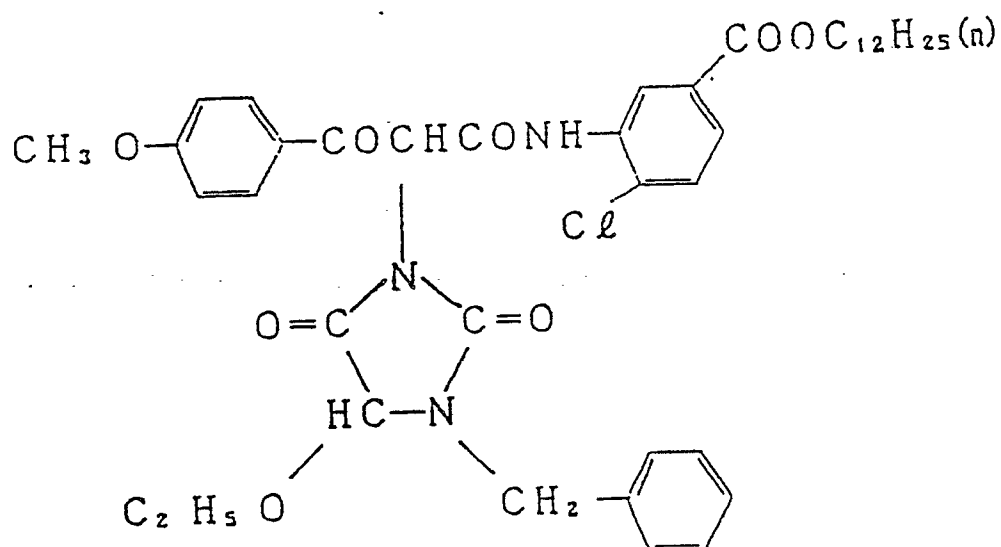
45

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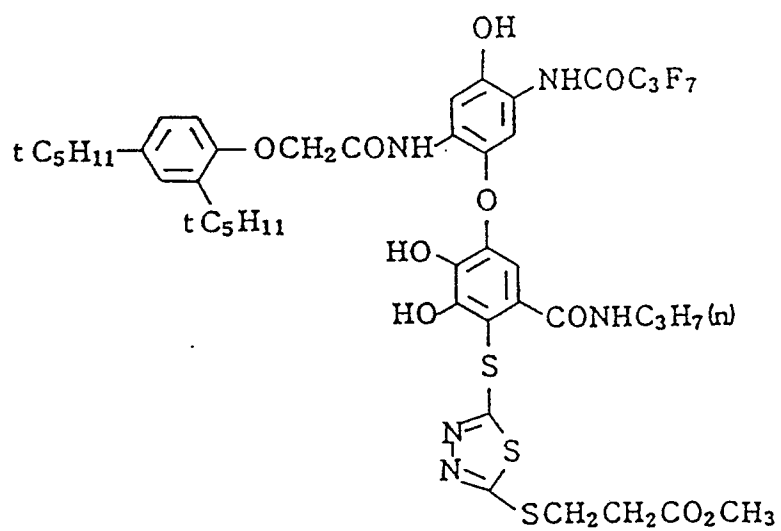
55



