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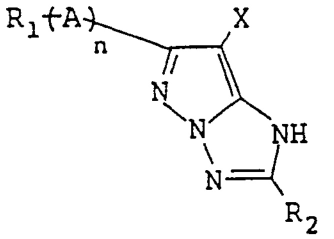
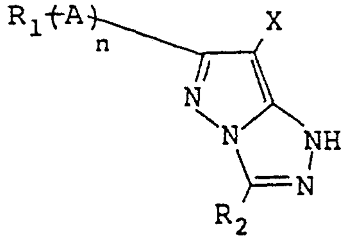
(54) Silver halide color photographic material and method for processing thereof.

(57) A silver halide color photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one light-insensitive layer, wherein at least one layer of the light-sensitive silver halide emulsion layers contains at least one dye forming coupler represented by the general formulas (I) or (II) described below and the weight ratio of an organic solvent having a high boiling point to the dye forming coupler in the layer is not more than 1:



(I)



(II)

wherein R_1 represents a branched chain alkyl group or an aryl group; R_2 represents a hydrogen atom or a substituent; X represents a hydrogen atom or a substituent being released upon a coupling reaction with an

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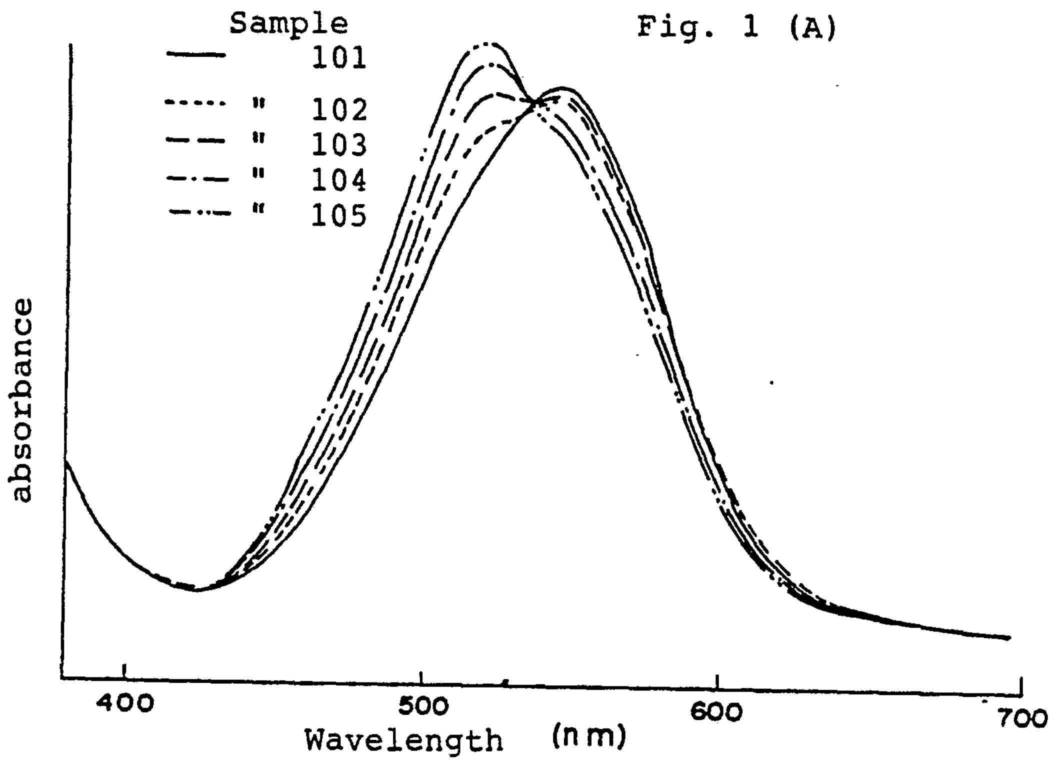
oxidation product of an aromatic primary amine developing agent; A represents an oxygen atom, a nitrogen atom or a sulfur atom; and n represents 0 or 1.

Fig. 1 (A)



SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL AND METHOD FOR PROCESSING THEREOF

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material.

BACKGROUND OF THE INVENTION

Among silver halide color photographic materials, those containing three kinds of color couplers which form yellow, magenta and cyan colors upon coupling with an oxidation product of an aromatic primary amine color developing agent, respectively, are most conventional.

As magenta couplers employed therein, pyrazolotriazole type magenta couplers, for example, those described in U.S. Patent 3,725,067, are preferred in view of color reproduction because they form azomethine dyes which have a less undesirable subsidiary absorption in the region around 430 nm. Also, they are preferred since the occurrence of stains in uncolored portions of the photographic material owing to heat or humidity is restrained.

It is important to reduce the dry layer thickness of color photographic light-sensitive materials for the purpose of improving image quality, particularly sharpness.

Couplers are usually dissolved in an organic solvent having a high boiling point and the emulsified dispersion thereof is coated on a support to prepare a color photographic light-sensitive material. Therefore, decreasing the amount of the organic solvent having a high boiling point is important to reduce the layer thickness. Since the amount of the organic solvent having a high boiling point is related to the mechanical strength of the layer, decreasing the amount of the organic solvent having a high boiling point results in a reduction of the amount of gelatin used.

Where pyrazoloazole type couplers are used, however, there is a serious problem in that when the amount of organic solvent having a high boiling point is reduced, a large subsidiary absorption on the short wavelength side is generated due to the occurrence of aggregation of the dyes formed upon processing. The generation of subsidiary absorption leads to degradation of color reproducibility. Therefore, it has been desired to develop pyrazoloazole type magenta couplers whose use does not lead to aggregation of the dyes formed upon processing.

In JP-A-63-321426 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), various additives for the purpose of eliminating such aggregation are disclosed. However, the introduction of additives leads to increased layer thickness, which results in deterioration of sharpness. Further, it is feared that the preservability of the photographic material is adversely affected.

Combinations of pyrazolotriazole type couplers and organic solvents having a high boiling point are described, for example, in JP-A-61-28948, JP-A-61-267760, JP-A-62-79451, JP-A-62-86363, JP-A-62-92946, JP-A-62-98352, JP-A-62-148951, and JP-A-63-10454. However, the particular combination of couplers and organic solvents having a high boiling point according to the present invention is not disclosed in these references. Nor is there any discussion bearing on preventing aggregation of the dyes formed.

The *Journal of The Society of Photographic Science and Technology of Japan*, Vol. 52, page 162 (1989), describes a relationship between the bulk of an alkyl group present at the 6-position of a pyrazolotriazole coupler and the absorption spectrum and light fading of the dye formed therefrom in a liquid phase. However, since the reported experiment was conducted in a diluted uniform solution, it is impossible to predict from this experiment a practical system which employs an organic solvent having a high boiling point.

Because of the poor light fastness of pyrazolotriazole type couplers, their use necessitates the addition of large amounts of color fading preventing agents. Further, their light fastness tends to decrease when the amount of organic solvent having a high boiling point is reduced.

Therefore, methods for preventing aggregation of dyes and for improving light fastness while decreasing the amount of organic solvent having a high boiling point have been investigated by modification of coupler structures.

Moreover, where pyrazolotriazole type couplers are used, magenta stains are apt to occur after development processing. This tendency is particularly serious when rapid processing is conducted or when processing is performed with a low level of replenishment. To solve such problems, it has been suggested to add an anti-staining agent to oil-droplets containing couplers. As a result, however, it is difficult to reduce the dry layer thickness.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a pyrazoloazole type coupler which forms a dye having good hue and which prevents the aggregation of dyes formed when the amount of organic solvent having a high boiling point which is employed with the coupler is reduced.

Another object of the present invention is to provide a color photographic light-sensitive material using a pyrazoloazole type coupler which has improved hue and sharpness.

Still another object of the present invention is to provide a pyrazolotriazole type coupler which exhibits only a small degree of light fading even when the amount of organic solvent having a high boiling point is reduced.

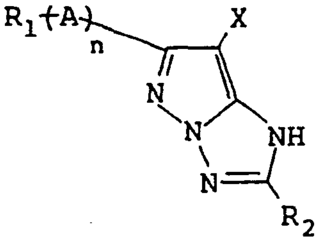
A further object of the present invention is to provide a silver halide color photographic material comprising a reflective support having coated thereon a layer containing a pyrazolotriazole type coupler and a reduced amount of an organic solvent having a high boiling point, which material has improved color reproducibility and light-fastness.

A still further object of the present invention is to provide a silver halide color photographic material containing a pyrazolotriazole type coupler and a reduced amount of an organic solvent having a high boiling point, which material has improved color reproducibility and light-fastness when it is processed by processing steps comprising black-and-white development and color development.

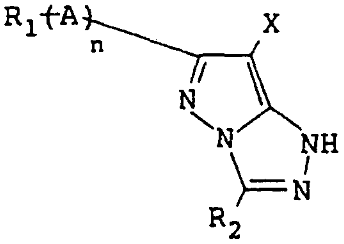
A still further object of the present invention is to provide a color photographic light-sensitive material which is improved in terms of the formation of stains and which has excellent color reproduction, even when it is subjected to rapid processing or processing with a low level of replenishment.

Other objects of the present invention will become apparent from the following detailed description and examples.

As a result of various investigations, it has been found that these objects of the present invention can be accomplished by a silver halide color photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one light-insensitive layer, wherein at least one layer of the light-sensitive silver halide emulsion layers contains at least one dye forming coupler represented by the general formulas (I) or (II) described below and the weight ratio of an organic solvent having a high boiling point to the dye forming coupler in the layer is not more than 1:



(I)



(II)

wherein R_1 represents a branched chain alkyl group or an aryl group; R_2 represents a hydrogen atom or a substituent; X represents a hydrogen atom or a substituent which is released upon a coupling reaction with an oxidation product of an aromatic primary amine developing agent; A represents an oxygen atom, a nitrogen atom or a sulfur atom; and n represents 0 or 1.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

Figs. 1(A) to 1(D) are graphs showing reflective spectra of color images obtained when Samples 101 to 120 were exposed to green light and subjected to development processing.

Figs. 2(A) to 2(D) are graphs showing transmitant spectra of color images obtained when only the green sensitive layers of Samples 201 to 216 were subjected to color formation.

DETAILED DESCRIPTION OF THE INVENTION

The pyrazolotriazole magenta couplers represented by the general formulas (I) and (II) are described in greater detail below.

In the general formulas (I) and (II), R_1 represents a substituted or unsubstituted branched chain alkyl group or a substituted or unsubstituted aryl group.

The unsubstituted branched chain alkyl group includes a branched chain alkyl group having from 3 to 24 carbon atoms. Suitable examples of substituents for the substituted branched chain alkyl group include a halogen atom (e.g., fluorine, chlorine, and bromine), a hydroxy group, a cyano group, a carboxy group, a sulfo group, an alkoxy group (e.g., methoxy, ethoxy, isopropyloxy, and butoxy), an aryloxy group (e.g., phenoxy, 2,4-di-tert-amylphenoxy, p-tert-octylphenoxy, and o-methoxyphenoxy), an alkylthio group (e.g., methylthio, ethylthio, butylthio, octylthio, and hexadecylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, and 2-pivaloylaminophenylthio), an acylamino group (e.g., acetylamino, pivaloylamino, 2-ethylhexanoylamino, and tetradecanoylamino), a sulfonamido group (e.g., methanesulfonamido, hexadecanesulfonamido, and p-toluenesulfonamido), a carbamoyl group (e.g., N-butylcarbamoyl, and N,N-diethylcarbamoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, and N,N-diisopropylsulfamoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, and 2-ethylhexyloxycarbonyl), an alkylamino group (e.g., ethylamino, isopropylamino, tert-octylamino, and dodecylamino), an anilino group, a carbamoylamino group, an alkoxycarbonylamino group, an acyloxy group, and a sulfonyl group.

The unsubstituted aryl group includes a phenyl group and a naphthyl group. Suitable examples of substituents for the substituted aryl group include a halogen atom (e.g., fluorine, chlorine, and bromine), a hydroxy group, a cyano group, a carboxy group, a sulfo group, an alkyl group (e.g., methyl, ethyl, tert-butyl, and tert-octyl), an alkoxy group (e.g., methoxy, ethoxy, isopropyloxy, and butoxy), an aryloxy group (e.g., phenoxy, p-tert-octylphenoxy, and o-methoxyphenoxy), an alkylthio group (e.g., methylthio, ethylthio, butylthio, and hexadecylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, and 2-pivaloylaminophenylthio), an acylamino group (e.g., acetylamino, pivaloylamino, 2-ethylhexanoylamino, and tetradecanoylamino), a sulfonamido group (e.g., methanesulfonamido, hexadecanesulfonamido, p-toluenesulfonamido, and 2-octyloxy-5-tert-octylbenzenesulfonamido), a carbamoyl group (e.g., N-methylcarbamoyl, N-butylcarbamoyl, N,N-diethylcarbamoyl, and N,N-diisopropylcarbamoyl), a sulfamoyl group (e.g., N-methylsulfamoyl, N-ethylsulfamoyl, N,N-diethylsulfamoyl, and N,N-diisopropylsulfamoyl), an alkoxycarbamoyl group (e.g., methoxycarbamoyl, ethoxycarbamoyl, 2-ethylhexyloxycarbamoyl, and dodecyloxycarbamoyl), an alkylamino group (e.g., ethylamino, isopropylamino, butylamino, dodecylamino, and N,N-dibutylamino), an anilino group, a carbamoylamino group, an alkoxycarbonylamino group, and a sulfonyl group.

In the general formulas (I) and (II), R_2 represents a hydrogen atom or a substituent. Suitable examples of the substituent include a straight chain or branched chain, substituted or unsubstituted alkyl group having from 1 to 30 carbon atoms (e.g., methyl, ethyl, isopropyl, tert-butyl, 2-ethylhexyl, cyclohexyl, and adamantyl), an aryl group (e.g., phenyl, p-tolyl, 2-methoxyphenyl, 2-pivaloylamidophenyl, 2,4-dimethoxyphenyl, naphthyl, 3,4-dichlorophenyl, 3,5-dichlorophenyl, and 2-methanesulfonamidophenyl), a heterocyclic group (e.g., 4-pyridyl, and 2-furyl), an alkoxy group (e.g., methoxy, ethoxy, isopropyloxy, 2-phenoxyethoxy, and 2-methoxyethoxy), an aryloxy group (e.g., phenoxy, 2-methoxyphenoxy, 2,4-dimethoxyphenoxy, 2-chlorophenoxy, and 2,5-di-tert-amylphenoxy), a heterocyclic oxy group (e.g., furyloxy), an amino group (e.g., N-methylamino, and N,N-dibutylamino), an anilino group (e.g., 2-methoxyanilino, and 2,4-dichloroanilino), a heterocyclic amino group (e.g., 4-pyridylamino), an amido group (e.g., acetamido, and benzamido), a methane group (e.g., N-hexylurethane, and N,N-dibutylurethane), a ureido group (e.g., N,N-dimethylureido, and N-phenylureido), a sulfonamido group (e.g., butanesulfonamido, and p-toluenesulfonamido), an alkylthio group (e.g., ethylthio, and octylthio), an arylthio group (e.g., phenylthio, and 4-dodecyloxyphenylthio), a sulfinyl group (e.g., benzenesulfinyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, and p-toluenesulfonyl), a sulfo group, a cyano group, and a nitro group.