## Ex Y-15



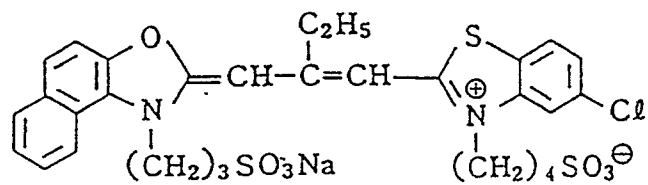
## Ex Y-16





ExS-1

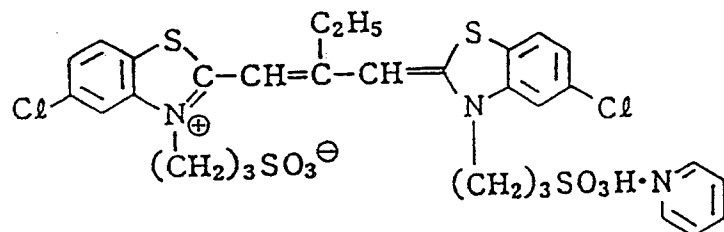
5



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ExS-2

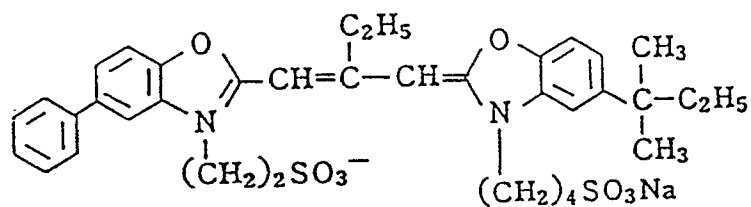
15



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ExS-3

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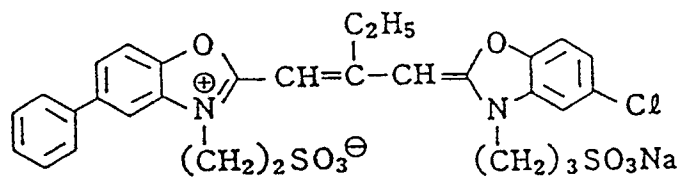


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ExS-4

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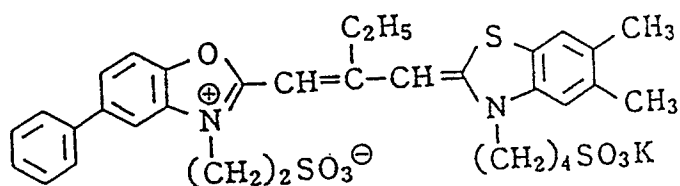


45

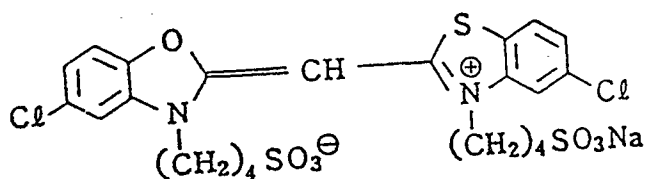
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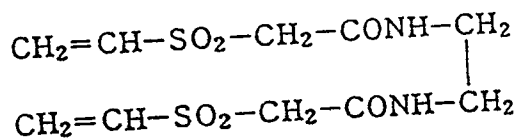
ExS-5



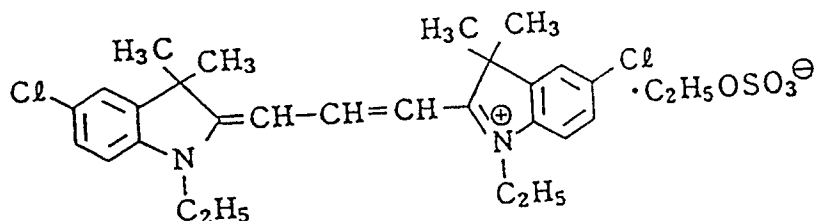
ExS-6



H-1



ExF-1



(Preparation of Samples 102 to 114)

Samples 102 to 114 were prepared with the same procedure as Sample 101, except that couplers shown in Table 1 were respectively added to the 11th layer and to the 12th layer in place of ExY-13 in such amount that the gradation when wedge-exposed by a blue light is to be equal.

(Preparation of Sample 120)

Sample 120 was prepared with the same procedure as Sample 101, except that ExY-15 was added to the 11th and to the 12th layer, respectively, in place of ExY-13 in the amount of equal mol to ExY-13.

(Evaluation of photographic characteristics)

The thus-prepared Samples 101 to 114 and 120 were evaluated for 1) sharpness, 2) interlayer effect, 3) stability of dye-image, and 4) sensitivity change after running processing according to the following procedures.

#### 1) Sharpness

After a light exposure to white light of a pattern for the MFT measurement, each sample was subjected to processing process I described below to evaluate a sharpness by the measurement of MFT.

#### 2) Interlayer effect

Each sample was subjected to an wedge exposure to a yellow light after a uniform exposure to a green light and then a development process according to processing process I described below. The thus-processed samples were evaluated as to density and the degree of interlayer effect by a green-density  $D_G$  at the portion of yellow density of 1.5.

#### 3) Stability of the dye image

Each sample was subjected to a wedge exposure to a white light and then to a development process according to the following processing process I. Then, each sample was subjected to a humidity and heat stability test by leaving samples in the atmosphere of 60 °C and 70 % RH. The density after the test for the portion having yellow density of 1.0 before test was shown.

#### 4) Evaluation of sensitivity change after the running processing.

The sensitivities (at the portion having density of fogging + 0.2) of a processed sample immediately after starting an automatic developer (processing process I shown below) and a processed sample after 20 days from starting (after running processing 800 meter for 35 mm film) were measured to evaluate the sensitivity change (as sample for the running test, film that had taken a photograph of a standard object was used).

(Processing process I)

The development processing was carried out in accordance with the following procedure by an automatic developer (until the accumulated replenishing amount reached 3 times the tank volume of the mother solution).

Processing procedure				
Step	Time (min.:sec.)	Temp. (° C)	Replenisher Amount(ml)*	Tank Volume(l)
Color developing	3 : 15	38	45	10
Bleaching	1 : 00	38	20	4
Bleach-fixing	3 : 15	38	30	8
Water-washing(1)	: 40	35	**	4
Water-washing(2)	1 : 00	35	30	4
Stabilizing	: 40	38	20	4
Drying	1 : 15	55		
Note:				

\* replenisher amount per 35 mm width 1 m length

\*\* counter current piping system from washing (2) to (1)

The compositions of the processing solutions were as follows:

Color-developing solution		Mother solution(g)	Replenisher (g)
Diethylenetriaminepentaacetate		1.0	1.1
1-Hydroxyethylidene-1,1-diphosphonate		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- $\beta$ -hydroxyethylamino)-2-methylaniline sulfate		4.5	5.5
Water to make		1.0 l	1.0 l
pH		10.05	10.10

#### Bleaching solution

(Both mother solution and replenisher are the same)

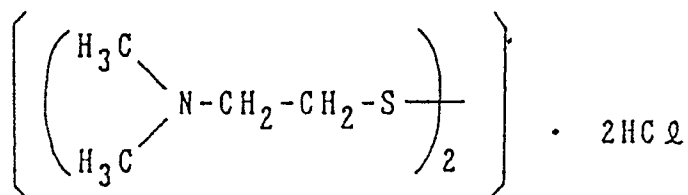
(g)

Ferric ammonium ethylenediamine-

5	tetraacetate dihydrate	120.0
	Disodium ethylenediaminetetraacetate	10.0
	Ammonium bromide	100.0
10	Ammonium nitrate	10.0
	Bleach accelerator	0.005 mol

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Aqueous ammonia (27%)	15.0 ml
Water to make	1.0 l
pH	6.3

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Bleach-fixing solution

(Both mother solution and replenisher are the same)

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	(g)
Ferric ammonium ethylenediaminetetraacetate dihydrate	50.0
Disodium ethylenediaminetetraacetate	5.0
Sodium sulfite	12.0
Ammonium thiosulfite aqueous solution (70%)	240.0 ml
Aqueous ammonia (27%)	6.0 ml
Water to make	1.0 l
pH	7.2

45

Water washing solution

(Both mother solution and replenisher are the same)

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Tap water was treated by passage through a hybrid-type column filled with an H-type strong acidic cation-exchange resin (Amberlite IR-120B, made by Rohm & Haas) and an OH-type strong alkaline anion-exchange resin (Amberlite IRA-400, made by the same company) to obtain water containing calcium and magnesium ions of each below 3mg/l. To the thus-treated water, 20 mg/l of sodium dichloro-isocyanurate and 150 mg/l of sodium sulfate were added. The pH of this solution was in a range of 6.5 to 7.5.