R_2 preferably represents a substituted or unsubstituted, straight chain or branched chain alkyl group or an aryl group.

In the general formulas (I) and (II), X represents a hydrogen atom or a substituent capable of being released upon coupling with an oxidation product of an aromatic primary amine developing agent. Suitable examples of the substituent include an aryloxy group (e.g., p-methylphenoxy, p-carboxyphenoxy, 2,4-di-tert-amylphenoxy, 2-pivaloylaminophenoxy, 2-methanesulfonamidophenoxy, and 2-methoxyphenoxy), a heterocyclic oxy group (e.g., furyloxy), an alkylthio group (e.g., dodecylthio, 2-hydroxyethylthio, carboxymethylthio, and 1-ethoxycarbonyltridecylthio), an arylthio group (e.g., 2-pivaloylaminophenylthio, and 2-butoxy-5-tert-octylphenylthio), a heterocyclic thio group, a halogen atom (e.g., fluorine, chlorine, and bromine), and a nitrogen-containing heterocyclic group bonded at the nitrogen atom therein (e.g., triazolyl, pyrazolyl, and imidazolyl).

In the general formulas (I) and (II), A represents an oxygen atom, a nitrogen atom or a sulfur atom, and n represents 0 or 1.

Of the couplers represented by the general formulas (I) and (II), these represented by the general formula (I) are preferred. Particularly, couplers represented by the general formula (I), wherein R_1 is a branched chain alkyl group and n is 0, wherein R_1 is a branched chain alkyl group, A is an oxygen atom and n is 1, and wherein R_1 is an aryl group, A is an oxygen atom and n is 1 are preferred.

A monomer containing the pyrazoloazole coupler moiety represented by general formula (I) or (II) may form a copolymer together with a non-color forming ethylenic monomer which does not undergo coupling with the oxidation product of an aromatic primary amine developing agent.

Examples of non-color forming ethylenic monomers which do not undergo coupling with the oxidation product of an aromatic primary amine developing agent include an acrylic acid such as acrylic acid, α-chloroacrylic acid, arid α-alkylacrylic acid (e.g., methacrylic acid), an ester or an amide derived from an acrylic acid (e.g., acrylamide, n-butylacrylamide, tert-butylacrylamide, diacetoneacrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, or β-hydroxy methacrylate), methylenedibisacrylamide, a vinyl ester (e.g., vinyl acetate, vinyl propionate, or vinyl laurate), acrylonitrile, methacrylonitrile, an aromatic vinyl compound (e.g., styrene and a derivative thereof, vinyltoluene, divinylbenzene, vinylacetophenone, or sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, a vinyl alkyl ether (e.g., vinyl ethyl ether), maleic acid, maleic anhydride, a maleic acid ester, N-vinyl-2-pyrrolidone, N-vinylpyridine, or 2- or 4-vinylpyridine.

Two or more kinds of non-color forming ethylenically unsaturated monomers can be used together. For example, a combination of n-butyl acrylate and methyl acrylate, a styrene and methacrylic acid, methacrylic acid and acrylamide, or methyl acrylate and diacetoneacrylamide can be used.

As is well known in the field of polymer color couplers, the non-color forming ethylenically unsaturated monomer which is copolymerized with a solid water-insoluble monomer coupler can be selected in such a manner that the copolymer formed has good physical properties and/or chemical properties (for example, solubility), compatibility with a binder such as gelatin in a photographic colloid composition, flexibility, and heat stability.

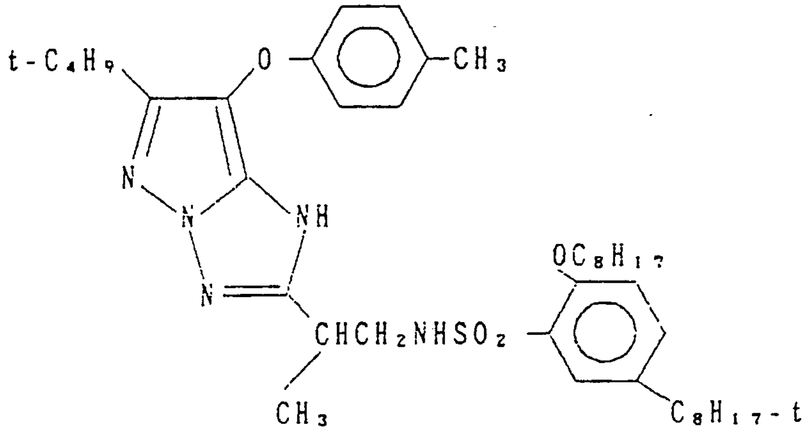
The polymer couplers used in the present invention may be water-soluble couplers or water-insoluble couplers, but polymer coupler latexes are particularly preferred as such polymer couplers.

Further, the couplers represented by the general formulas (I) or (II) may form a dimer through R_1, R_2 or X.

Specific examples of the pyrazoloazole couplers used in the present invention are set forth below, but the present invention should not be construed as being limited thereto.

The couplers represented by the general formulae (I) and (II) may be prepared according to a prior known process, for example, 1H-pyrazolo[1,5-b]-1,2,4-triazole of formula (I) is prepared by the process according to U.S. Patent 4,621,046 or 4,540,654 and 1H-pyrazolo[5,1-c]-1,2,4-triazole is prepared by the process according to U.S. Patent 3,725,067, Research Disclosure, item No. 12443, or J. Chem. Soc., Perkin I, p. 2047 (1977).

M－1



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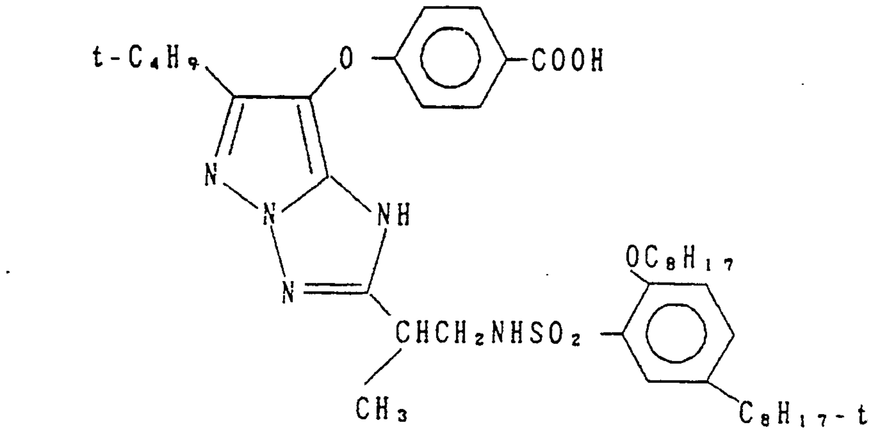
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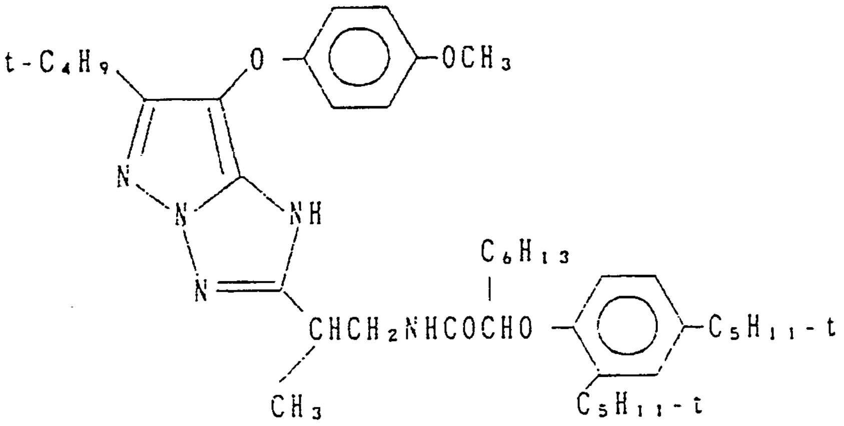
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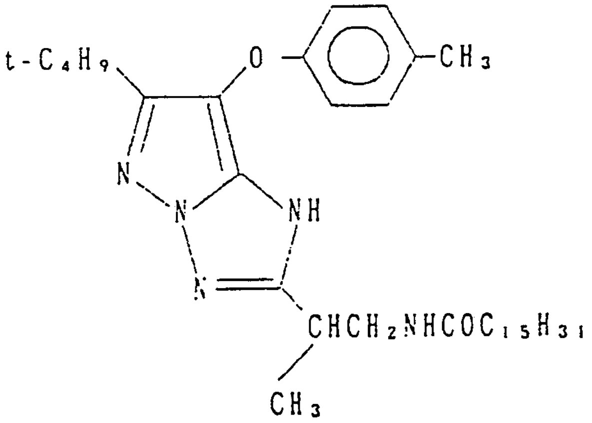
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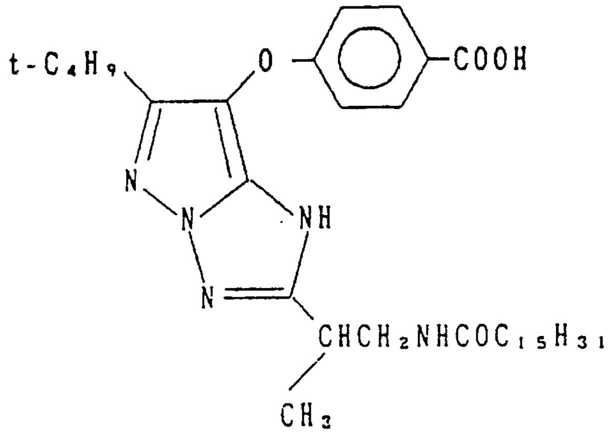
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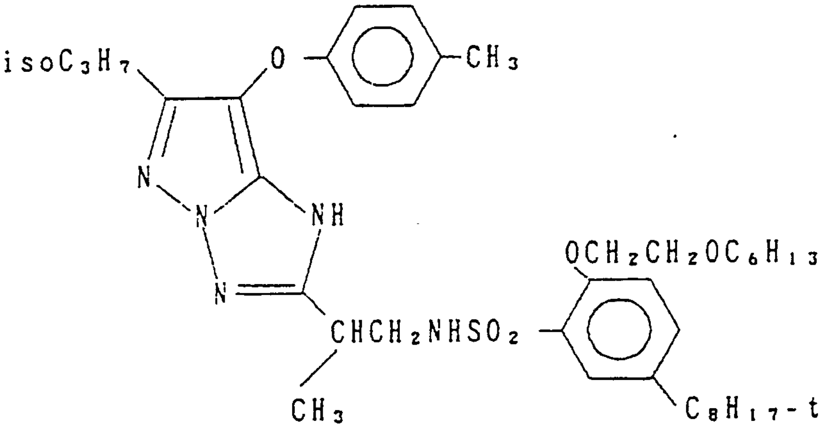
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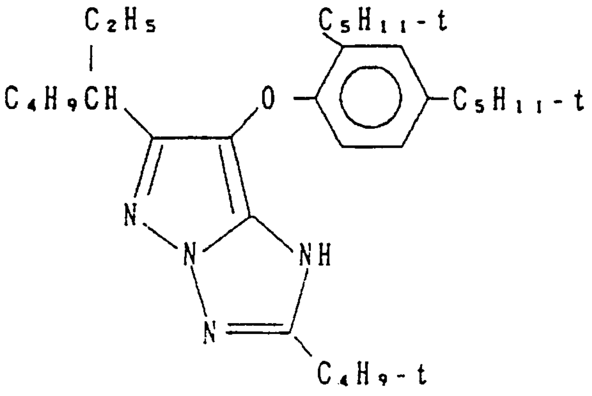

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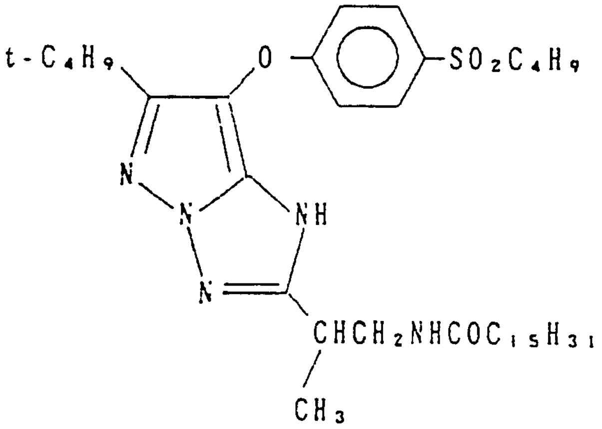

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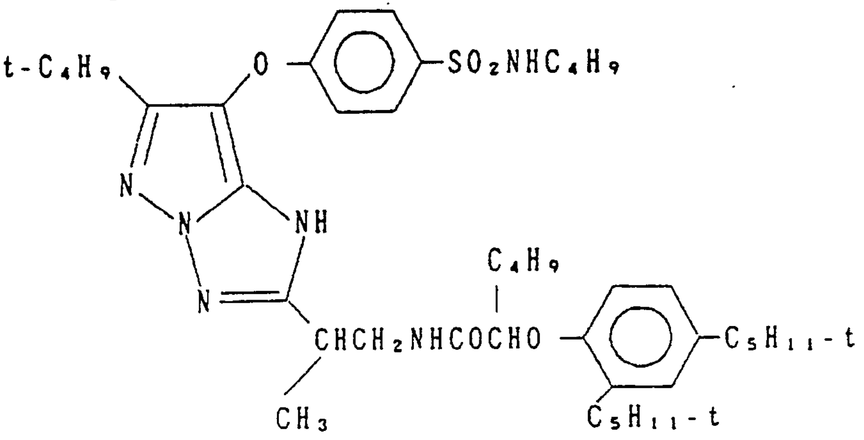
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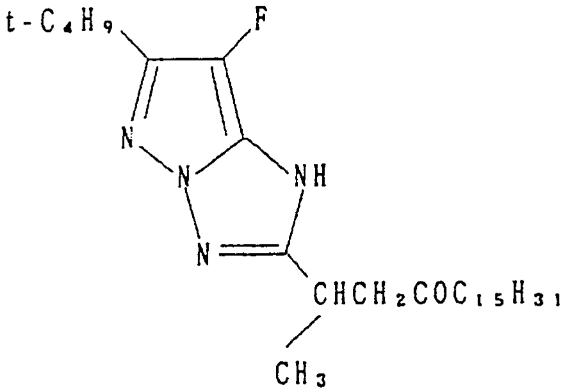
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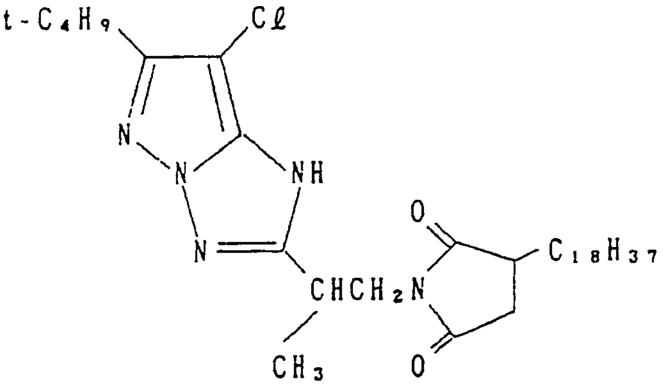
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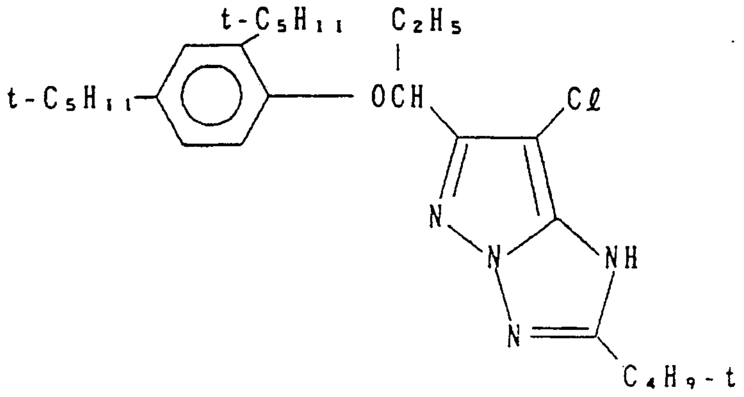