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Stabilizing solution

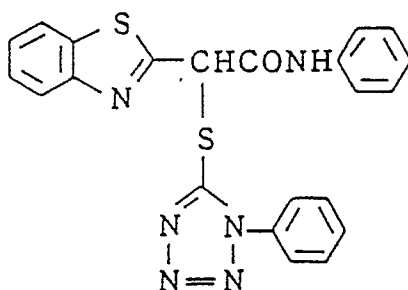
(Both mother solution and replenisher are the same)

	(g)
Formalin (37 %)	2.0 ml
Polyoxyethylene-p-monononylphenyl ether (av. polymerization degree of 10)	0.3
Disodium ethylenediaminetetraacetate	0.05
Water to make	1.0 l
pH	5.0 - 8.0

Comparative couplers used are as follows:

### Comparative coupler (1)

(coupler described in JP-A No. 82423/1977)



## Comparative coupler (2)

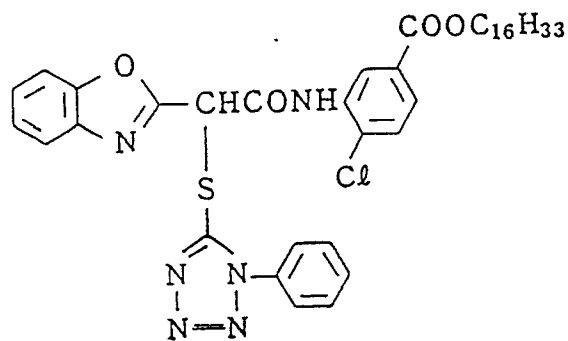
(coupler described in JP-A No. 82423/1977)

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## Comparative coupler (3)

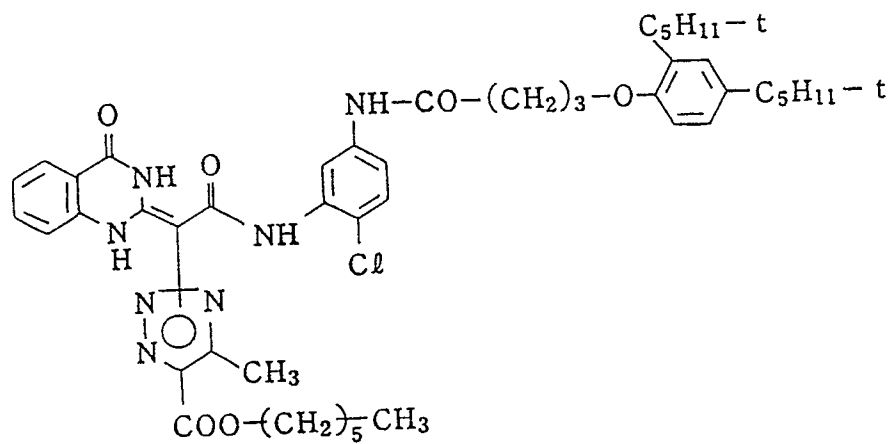
(coupler described in JP-A No. 261262/1988)

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Table 1

Sample No.	Coupler in the 11th and the 12th layers		MTF-value*	D <sub>G</sub> **	Fastness of Image	Sensitivity Change
101(Comparative Example)	ExY-13		+ 0.15	- 0.23	0.73	± 0
102( " )	Comparative Coupler	(1)	+ 0.12	- 0.15	0.97	- 0.18
103( " )	"	(2)	+ 0.13	- 0.16	0.97	- 0.16
104( " )	"	(3)	+ 0.14	- 0.19	0.82	- 0.10
105(This Invention)	Exemplified Coupler	(1)	+ 0.15	- 0.24	0.96	± 0
106( " )	"	(2)	+ 0.16	- 0.23	0.97	± 0
107( " )	"	(3)	+ 0.16	- 0.24	0.98	± 0
108( " )	"	(6)	+ 0.15	- 0.23	0.97	- 0.01
109( " )	"	(10)	+ 0.15	- 0.23	0.97	± 0
110( " )	"	(21)	+ 0.16	- 0.24	0.98	± 0
111( " )	"	(22)	+ 0.15	- 0.23	0.97	- 0.01
112( " )	"	(32)	+ 0.12	- 0.16	0.99	± 0
113( " )	"	(33)	+ 0.13	- 0.15	0.96	± 0
114( " )	"	(34)	+ 0.12	- 0.15	0.97	- 0.01
120(Contrast)	ExY-15		0	0	0.98	± 0
Notes:						

\* MTF-value of green-sensitive layer, spatial frequency 5c/mm is shown by the difference between the MTF-value of sample 120

\*\* It is shown by the difference between the D<sub>G</sub> of sample 120

As is apparent from the results in Table 1, Sample 101, which employed a coupler described in U.S. Patent No. 4,477,563, has a problem of image-dye fastness, although a change of sensitivity is not observed. On the other hand, Samples 102 and 104 which employed couplers described in JP-A Nos. 82423/1972 and 261262/1988, have a problem such that the sensitivity lowers during the running processing, although there is no problem with image-dye fastness.

In contrast with the above, Samples 105 to 114 solved these problems, being excellent in sharpness and color reproduction.

## Example 2

The same evaluation as in Example 1 was carried out, except that the processing process was changed to the following processing process II.

As results, the photographic images obtained by samples of the present invention were the same as in Example 1, with excellent image-dye fastness, sharpness, and color reproduction, and no change in sensitivity after the running processing.



Processing process II			
Step	Processing Time	Temperature	Replenisher Amount *
Color developing	3 min.15 sec.	38 °C	38 ml
Bleaching	45 sec.	38 °C	4 ml
Fixing	1 min.30 sec.	38 °C	30 ml
Stabilizing 1	20 sec.	38 °C	-
Stabilizing 2	20 sec.	38 °C	-
Stabilizing 3	20 sec.	38 °C	35 ml**
Drying	1 min.	50-70 °C	-
Notes:			

\* replenisher amount per 35 mm width 1 m length

\*\* three tanks counter current flow system from stabilizing 3 to 2, and 2 to 1

The compositions of the processing solutions were as follows:

Color-developing solution	Mother solution(g)	Replenisher (g)
Diethylenetriaminepentaacetate	5.0	6.0
Sodium sulfite	4.0	4.4
Potassium carbonate	30.0	37.0
Potassium bromide	1.3	0.9
Potassium iodide	1.2 mg	-
Hydroxylamine sulfate	2.0	2.8
4-(N-ethyl-N- $\beta$ -hydroxyethylamino)-2-methylaniline sulfate	4.7	5.3
Water to make	1.0 l	1.0 l
pH	10.00	10.05

Bleaching solution

Mother

Replenisher

solution(g)

(g)

5 Ferric ammonium ethylenediamine-

tetraacetate dihydrate

72.0

107.0

10 Ferric ammonium 1, 3-diaminopropane-

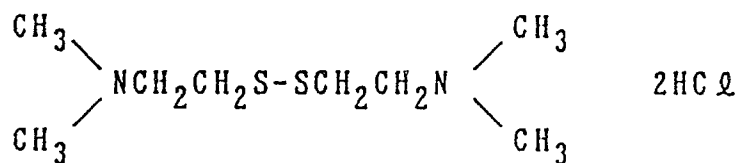
teraacetate

38.0

56.0

Bleach accelerator

0.005 mol



1,3-Diaminopropanetetraacetate 4.0

5.0

25 Ammonium bromide

100.0

160.0

Ammonium nitrate

30.0

50.0

Aqueous ammonia (27%)