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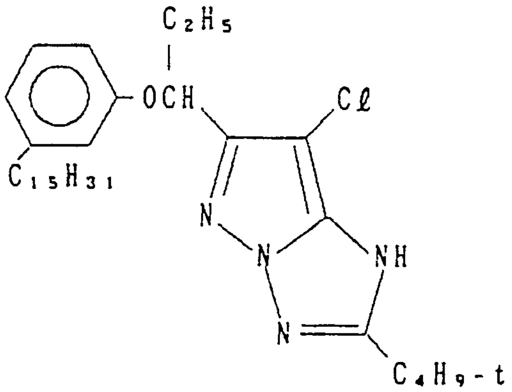

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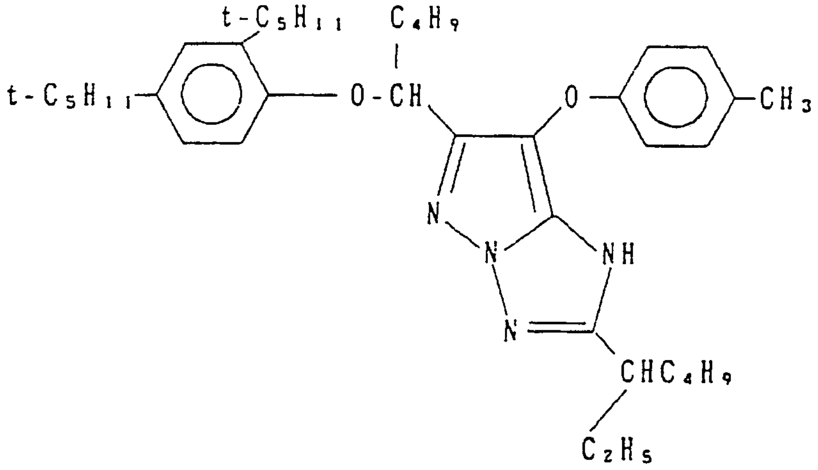

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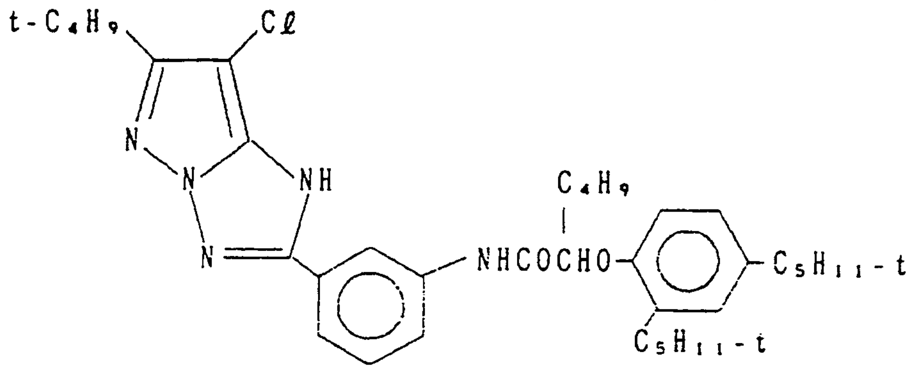
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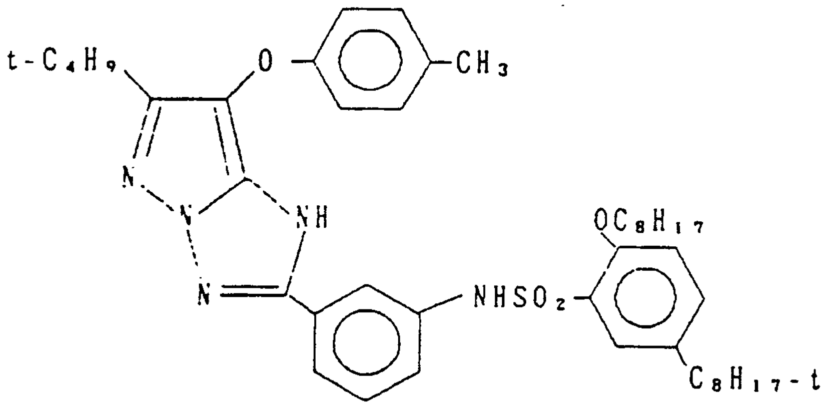
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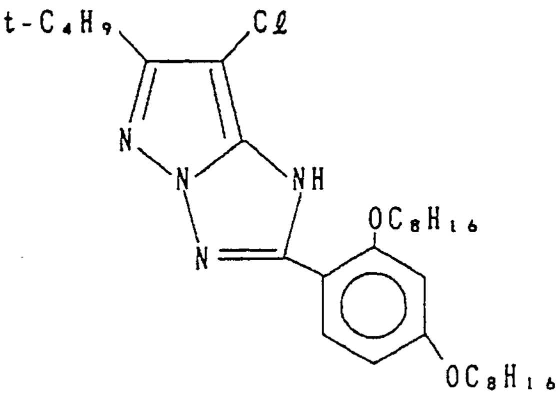
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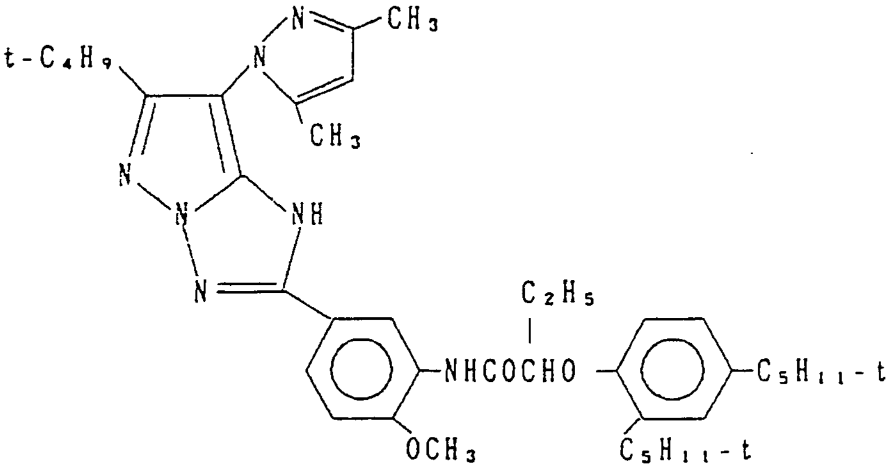
M－18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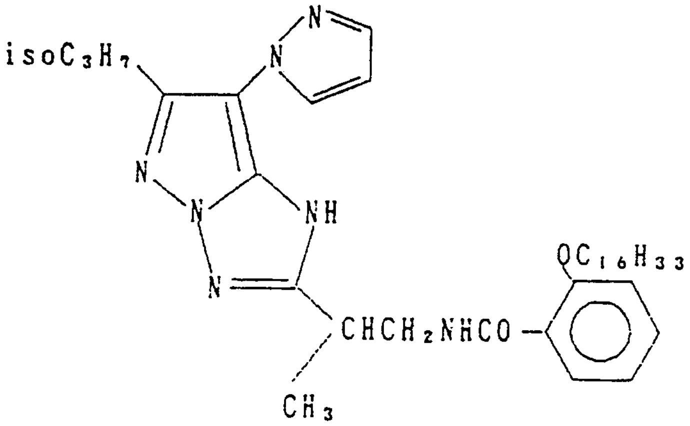
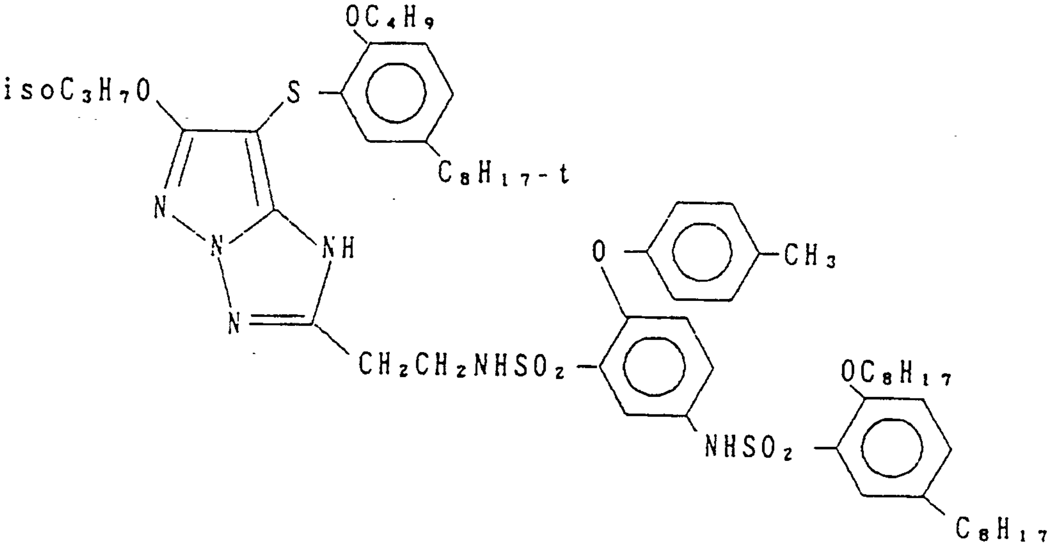
CH₃
CH₃
N
N
NH
N
C₂H₅
NHCOCHO
C₅H₁₁-t
OCH₃
C₅H₁₁-t