20.0 ml

23.0 ml

30 Acetic acid (98 %)

9.0 ml

15.0 ml

Water to make

1.0 l

1.0 l

35 pH

5.4

4.5

Fixing solution

Mother

Replenisher

40 solution(g)

(g)

1-Hydroxyethylidene-1,1-diphosphate

		5.0	6.0
	Sodium sulfite	7.0	8.0
5	Sodium hydrogensulfite	5.0	5.5
	Ammonium thiosulfite aqueous solution (70%)		
		170.0 ml	200.0 ml
10	Water to make	1.0 l	1.0 l
	pH	6.7	6.8

15

Stabilizing solution

20 (Both mother solution and replenisher are the same)

		(g)
25	Formalin (37 %)	1.2 ml
	5-Chloro-2-methyl-4-isothiazoline-3-on	
		6.0 mg
30	2-Methyl-4-isothiazoline-3-on	3.0 mg
	Surface-active agent	0.4
35	$[C_{10}H_{21}-O-(CH_2CH_2O)_{10}H]$	
	Ethylene glycol	1.0
	Water to make	1.0 l
40	pH	5.0 - 7.0

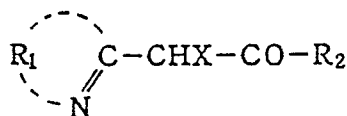
45 Having described our invention as related to the embodiment, it is our intention that the invention be not limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

**Claims**

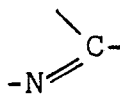
50 1. A silver halide color photographic material wherein a compound represented by the formula (I) given below is contained in at least one hydrophilic colloid layer formed on a support:

Formula (I)

55

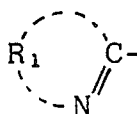


wherein R<sub>1</sub> represents a group of non-metallic atoms required to form a heterocyclic group together with the



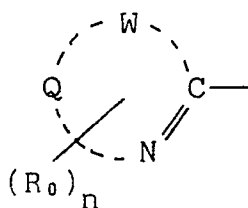
residue, R<sub>2</sub> represents an organic residue, and X represents a group of such a nature that when the compound reacts with the oxidized product of an aromatic primary amine developing agent, X splits off to act as a development retarder or a development retarder precursor that will be decomposed into a substantially photographically noninfluential compound after flowing into the color-developing solution.

2. The silver halide color photographic material as claimed in claim 1, wherein the heterocyclic group represented by

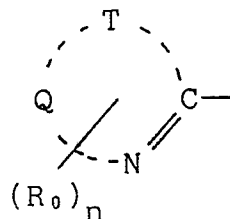


in formula (I) is represented by formula (IIa), (IIb), (IIc), or (IId):

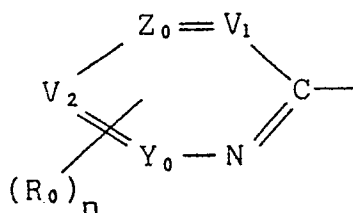
Formula (IIa)



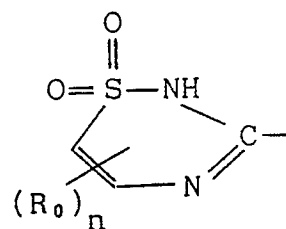
Formula (IIb)



Formula (IIc)

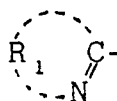


Formula (IIId)



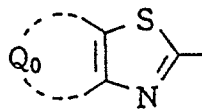
wherein W represents N, O, or S; Q represents a group of nonmetallic atoms which form a 5- to 7-membered ring together with W and -N=C; R<sub>0</sub> represents a substituent; n is an integer of 0 to 2; T represents a carbonyl or a sulfonyl group, T, Q, and -N=C together form a 5- or 7-membered ring; at least one of Y<sub>0</sub> and Z<sub>0</sub> represents N, otherwise being C; V<sub>1</sub> and V<sub>2</sub> each represent N or C; and when n is 2, two R<sub>0</sub>'s each may be the same or different, including either to form a ring together or not to form a ring.

3. The silver halide color photographic material as claimed in claim 1, wherein the heterocyclic group represented by

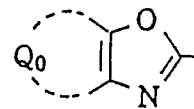


in formula (I) is selected from the group consisting of rings represented by formulae (III), (IV), (V), (VI), (VII), and (VIII):

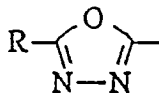
Formula (III)



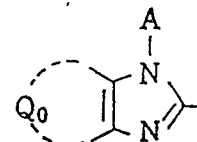
Formula (IV)



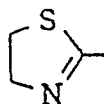
Formula (V)



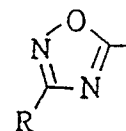
Formula (VI)



Formula (VII)

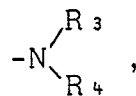


Formula (VIII)



wherein  $Q_0$  represents a substituted or unsubstituted 1,2-condensed benzene ring, A represents a hydrogen atom, a monovalent group selected from the group consisting of an alkyl, an alkoxyalkyl, a halogenoalkyl, an aralkyl and an aryl, and R represents a hydrogen atom, or a substituent selected from the group consisting of an alkyl group, an aryl group, a halogen atom, an alkoxy group, an acylamino group and or an alkylthio group.

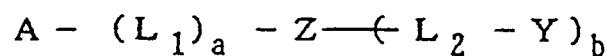
4. The silver halide color photographic material as claimed in claim 1, wherein the organic residue represented by  $R_2$  in formula (I) is a straight-chain or branched, or chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, or a group



in which  $R_3$  and  $R_4$  each represent a hydrogen atom, an aliphatic group, an aromatic group, or a heterocyclic group.

5. The silver halide color photographic material as claimed in claim 1, wherein X in the formula (I) is represented by formula (IX) in which X is linked to a coupler residue A:

Formula (IX)



wherein A represents the coupler residue, Z represents a basic part of the compound that exhibits a

development-retarding effect and is linked to the coupling position of the coupler directly or through a linking group  $L_1$ , Y represents a substituent that causes the development-retarding effect of Z to be exhibited, the linking group represented by  $L_2$  includes a chemical bond that is cleaved in the developing solution, a is 0 or 1, b is 1 or 2, and when b is 2,  $-L_2-Y$ 's may be the same or different.

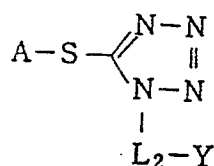
6. The silver halide color photographic material as claimed in claim 5, wherein the basic part of the development retarder represented by Z in formula (IX) is a divalent nitrogen-containing heterocyclic group or nitrogen-containing heterocyclic thio group.

7. The silver halide color photographic material as claimed in claim 6, wherein said heterocyclic is selected from the group consisting of tetrazolyl, benzthiazolyl, benzimidazolyl, thiazolyl, oxadiazolyl, triazolyl, and imidazolyl.

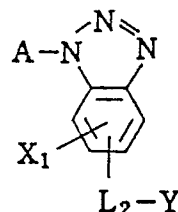
8. The silver halide color photographic material as claimed in claim 5, wherein the group represented by Y in formula (IX) is an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an aryl group, an aralkyl group, or a heterocyclic group.