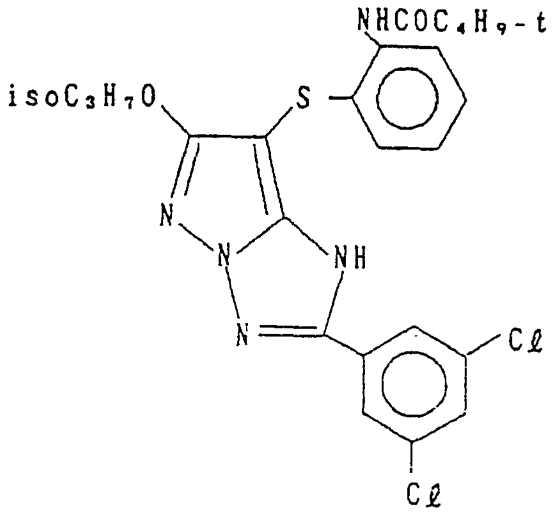
M－19


isoC3H7
N
N
N
N
NH
N
OC16H33
CHCH2NHCO
CH3

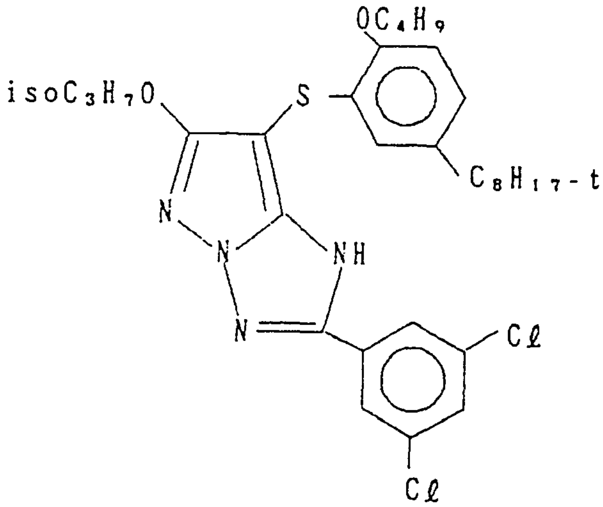
M－20


OC4H9
isoC3H7O
S
C8H17-t
N
N
NH
N
O
CH3
CH2CH2NHSO2
OC8H17
NHSO2
C8H17

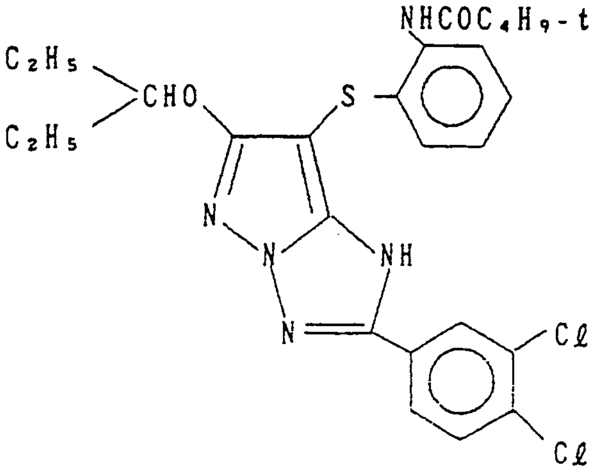
M－21


NHCOC₄H₉-t
isoC₃H₇O
S
N
N
NH
N
Cℓ
Cℓ

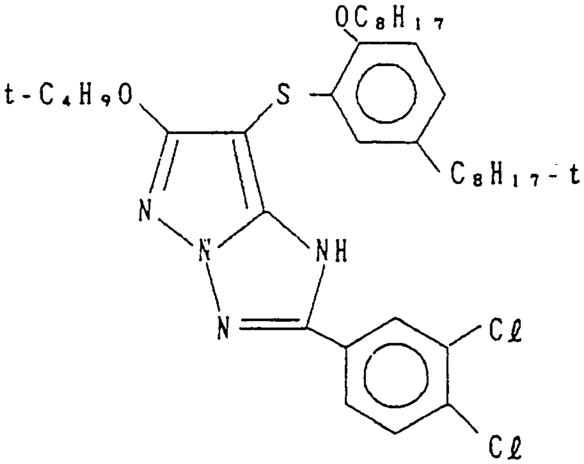
M－22


OC₄H₉
isoC₃H₇O
S
C₈H₁₇-t
N
N
NH
N
Cℓ
Cℓ

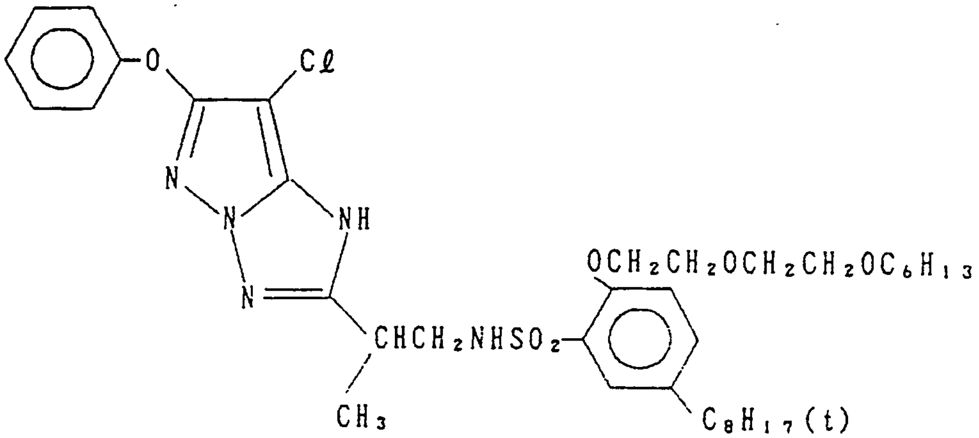
M－２３


NHCOC₄H₉-t
C₂H₅
CHO
C₂H₅
S
N
N
NH
N
Cℓ
Cℓ

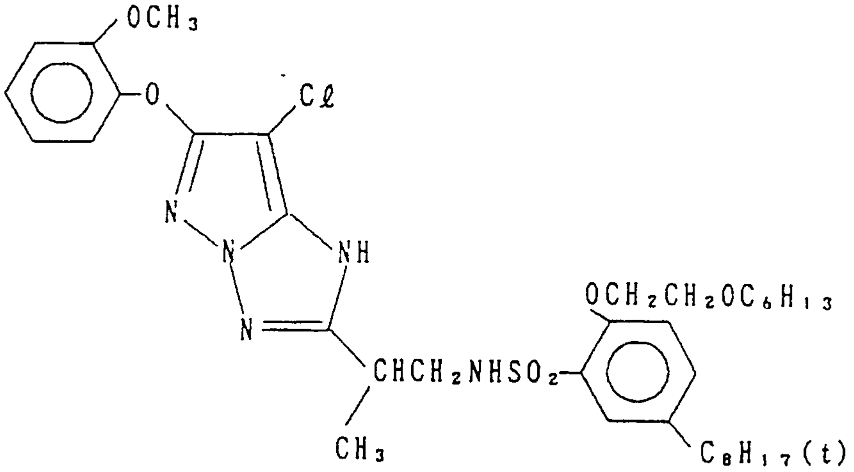
M－２４


OC₈H₁₇
t-C₄H₉O
S
C₈H₁₇-t
N
N
NH
N
Cℓ
Cℓ

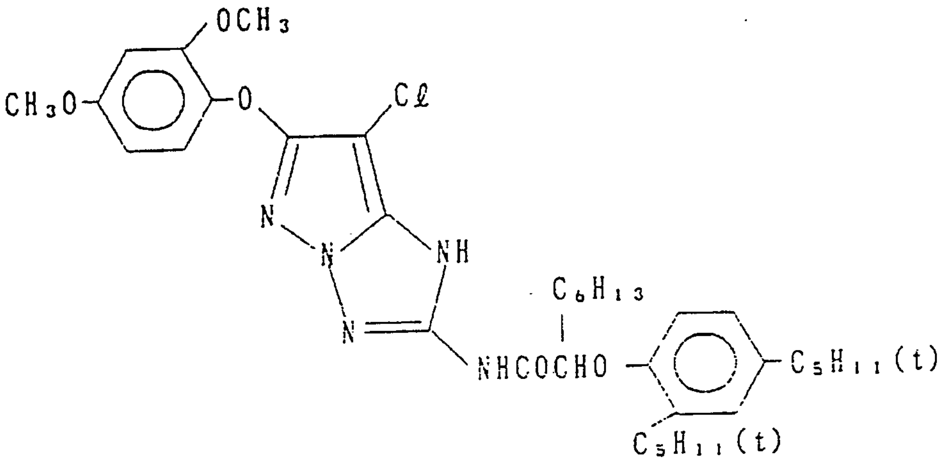
M－２５


O
Cℓ
N
N
NH
N
OCH₂CH₂OCH₂CH₂OC₆H₁₃
CHCH₂NHSO₂
CH₃
C₈H₁₇(t)

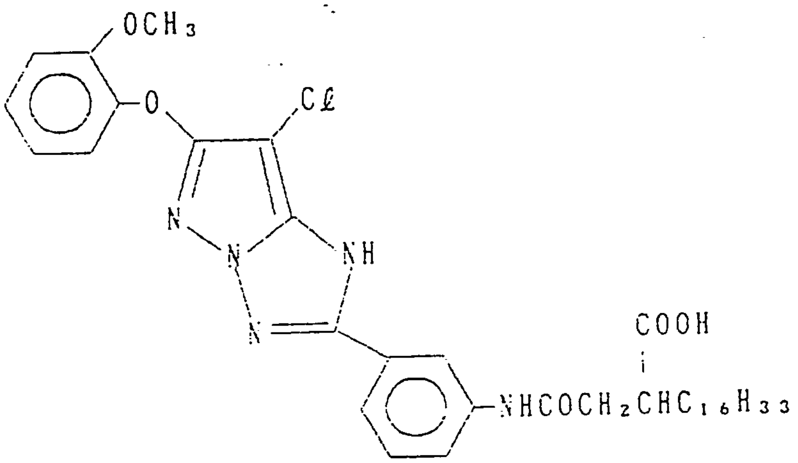
M－２６


OCH₃
O
Cℓ
N
N
NH
N
OCH₂CH₂OC₆H₁₃
CHCH₂NHSO₂
CH₃
C₈H₁₇(t)

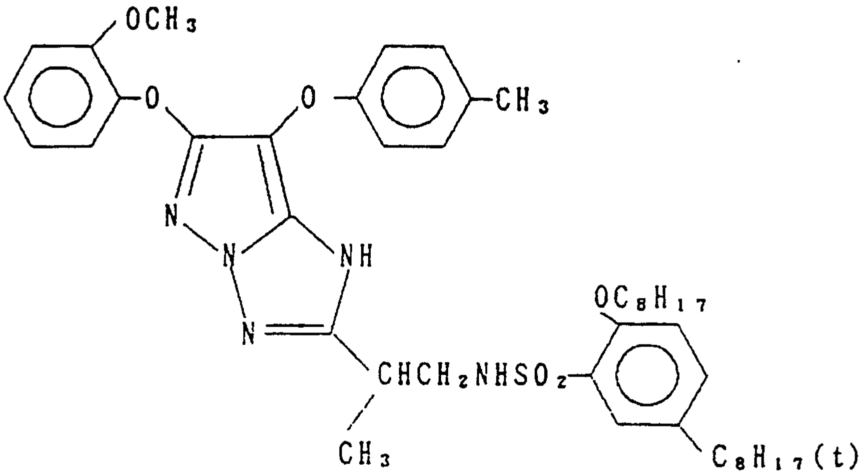
M－２７


OCH₃
CH₃O
O
Cℓ
N
N
NH
N
C₆H₁₃
NHCOCHO
C₅H₁₁(t)
C₅H₁₁(t)

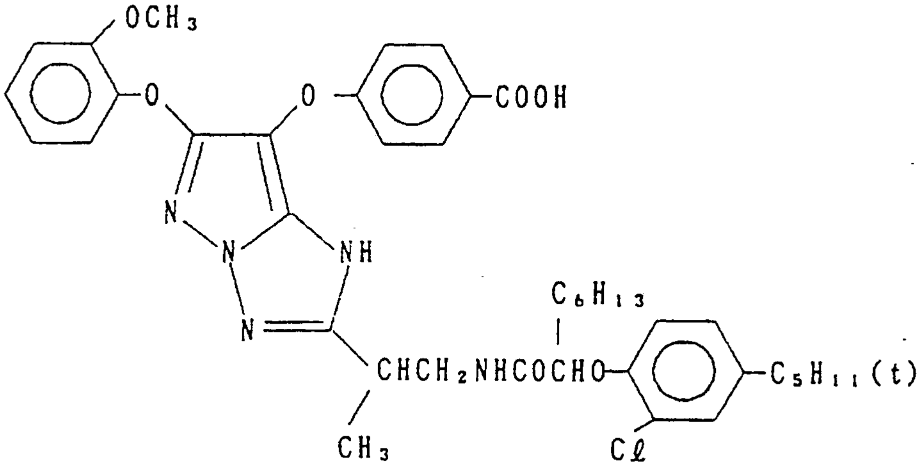
M－２８


OCH₃
O
Cℓ
N
N
NH
N
COOH
NHCOCH₂CHC₁₆H₃₃

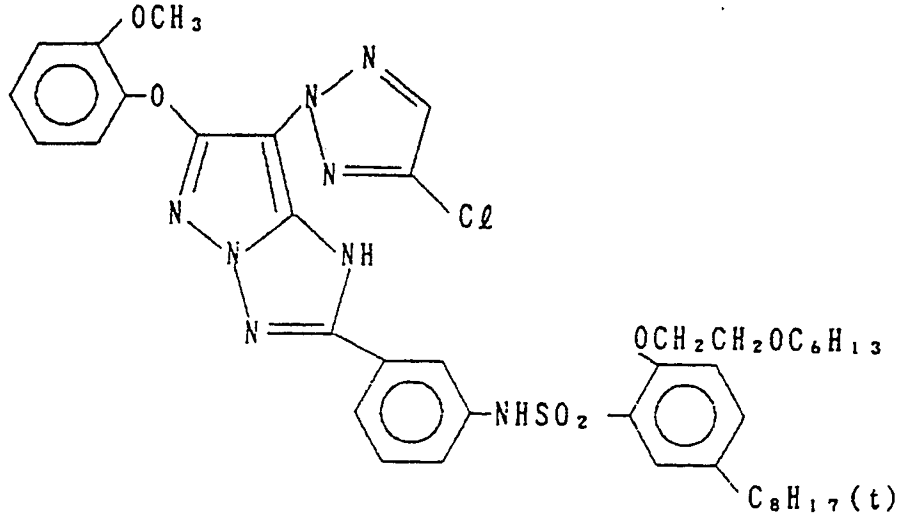
M－２９


OCH₃
O
O
CH₃
N
N
NH
N
OC₈H₁₇
CHCH₂NHSO₂
CH₃
C₈H₁₇(t)

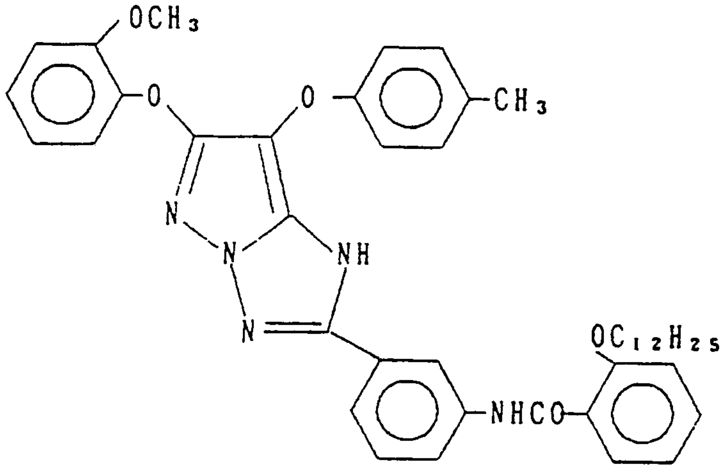
M－３０


OCH₃
O
O
COOH
N
N
NH
N
C₆H₁₃
CHCH₂NHCOCHO
C₅H₁₁(t)
CH₃
Cℓ

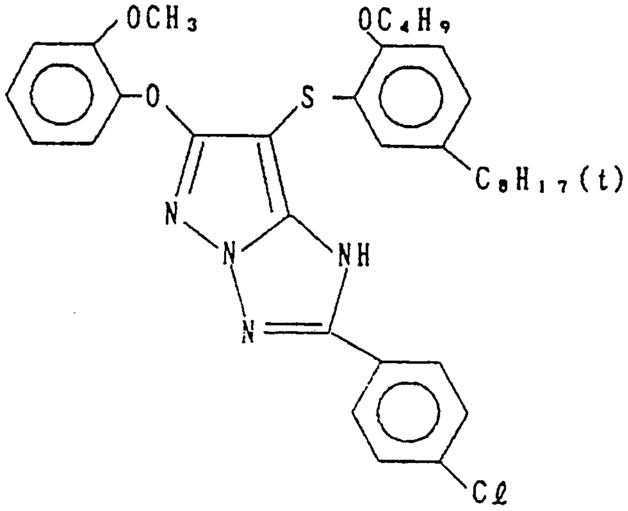
M－31


OCH₃
O
N
N
N
Cℓ
N
N
NH
N
OCH₂CH₂OC₆H₁₃
NHSO₂
C₈H₁₇(t)

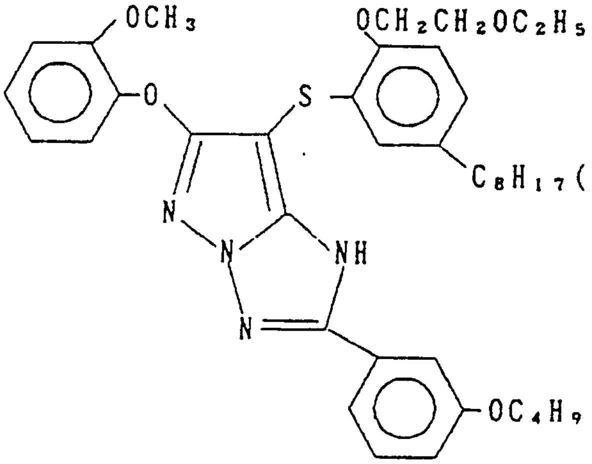
M－32


OCH₃
O
O
CH₃
N
N
NH
N
OC₁₂H₂₅
NHCO

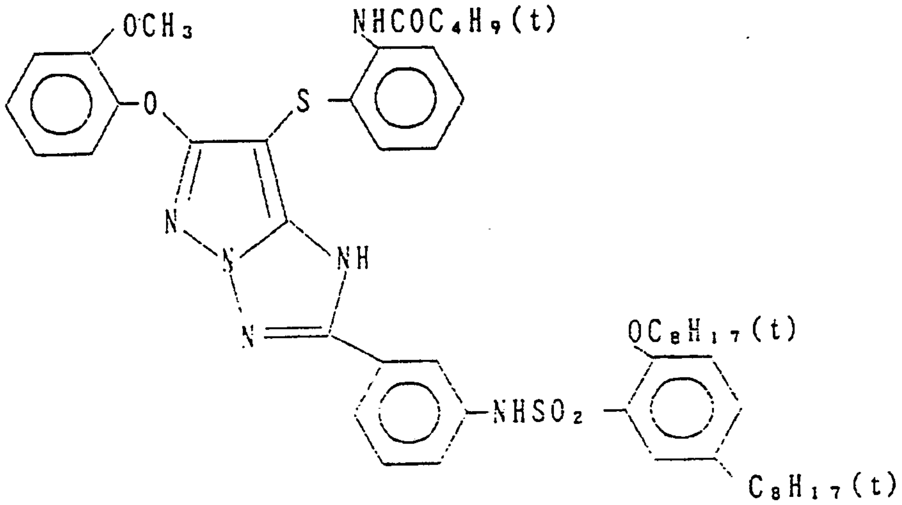
M－３３


OCH₃
OC₄H₉
O
S
C₈H₁₇(t)
N
N
NH
N
Cℓ

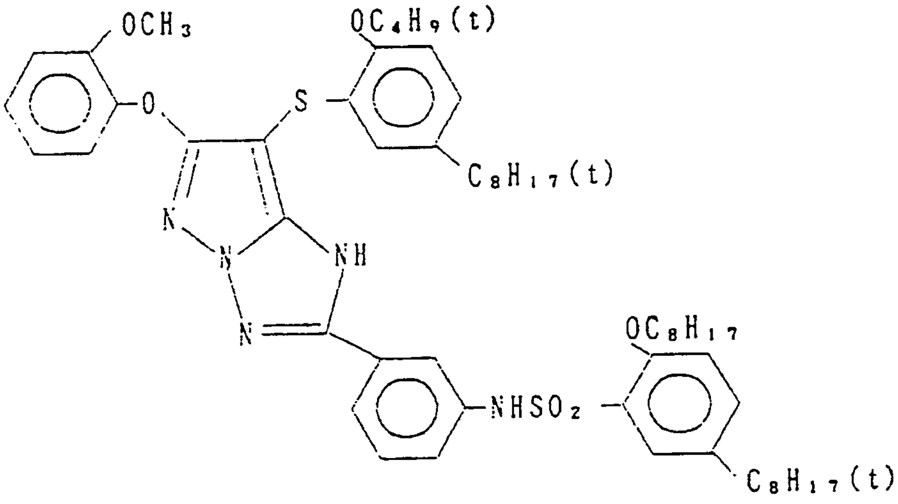
M－３４


OCH₃
OCH₂CH₂OC₂H₅
O
S
C₈H₁₇(t)
N
N
NH
N
OC₄H₉

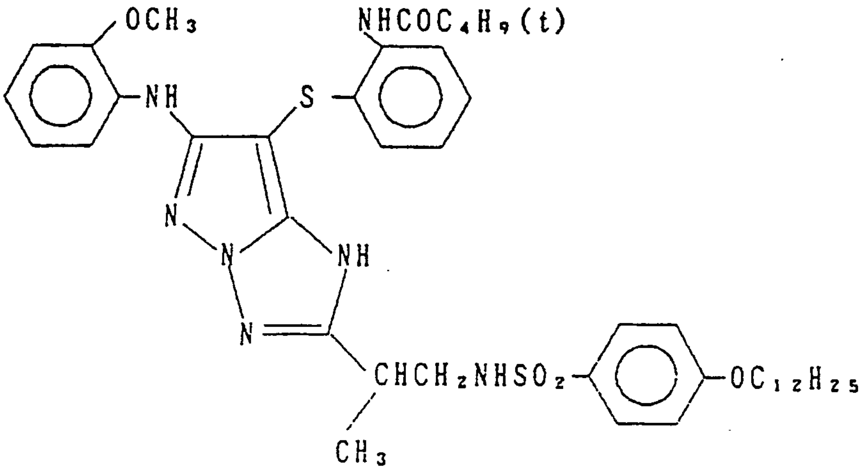
M－35


OCH3
NHCOC4H9(t)
O
S
N
N
NH
N
OC8H17(t)
NHSO2
C8H17(t)

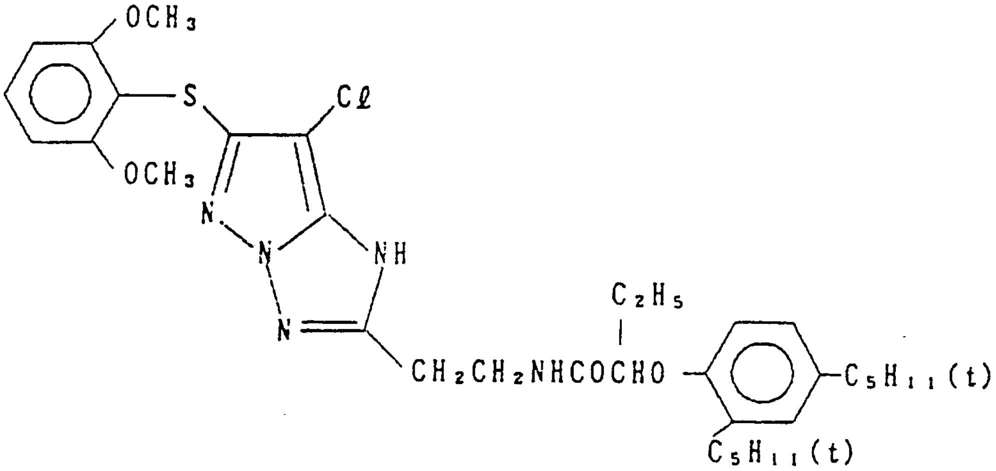
M－36


OCH3
OC4H9(t)
O
S
C8H17(t)
N
N
NH
N
OC8H17
NHSO2
C8H17(t)

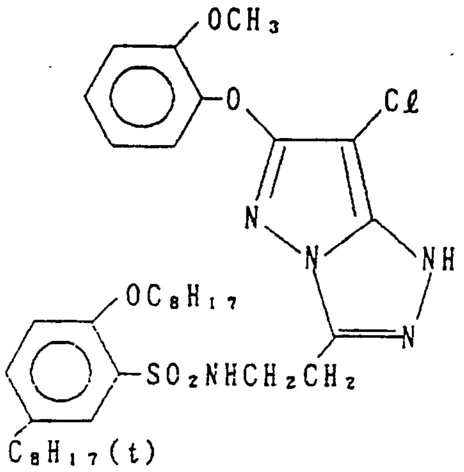
M－３７


OCH3
NHCOC4H9(t)
NH
S
N
N
NH
N
CHCH2NHSO2
OC12H25
CH3

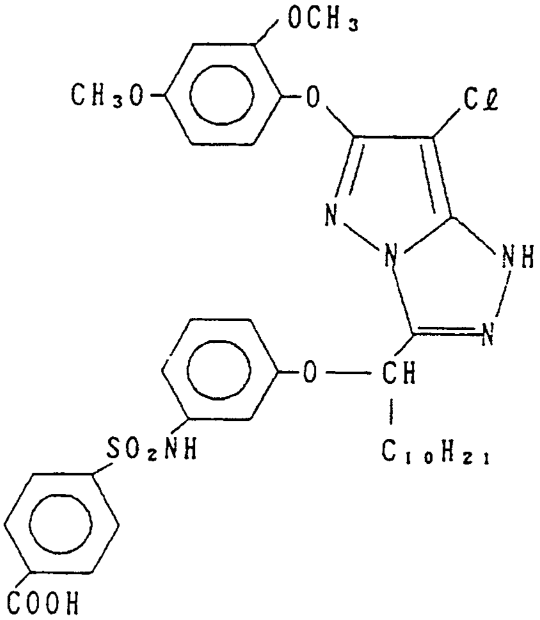
M－３８


OCH3
S
Cl
OCH3
N
N
NH
C2H5
N
CH2CH2NHCOCHO
C5H11(t)
C5H11(t)