9. The silver halide color photographic material as claimed in claim 5, wherein the coupler represented by formula (IX) is selected from the group, consisting of compounds represented by the following formulae (X), (XI), (XII), (XIII), (XIV), (XV), and (XVI):

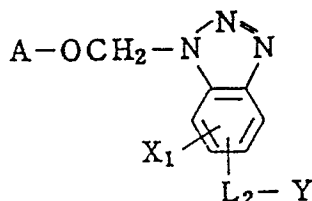
Formula (X)



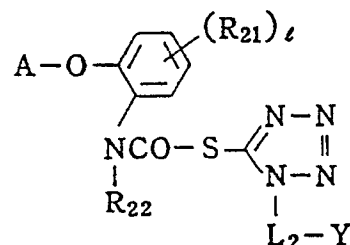
Formula (XI)



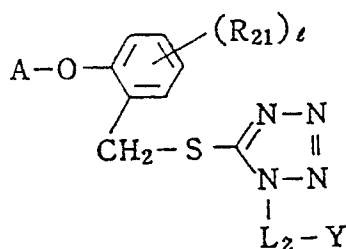
Formula (XII)



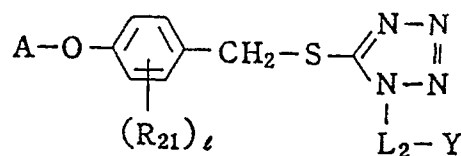
Formula (XIII)



Formula (XIV)



Formula (XV)

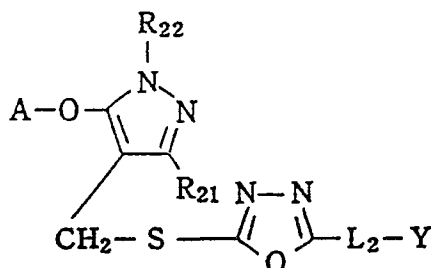


## Formula (XVI)

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wherein A, L<sub>2</sub>, and Y have the same meanings as those in formula (IX), R<sub>21</sub> represents a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an aralkyl group, an alkoxy group, an alkoxy carbonyl group, an anilino group, an acylamino group, an ureido group, a cyano group, a nitro group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, an aryl group, a carboxy group, a sulfo group, a cycloalkyl group, an alkanesulfonyl group, an arylsulfonyl group, or an acyl group; R<sub>22</sub> represents a hydrogen atom, an alkyl group, an alkenyl group, an aralkyl group, a cycloalkyl group, or an aryl group;  $\ell$  is 1 or 2, and when  $\ell$  is 2, R<sub>21</sub> and R<sub>22</sub> may bond together to form a condensed ring.

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10. The silver halide color photographic material as claimed in claim 1, wherein the compound represented by formula (I) is included in an amount of  $1 \times 10^{-7}$  to 0.5 mol per mol of silver present in the same layer or in the adjacent layer.

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11. The silver halide color photographic material as claimed in claim 1, wherein the compound represented by formula (I) is included in an amount of  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol per mol of silver present in the same layer or in the adjacent layer.

12. The silver halide color photographic material as claimed in claim 1, wherein the compound represented by formula (I) is used in combination with another color image-forming coupler.

13. The silver halide color photographic material as claimed in claim 11, wherein the molar ratio of the compound represented by formula (I) to the other color image-forming coupler is from 0.1/99.9 to 90/10.

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14. The silver halide color photographic material as claimed in claim 11, wherein the molar ratio of the compound represented by formula (I) to the other color image-forming coupler is from 1/99 to 50/50.

15. The silver halide color photographic material as claimed in claim 1, wherein the silver halide color photographic material has on a support at least one silver halide emulsion layer selected from a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer.

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16. The silver halide color photographic material as claimed in claim 15, wherein the silver halide color photographic material has on the support at least one photosensitive layer consisting of several silver halide emulsion layers, whose color sensitivities are substantially the same and whose photographic sensitivities are different, the photosensitive layer being one having a color sensitivity to any one of blue light, green light, and red light.

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17. The silver halide color photographic material as claimed in claim 15, wherein the silver halide emulsion layer constitutes a unit photosensitive layer made of a two-layer constitution consisting of a high-speed emulsion layer and a slow-speed emulsion layer.

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