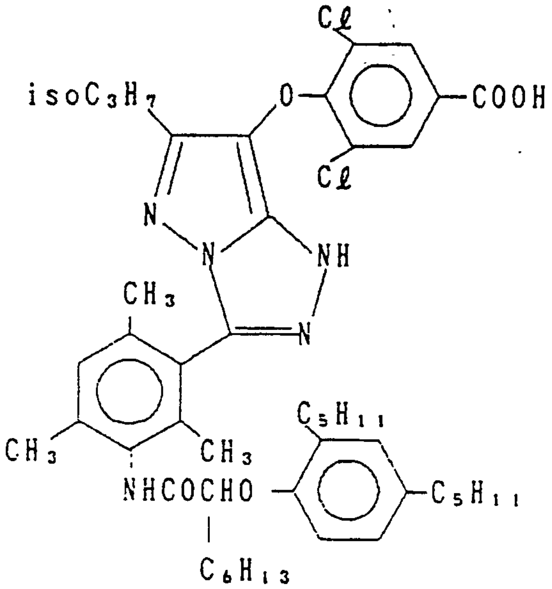
M－39



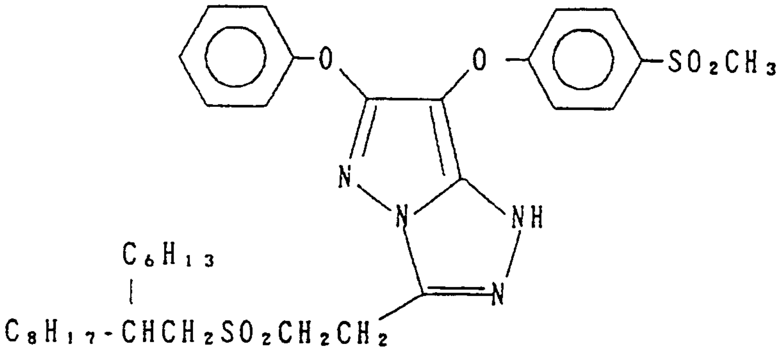
M－40



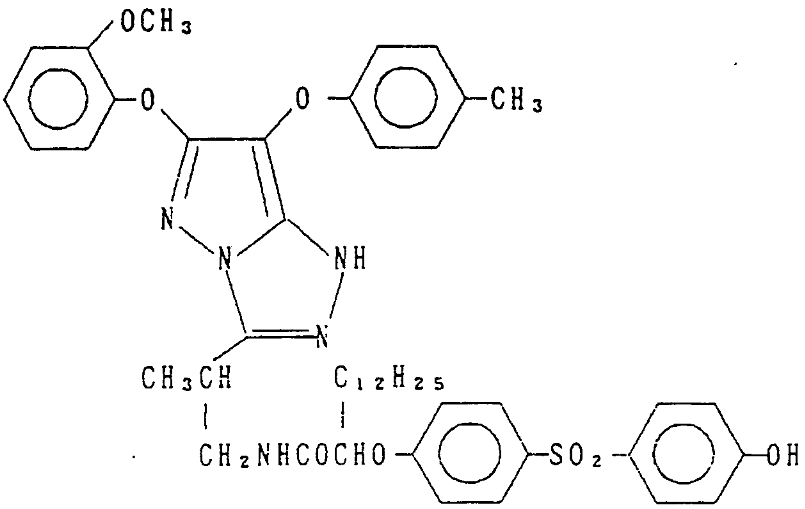
M－41


isoC3H7
O
Cℓ
Cℓ
COOH
N
N
NH
N
CH3
CH3
CH3
NHCOCHO
C6H13
C5H11
C5H11

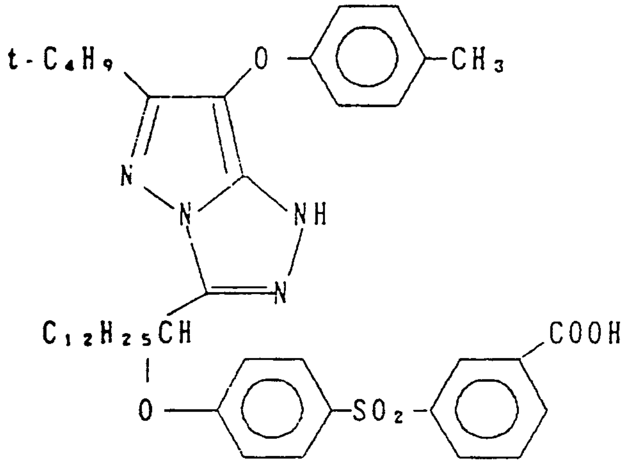
M－42


O
O
SO2CH3
N
N
NH
N
C6H13
C8H17-CHCH2SO2CH2CH2

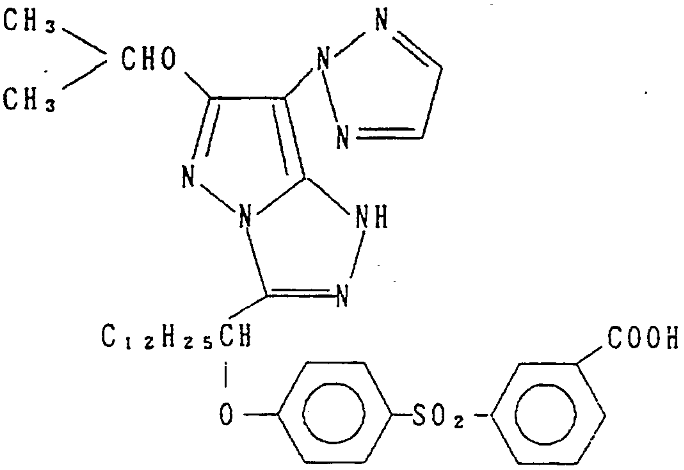
M－４３



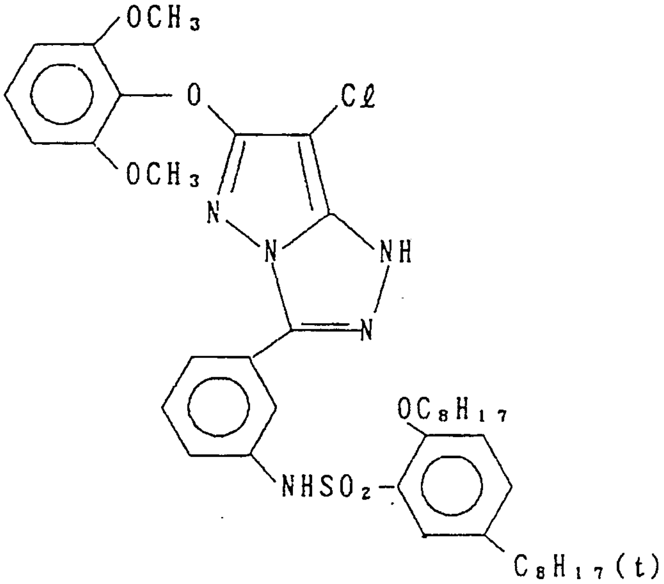
M－４４



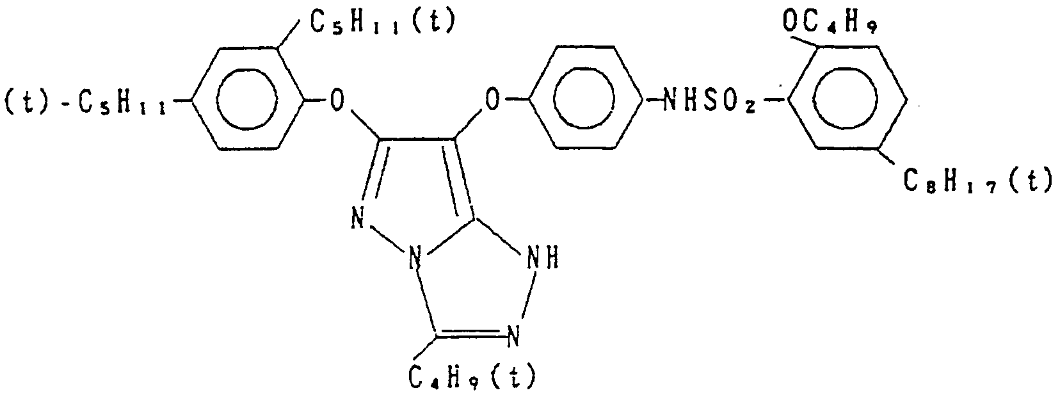
M－４５


CH3
CHO
CH3
N
N
N
N
N
NH
N
C12H25CH
O
SO2
COOH

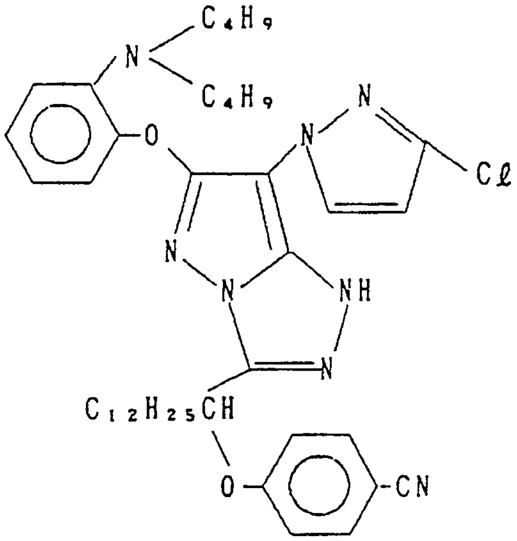
M－４６


OCH3
O
Cℓ
OCH3
N
N
NH
N
OC8H17
NHSO2
C8H17(t)

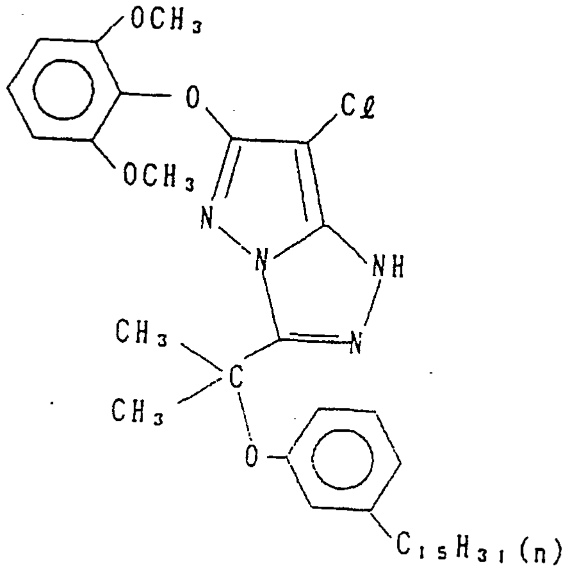
M－４７



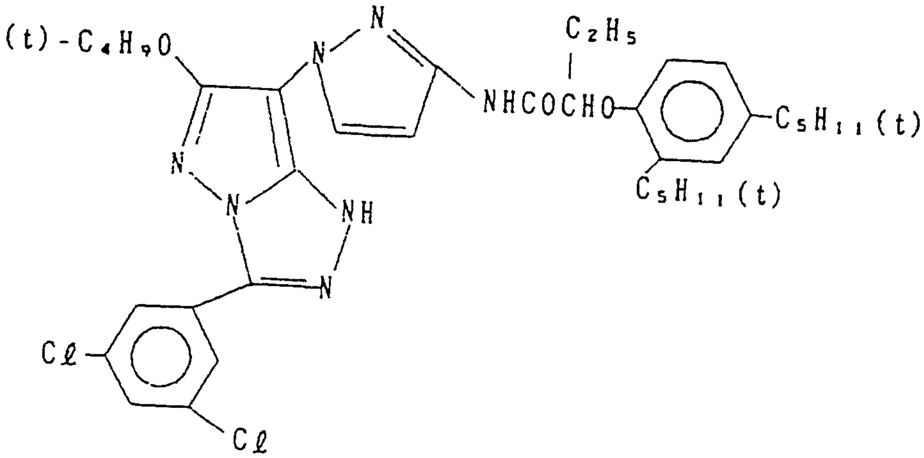
M－４８



M－49



M－50



Of the couplers represented by the general formulas (I) and (II) used in the present invention, those represented by general formula (I) are more preferred for the purposes of the present invention, because the degradation of light-fastness is small when the amount of organic solvent having a high boiling point is reduced.

Further, where R_1 is a branched chain alkyl group in the pyrazolotriazole coupler according to the present invention, the effect of the present invention increases as the bulk of the alkyl group increases. Specifically, a substituted or unsubstituted isopropyl group and a substituted or unsubstituted tert-butyl group are most preferred as R_1.

When R_1 is an aryl group, an aryl group having a bulky group at its ortho position is preferred, and an aryl group having substituents at its 2- and 6-positions is more preferred in view of the effect of the present invention.

The amount of the pyrazolotriazole coupler used in the present invention is generally 0.01 mmol or more, preferably from 0.1 mmol to 1.5 mmol, per m^2 of the light-sensitive material.

The couplers which are used in the present invention can be dissolved in an organic solvent having a high boiling point and then emulsified and dispersed, or they can be emulsified and dispersed without using an organic solvent having a high boiling point. Couplers dispersed in the form of a latex can be mixed with a photographic emulsion as they are or they can be mixed with a binder such as gelatin and then mixed with a photographic emulsion.

Methods for dispersing the oleophilic couplers of this invention in organic solvents having a high boiling point which can be used in the present invention are described in greater detail below.

To incorporate oleophilic photographic organic compounds such as couplers into light-sensitive materials, various known dispersing methods can be employed in the present invention.

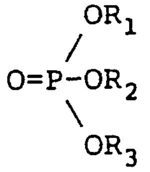
For example, according to the oil droplet-in-water type dispersing method described, for example, in U.S. Patent 2,322,027, oleophilic photographic organic compounds are dissolved in (i) an organic solvent having a high boiling point above about 175° C at normal pressure, for example, a phthalic acid ester, a phosphoric acid ester, a benzoic acid ester, a fatty acid ester, an amide, a phenol, an alcohol, a carboxylic acid, an N,N-dialkylaniline, a hydrocarbon, an oligomer and a polymer and/or (ii) an organic solvent having a low boiling point of from about 30° C to about 160° C at normal pressure, for example, an ester (e.g., ethyl acetate, butyl acetate, ethyl propionate, β-ethoxyethyl acetate, and methyl cellosolve acetate), an alcohol (e.g., secondary butyl alcohol), a ketone (e.g., methyl isobutyl ketone, methyl ethyl ketone, and cyclohexanone), an amide (e.g., dimethylformamide, and N-methylpyrrolidone), and an ether (e.g., tetrahydrofuran, and dioxan), and then emulsified and dispersed in a hydrophilic colloid such as gelatin.

The processes and effects of latex dispersing methods and specific examples of latexes for loading are described, for example, in U.S. Patent 4,199,363, West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230, and European Patent 294,104A.

The organic solvent having a high boiling point or latex not only functions as a dispersion medium, but may have various additional functions, for example, improving the physical properties of the gelatin layer, accelerating color formation, controlling the hue of the color image formed, and improving the fastness of the color image.

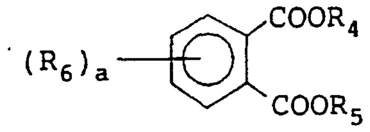
The organic solvent having a high boiling point can be employed in any liquid, wax or solid form.

The organic solvent having a high boiling point used in the present invention is preferably represented by the following general formulas (S-1), (S-2), (S-3), (S-4), (S-5), (S-6), (S-7), (S-8) or (S-9):



$$O{=}P(OR_1)(OR_2)(OR_3)$$

(S-1)

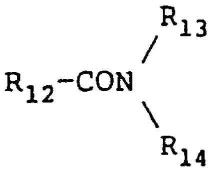


(S-2)

$(Ar\text{-}COO)_b R_7$ (S-3)

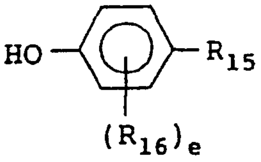
$(R_8\text{-}COO)_c R_9$ (S-4)

$R_{10}(COO\text{-}R_{11})_d$ (S-5)

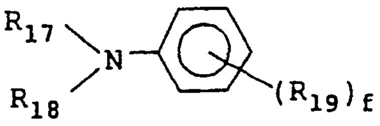


$$R_{12}\text{-}CON(R_{13})(R_{14})$$

(S-6)



(S-7)



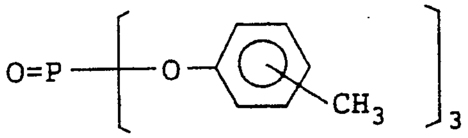
(S-8)

$$-(A_1)_{a1}-(A_2)_{a2}-\cdots\cdots\cdots-(A_n)_{an}-$$ (S-9)

wherein R_1, R_2 and R_3 of formula (S-1) each represents an alkyl group, a cycloalkyl group or an aryl group; R_4 and R_5 each represents an alkyl group, a cycloalkyl group or an aryl group; R_6 represents a halogen atom (e.g., F, Cl, Br, and I), an alkyl group, an alkoxy group, an aryloxy group or an alkoxycarbonyl group; a represents an integer of from 0 to 3, when a represents 2 or 3, two or three R_6's may be the same or different; Ar represents an aryl group; b represents an integer of from 1 to 6; R_7 represents a b-valent hydrocarbon group or hydrocarbon group connected via an ether bond; R_8 represents an alkyl group or a cycloalkyl group; c represents an integer of from 1 to 6; R_9 represents a c-valent hydrocarbon group or hydrocarbon group connected via an ether bond; d represents an integer of from 2 to 6; R_{10} represents a d-valent hydrocarbon group provided that an aromatic group is excluded; R_{11} represents an alkyl group, a cycloalkyl group or an aryl group; R_{12}, R_{13} or R_{14} each represents an alkyl group, a cycloalkyl group and an aryl group, or R_{12} and R_{13} or R_{13} and R_{14} may combine with each other to form a ring; R_{15} represents an alkyl group, a cycloalkyl group, an alkoxycarbonyl group, an alkylsulfonyl group, an arylsulfonyl group, an aryl group or a cyano group; R_{16} represents a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, an alkoxy group or an aryloxy group; e represents an integer of from 0 to 3, when e represents 2 or 3, two or three R_{16}'s may be the same or different; R_{17} and R_{18} each represents an alkyl group, a cycloalkyl group or an aryl group; R_{19} represents a halogen atom, a cycloalkyl group, an alkyl group, an aryl group, an alkoxy group or an aryloxy group; f represents an integer of from 0 to 4, when f represents 2, 3 or 4, two, three or four R_{19}'s may be the same or different; A_1, A_2, ... and An each represents a polymer unit formed from a non-color forming ethylenic monomer different from each other; a_1, a_2, ... and a_n each represents a weight ratio of the polymer unit; and n represents an integer of from 1 to 30.

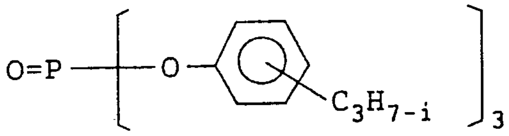
Specific examples of the organic solvent having a high boiling point which are employed in the present invention are set forth below, but the present invention should not be construed as being limited thereto.

S-1

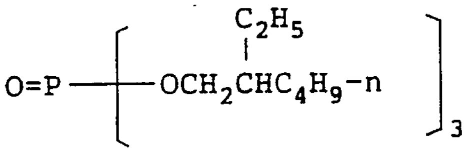


dielectric constant: 7.33

S-2

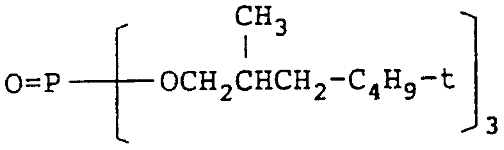


S-3



$$O{=}P\left[OCH_2\overset{C_2H_5}{\overset{|}{C}}HC_4H_9\text{-}n\right]_3$$

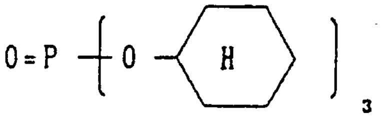
S-4



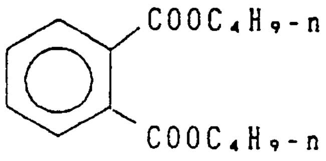
$$O{=}P\left[OCH_2\overset{CH_3}{\overset{|}{C}}HCH_2\text{-}C_4H_9\text{-}t\right]_3$$

dielectric constant: 4.80

S − 5

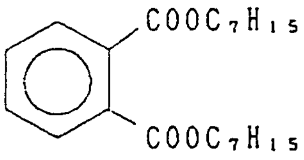


S − 6

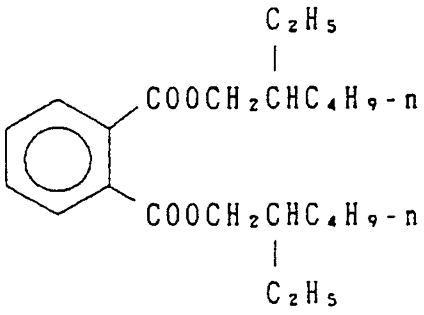


dielectric constant: 6.45

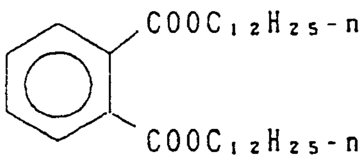
S − 7



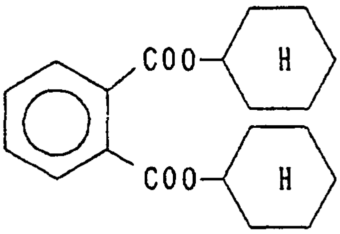
S − 8



S − 9

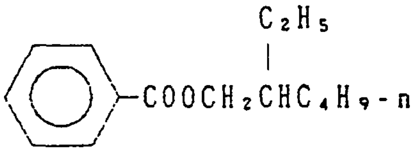


S-10

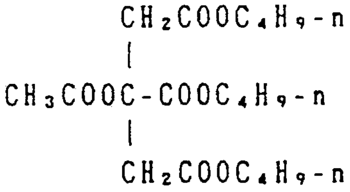


dielectric constant: 6.45

S-11

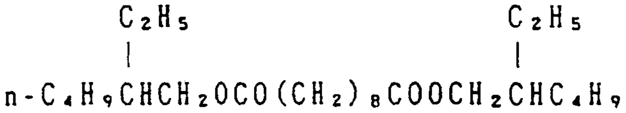


S-12



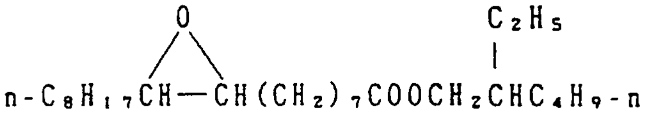
$$\mathrm{CH_3COO}\overset{\displaystyle \mathrm{CH_2COOC_4H_9\text{-}n}}{\underset{\displaystyle \mathrm{CH_2COOC_4H_9\text{-}n}}{\mathrm{C}}}\mathrm{\text{-}COOC_4H_9\text{-}n}$$

S-13

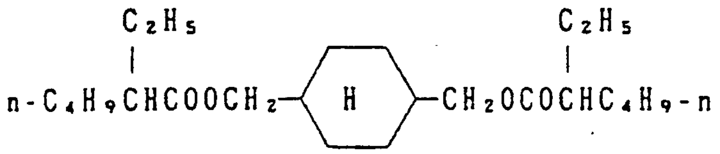


$$\mathrm{n\text{-}C_4H_9}\overset{\displaystyle \mathrm{C_2H_5}}{\mathrm{CH}}\mathrm{CH_2OCO(CH_2)_8COOCH_2}\overset{\displaystyle \mathrm{C_2H_5}}{\mathrm{CH}}\mathrm{C_4H_9}$$

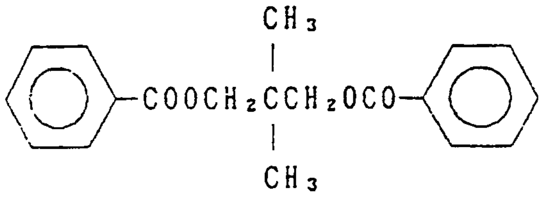
S-14



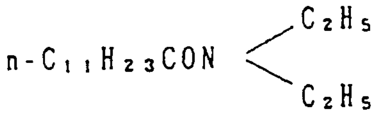
S-15



S-16

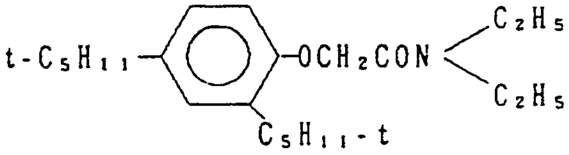


S-17

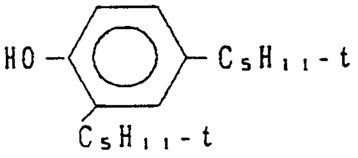


dielectric constant: 13.45

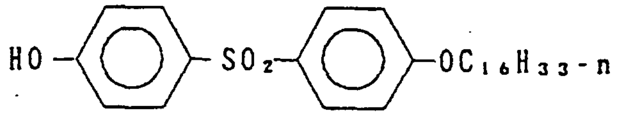
S-18



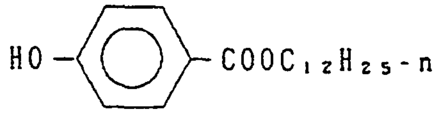
S-19



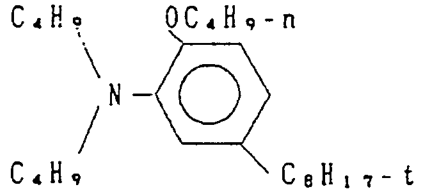
S - 20



S - 21

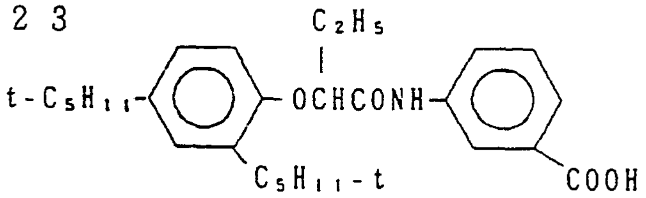


S - 22



dielectric constant: 2.76

S - 23



S-24 Polymethylmethacrylate
(average molecular weight 20.000)
S-25 Poly(N-t-butylacrylamido) (average molecular weight 60,000)
S-26 Chlorinated paraffin
(Average composition: $C_{12}H_{18}Cl_8$)

Other examples of organic solvents having a high boiling point which can be used in the present invention and/or synthesis methods thereof are described, for example, in U.S. Patents 2,322,027, 2,533,514, 2,772,163, 2.835,679, 3,676,137, 3,912,515, 3,936,303, 4,080,209, 4,127,413, 4,193,802, 4,239,851, 4,278,757, 4.363,873, 4,483,918 and 4,745,049, European Patent 276,319A, JP-A-48-47335, JP-A-51-149028, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-64-68745 and JP-A-1-101543.

In the present invention, when the weight ratio of the organic solvent having a high boiling point to the coupler is not more than 1.0, the effect of the present invention becomes significant. On the other hand, where couplers other than those of the present invention are used, aggregation of the dyes formed during processing can be substantially restrained if the amount of organic solvent having a high boiling point is increased. The weight ratio of the organic solvent having a high boiling point to the coupler is preferably not more than 0.7, more preferably not more than 0.5, and most preferably not more than 0.2. As the weight ratio becomes small, the difference between the couplers according to the present invention and couplers being out of those of the present invention becomes large with respect to hue due to an aggregation of the dyes.

Further, of the organic solvents having a high boiling point which are used in the present invention, those having a dielectric constant of 5 or more are preferred, because they have a high coupling activity when the amount thereof is reduced. The dielectric constant can be measured by a bridge method using a

TRS-10T instrument (manufactured by Ando Denki Co.) under conditions of 25° C and 10 MHz.

The color photographic light-sensitive material of the present invention may have at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one red-sensitive silver halide emulsion layer on a support. The number of silver halide emulsion layers and light-insensitive layers and the order thereof are not particularly restricted. One typical example is a silver halide photographic material comprising a support having thereon at least one light-sensitive layer group composed of a plurality of silver halide emulsion layers which have substantially the same spectral sensitivity but different speeds. The light-sensitive layer group is a unit light-sensitive layer having a spectral sensitivity to any of blue light, green light and red light. In a multilayer silver halide color photographic material, unit light-sensitive layers are generally provided in the order of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer from the support side on the support. The order of these layers can be varied depending on the purpose. Further, a layer structure wherein between two layers having the same spectral sensitivity, a light-sensitive layer having a different spectral sensitivity is sandwiched may be used.

Between the above described silver halide light-sensitive layers or as the uppermost layer or the undermost layer, various light-insensitive layers such as an intermediate layer can be provided.

Into such an intermediate layer, couplers and DIR compounds as described, for example, in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038 may be incorporated. Further, the intermediate layer may contain conventionally employed color mixing preventing agents.

The plurality of silver halide emulsion layers which constitute the unit light-sensitive layer preferably have a two layer construction consisting of a high speed emulsion layer and a low speed emulsion layer as described, for example, in West German Patent 1,121,470 and British Patent 923,045. It is preferred that these layers be disposed in order of increasing speed from the support side. Further, a light-insensitive layer may be provided between silver halide emulsion layers. Moreover, a low speed emulsion layer may be provided further away from the support and a high speed emulsion layer may be provided on the side closest to the support as described, for example, in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

Specific examples of the layer construction include an order of a low speed blue-sensitive layer (BL)/a high speed blue-sensitive layer (BH)/a high speed green-sensitive layer (GH)/a low speed green-sensitive layer (GL)/a high speed red-sensitive layer (RH)/a low speed red-sensitive layer (RL) from the farthest from the support, an order of BH/BL/GL/GH/RH/RL, or an order of BH/BL/GH/GL/RL/RH.

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

Furthermore, a layer construction of three layers having different speeds consisting of an upper silver halide emulsion layer having the highest speed, an intermediate silver halide emulsion layer having lower speed than that of the upper layer, and an under silver halide emulsion layer having lower speed than that of the intermediate layer in order of increasing speed from the support side as described in JP-B-49-15495 may also be employed. In cases where the unit light-sensitive layer of the same spectral sensitivity is composed of three layers having different speeds, an order of an intermediate speed emulsion layer/a high speed emulsion layer/a low speed emulsion layer from the farthest from the support may be employed as described in JP-A-59-202464.

In addition, an order of a high speed emulsion layer/a low speed emulsion layer/an intermediate speed emulsion layer, or an order of a low speed emulsion layer/an intermediate speed emulsion layer/a high speed emulsion layer may be employed.

Where the unit light-sensitive layer consists of four layers or more, the order can be varied as described above.

In order to improve color reproducibility, it is preferred that a donor layer (CL) of interimage effect having a spectral sensitivity distribution different from that of the main light-sensitive layer such as BL, GL or RL be provided adjacent or close to the main layer as described, for example, in U.S. Patents 4,663,271, 4,705,744 and 4,707,436, JP-A-62-160448 and JP-A-63-89580.

As described above, various layer constructions and dispositions may be appropriately selected depending on the purpose of the photographic light-sensitive material.

In cases where the color photographic light-sensitive material of the present invention is a color negative film or a color reversal film, the silver halide preferably employed in the photographic emulsion layers thereof is silver iodobromide, silver iodochloride or silver iodochlorobromide,each containing about 30 mol% or less of silver iodide. Silver iodobromide or silver iodochlorobromide each containing from about 2 mol% to about 25 mol% of silver iodide is particularly preferred.

In cases where the color photographic light-sensitive material of the present invention is a color printing paper, the silver halide preferably employed in the photographic emulsion layers thereof is silver chlorobromide or silver chloride, each containing substantially no silver iodide. The terminology "containing substantially no silver iodide" as used herein means that the silver iodide content of the emulsion is not more than 1 mol%, preferably not more than 0.2 mol%.

With respect to the halogen composition of the silver chlorobromide emulsion, any silver bromide/silver chloride ratio may be employed. The ratio may be widely varied depending on the purpose, but emulsions having a silver chloride content ratio of 2 mol% or more are preferably employed.

In photographic light-sensitive materials suitable for rapid processing, a so-called high silver chloride content emulsion which has a high silver chloride content ratio is preferably used. The silver chloride content ratio in such a high silver chloride content emulsion is preferably 90 mol% or more, more preferably 95 mol% or more.

Further, for the purpose of reducing the amount of replenisher for the developing solution, an almost pure silver chloride emulsion such as one wherein the silver chloride content is from 98 mol% to 99.9 mol% is preferably employed.

The silver halide grains in the silver halide emulsion may have a regular crystal structure, for example, a cubic, octahedral or tetradecahedral structure, an irregular crystal structure, for example, a spherical or tabular structure, a crystal defect, for example, a twin plane, or a composite structure thereof.

The particle size of the silver halide may be varied and the emulsion may include fine grains having a diameter of projected area from about 0.2 micron or less to large size grains having a diameter of projected area of about 10 microns. Further, a polydispersed emulsion and a monodispersed emulsion may be used.

The silver halide photographic emulsion which can be used in the present invention can be prepared using known methods, for example, those described in Research Disclosure, No. 17643 (December, 1978), pages 22 to 23, "I. Emulsion Preparation and Types" and ibid., No. 18716 (November, 1979), page 648, P. Glafkides, Chimie et Physique Photographique, Paul Montel (1967), G.F. Duffin, Photographic Emulsion Chemistry, The Focal Press (1966), and V.L. Zelikman et al., Making and Coating Photographic Emulsion, The Focal Press (1964).

Monodispersed emulsions as described, for example, in U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are preferably used in the present invention.

Further, tabular silver halide grains having an aspect ratio of about 5 or more can be employed in the present invention. The tabular grains may be easily prepared by the method as described, for example, in Gutoff, Photographic Science and Engineering, Vol. 14, pages 248 to 257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and British Patent 2,112,157.

The crystal structure of the silver halide grains may be uniform, or may be composed of different halide compositions between the inner portion and the outer portion, or may have a stratified structure.

Further, silver halide emulsions in which silver halide grains having different compositions are connected upon epitaxial junctions or silver halide emulsions in which silver halide grains are connected with compounds other than silver halide such as silver thiocyanate, or lead oxide, may also be employed.

Moreover, a mixture of grains having a different crystal structure may be used.

The silver halide emulsions used in the present invention are usually subjected to physical ripening, chemical ripening and spectral sensitization. Various kinds of additives which can be employed in these steps are described in Research Disclosure, No. 17643, (December, 1978) and ibid., No. 18716 (November, 1979) and relevant items therefrom are summarized in the table shown below.

Further, known photographic additives which can be used in the present invention are also described in the above mentioned publications and relevant items therefrom are summarized in the table below.

Kind of Additives	RD 17643	RD 18716
1. Chemical Sensitizers	Page 23	Page 648, right column
2. Sensitivity Increasing Agents		- ditto -
3. Spectral Sensitizers and Supersensitizers	Pages 23 to 24	Page 648, right column to page 649, right column
4. Whitening Agents	Page 24	
5. Antifoggants and Stabilizers	Pages 24 to 25	Page 649, right column
6. Light-Absorbers, Filter Dyes and Ultraviolet Ray Absorbers	Pages 25 to 26	Page 649, right column to page 650, left column
7. Antistaining Agents	Page 25, right column	Page 650, left column to right column
8. Dye Image Stabilizers	Page 25	
9. Hardeners	Page 26	Page 651, left column
10. Binders.	Page 26	- ditto -
11. Plasticizers and Lubricants	Page 27	Page 650, right column
12. Coating Aids and Surfactants	Pages 26 to 27	Page 650, right column
13. Antistatic Agents	Page 27	- ditto -

In the color photographic light-sensitive material according to the present invention, various color fading preventing agents can be employed. More specifically, representative examples of organic color fading preventing agents for cyan, magenta and/or yellow images include hindered phenols (for example, hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, or bisphenols), gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, or ether or ester derivatives thereof derived from each of these compounds by sililation or alkylation of the phenolic hydroxy group thereof. Further, metal complexes representatively illustrated by (bissalicylaldoxymate) nickel complexes and (bis-N,N-dialkyldithiocarbamate) nickel complexes may be employed.

Specific examples of the organic color fading preventing agents are described in the following patents or patent applications.

Hydroquinones: U.S. Patents 2,360,290, 2,418,613, 2,700,453, 2,701,197, 2,728,659, 2,732,300, 2,735,765, 3,982,944 and 4,430,425, British Patent 1,363,921, U.S. Patents 2,710,801 and 2,816,028; 6-hydroxychromanes, 5-hydroxycoumaraus and spirochromanes: U.S. Patents 3,432,300, 3,573,050, 3,574,627, 3,698,909 and 3,764,337, JP-A-52-152225; spiroindanes: U.S. Patent 4,360,589; p-alkoxyphenols: U.S. Patents 2,735,765, British Patent 2,066,975, JP-A-59-10539, JP-B-57-19765; hindered phenols: U.S. Patent 3,700,455, JP-A-52-72224, U.S. Patent 4,228,235, JP-B-52-6623; gallic acid derivatives, methylenedioxybenzenes and aminophenols: U.S. Patents 3,457,079 and 4,332,886, JP-B-56-21144; hindered amines: U.S. Patents 3,336,135 and 4,268,593, British Patents 1,326,889, 1,354,313 and 1,410,846, JP-B-51-1420, JP-A-58-114036, JP-A-59-53846, JP-A-59-78344.

Further, specific examples of the metal complexes are described in U.S. Patents 4,050,938 and 4,241,155, and British Patent 2,027,731A.

The color fading preventing agents are co-emulsified with the corresponding color coupler in an amount of from 5 to 100% by weight of the color coupler and incorporated into the light-sensitive layer to achieve the effects thereof.

Further, to prevent degradation of photographic properties due to formaldehyde gas, it is preferred to add a compound capable of reacting with formaldehyde to fix it to the photographic light-sensitive material as described in U.S. Patents 4,411,987 and 4,435,503.

In the present invention, various color couplers can be employed and specific examples thereof are described in the patents cited in Research Disclosure, No. 17643, "VII-C" to "VII-G".

As yellow couplers used in the present invention, for example, those described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752 and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023 and 4,511,649, and European Patent 249,473A are preferred.

As magenta couplers used in the present invention 5-pyrazolone type and pyrazoloazole type compounds are preferred. Magenta couplers as described, for example, in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure, No. 24220

(June, 1984), JP-A-60-33552, Research Disclosure, No. 24230 (June, 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, and U.S. Patents 4,500,630, 4,540,654 and 4,556,630, and WO(PCT) 88/04795 are particularly preferred.

As cyan couplers used in the present invention phenol type and naphthol type couplers are illustrative. Cyan couplers as described, for example, in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011 and 4,327,173, West German Patent Application (OLS) No. 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658 are preferred.

As colored couplers for correcting undesirable absorptions of the dyes formed during processing, those described, for example, in Research Disclosure, No. 17643, "VII-G", U.S. Patent 4,163,670, JP-B-57-39413, US. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368 are preferably employed. It is also preferred to use couplers for correcting undesirable absorptions of dyes formed by a fluorescent dye released upon coupling as described, for example, in U.S. Patent 4,774,181, or couplers having a dye precursor group capable of forming a dye upon a reaction with a developing agent, as a releasing group, as described, for example, in U.S. Patent 4,777,120.

As couplers capable of forming appropriately diffusible dyes, those described, for example, in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Patent Application (OLS) No. 3,234,533 are preferably employed.

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

Couplers capable of releasing a photographically useful moiety during the course of coupling can be also employed preferably in the present invention. As DIR couplers capable of releasing a development inhibitor, those described, for example, in the patents cited in Research Disclosure, No. 17643, "VII-F" described above, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012 are preferred.

As couplers which release imagewise a nucleating agent or a development accelerator at the time of development, those as described, for example, in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840 are preferred.

Furthermore, competing couplers such as those described, for example, in U.S. Patent 4,130,427; polyequivalent couplers such as those described, for example, in U.S. Patents 4,283,472, 4,338,393 and 4,310,618; DIR redox compounds or DIR coupler releasing couplers or DIR couplers or DIR redox compounds releasing redox compounds such as those described, for example, in JP-A-60-185950 and JP-A-62-24252; couplers capable of releasing a dye which turns to a colored form after being released such as those described, for example, in European Patent 173,302A; bleach accelerator releasing couplers such as those described, for example, in Research Disclosure, No. 11449, ibid, No. 24241 and JP-A-61-201247; ligand releasing couplers such as those described, for example, in U.S. Patent 4,553,477; couplers capable of releasing a leuco dye such as those described, for example, in JP-A-63-75747; and couplers capable of releasing a fluorescent dye such as those described, for example, in U.S. Patent 4,774,181 may be employed in the photographic light-sensitive material of the present invention.

The couplers which are used in the present invention can be introduced into the photographic light-sensitive material according to various dispersing methods as described hereinbefore.

It is preferred to add various kinds of antiseptics or antimolds to the color photographic light-sensitive material of the present invention, for example, 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, or 2-(4-thiazolyl)benzimidazole, as described, for example, in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941.

The present invention can be applied to various color photographic light-sensitive materials, and typical examples thereof include color negative films for general use or cinematography, color reversal films for slides or television, color papers, color positive films, and color reversal papers.

Suitable supports which can be used in the present invention are described, for example, in Research Disclosure, No. 17643, page 28 and ibid., No. 18716, page 647, right column to page 648, left column, as mentioned above.

The term "reflective support" which can be employed in the present invention means a support having an increased reflection property for the purpose of rendering the dye images formed in the silver halide emulsion layer clear. Examples of reflective supports include supports having coated thereon a hydrophobic resin containing a light reflective substance such as titanium oxide, zinc oxide, calcium carbonate, or calcium sulfate dispersed therein and supports composed of a hydrophobic resin containing a light reflective substance dispersed therein. More specifically, they include baryta coated paper; polyethylene coated paper; polypropylene type synthetic paper; transparent supports, for example, glass plate, polyester film such as polyethylene terephthalate film, cellulose triacetate film or cellulose nitrate film, polyamide film, polycarbonate film, polystyrene film, or vinyl chloride resin, having a reflective layer or having incorporated therein a reflective substance.

Other examples of the reflective support which can be used are supports having a metal surface of mirror reflectivity or secondary diffuse reflectivity. The metal surface preferably has a spectral reflectance of 0.5 or more in the visible wavelength range. The metal surfaces are preferably produced by roughening or imparting diffusion reflectivity using metal powders. Suitable examples of metals include aluminum, tin, silver, magnesium or alloys thereof. The metal surfaces includes metal plates, metal foils or thin metal layers obtained by rolling, vacuum evaporation or plating. Among them, a metal surface obtained by vacuum evaporation of metal on a substrate is preferably employed.

On the metal surface it is preferred to provide a water-proof resin layer, particularly a thermoplastic resin layer. On the side of the support opposite to the metal surface according to the present invention, an antistatic layer is preferably provided. Details of these supports are described, for example, in JP-A-61-210346, JP-A-63-24247, JP-A-63-24251 and JP-A-63-24255.

It is preferred that the total layer thickness of all hydrophilic colloid layers provided on the emulsion layer side of the photographic light-sensitive material according to the present invention be not more than 28 µm, more preferably not more than 23 µm, and further more preferably not more than 20 µm. Also, the layer swelling rate of $T_{\frac{1}{2}}$ is preferably not more than 30 seconds, more preferably not more than 20 seconds. The layer thickness means the thickness of the layer measured after preservation under conditions of 25° C and relative humidity of 55% for 2 days. The layer swelling rate of $T_{\frac{1}{2}}$ is determined according to methods known in the art. For instance, the degree of swelling can be measured using a swellometer of the type described in A. Green, Photogr. Sci. Eng., Vol. 19, No. 2, page 124 to 129, and $T_{\frac{1}{2}}$ is defined as the time necessary for reaching a layer thickness to a saturated layer thickness which is 90% of the maximum swelling layer thickness obtained when treated in a color developing solution at 30° C for 3 minutes and 15 seconds.

The layer swelling rate of $T_{\frac{1}{2}}$ can be controlled by adding a hardening agent to the gelatin binder or by changing the aging condition after coating.

The rate of swelling is preferably from 150% to 400%. The rate of swelling can be calculated by the formula of (maximum swelling layer thickness - layer thickness)/layer thickness, wherein the maximum swelling layer thickness has the same meaning as defined above.

The color photographic light-sensitive material according to the present invention can be subjected to development processing in a conventional manner as described in Research Disclosure, No. 17643, pages 28 to 29 and ibid., No. 18716, page 651, left column to right column, as mentioned above.

The color developing solution which can be used in development processing of the color photographic light-sensitive material according to the present invention is an alkaline aqueous solution containing preferably an aromatic primary amine type color developing agent as the main component. As the color developing agent, while an aminophenol type compound is useful, a p-phenylenediamine type compound is preferably employed. Typical examples of p-phenylenediamine type compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, or the sulfates, hydrochlorides or p-toluene sulfonates thereof. Among these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline sulfate is particularly preferred.

Two or more kinds of color developing agents may be employed in a combination thereof, depending on the purpose.

The color developing solution can ordinarily contain pH buffering agents, such as carbonates, borates or phosphates of alkali metals; and development inhibitors or anti-fogging agents such as chlorides, bromides, iodides, benzimidazoles, benzothiazoles, or mercapto compounds. Further, if necessary, the color developing solution may contain various preservatives, for example, hydroxylamine, diethylhydroxylamine, sulfites, hydrazines such as N,N-biscarboxymethylhydrazine, phenylsemicarbazides, triethanolamine, or catechol sulfonic acids; organic solvents such as ethyleneglycol, cr diethylene glycol; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, or amines; dye forming couplers; competing couplers; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; viscosity imparting agents; and various chelating agents representatively illustrated by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids, or phosphonocarboxylic acids. Representative examples of the chelating agents include ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphcnic acid, ethylenediamine-

N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof.

Processing solutions other than the color developing solution and processing steps for color reversal photographic materials will be described in detail below.

Of the processing steps for color reversal photographic materials, the steps from black-and-white development to color development are as follows:

1) Black-and-White Development-Washing with Water-Reversal Color Development
2) Black-and-White Development-Washing with Water-Light Reversal-Color Development
3) Black-and-White Development-Washing with Water-Color Development

The washing with water steps in 1) to 3) above can be substituted with a rinse step as described in U.S. Patent 4,804,616 to simplyfy the processing and reduce waste.

Steps after color development are described below.

4) Color Development-Conditioning-Bleaching-Fixing-Washing with Water-Stabilizing
5) Color Development-Washing with Water-Bleaching-Fixing-Washing with Water-Stabilizing
6) Color Development-Conditioning-Bleaching-Washing with Water-Fixing-Washing with Water-Stabilizing
7) Color Development-Washing with Water-Bleaching-Washing with Water-Fixing-Washing with Water-Stabilizing
8) Color Development-Bleaching-Fixing-Washing with Water-Stabilizing
9) Color Development-Bleaching-Bleach-Fixing-Washing with Water-Stabilizing
10) Color Development-Bleaching-Bleach-Fixing-Fixing-Washing with Water-Stabilizing
11) Color development-Bleaching-Washing with Water-Fixing-Washing with Water-Stabilizing
12) Color Development-Conditioning-Bleach-Fixing-Washing with Water-Stabilizing
13) Color Development-Washing with Water-Bleach-Fixing-Washing with Water-Stabilizing
14) Color Development-Bleach-Fixing-Washing with Water-Stabilizing
15) Color Development-Fixing-Bleach-Fixing-Washing with Water-Stabilizing

The washing with water steps just before the stabilizing steps in 4) to 15) may be omitted, and the final stabilizing steps may also be omitted.

The color reversal steps are composed of one of 1) to 3) and one of 4) to 15) described above.

Processing solutions for color reversal processing steps are described below.

In the black-and-white developing solution used in the present invention, known black-and-white developing agents can be used, including, for example, dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone), aminophenols (e.g., N-methyl-p-aminophenol), 1-phenyl-3-pyrazolines, ascorbic acid, heterocyclic compounds wherein a 1,2,3,4-tetrahydroquinoline ring is fused to an indolene ring as described in U.S. Patent No. 4,067,872, and the like, which can be used alone or in combination.

The black-and-white developing solution used in the present invention may contain, if desired, preservatives (e.g., sulfites, or bisulfites), buffering agents (e.g., carbonates, boric acid, borates, or alkanolamines), alkali agents (e.g., hydroxides, or carbonates), dissolution aids (e.g., polyethylene glycols, or esters thereof), pH controlling agents (e.g., organic acids such as acetic acid), sensitizers (e.g., quaternary ammonium salts), development accelerators, surface active agents, defoaming agents, hardeners or viscosity imparting agents.

In the black-and-white developing solution used in the present invention, a compound which functions as a silver halide solvent should be incorporated. Usually, the above-described sulfites added as preservatives also act as the solvent. Specific examples of the sulfites and other silver halide solvents which can be used include KSCN, NaSCN, K_2SO_3, Na_2SO_3, $K_2S_2O_5$, $Na_2S_2O_5$, $K_2S_2O_3$, and $Na_2S_2O_3$.

Although a suitable amount of the silver halide solvent should be used because too small an amount causes delay of development and too large an amount causes fogging of the silver halide emulsion, a suitable amount can be easily determined by persons skilled in the art.

For example, it is preferred to use SCN^- in a range of from 0.005 to 0.02 mol, particularly from 0.01 to 0.015 mol, and SO_3^{2-} in a range of from 0.05 to 1 mol, particularly from 0.1 to 0.5 mol, per liter of the developing solution.

In order to accelerate development, a development accelerator can be used. Particularly, organic thioether compounds as described in JP-A-57-63580 can be employed.

When these compounds are added to the black-and-white developing solution used in the present invention, the amount thereof is preferred to be in a range of from 5×10^{-6} mol to 5×10^{-1}mol, more preferably from 1×10^{-4} mol to 2×10^{-1} mol, per liter of the developing solution.

In the black-and-white developing solution used in the present invention various chelating compounds are employed for the purpose of water-softening. Preferably used chelating compounds are aminopolycarboxylic acids, organic phosphonic acids and phosphonocarboxylic acids as described with respect to the color developing solution.

Further, in the black-and-white developing solution used in the present invention, various compounds as described with respect to the color developing solution are added in addition to the above described sulfites as preservatives.

As anti-fogging agents, alkali metal halides such as potassium bromide, sodium bromide and potassium iodide and organic anti-fogging agents are preferred. Suitable examples of organic anti-fogging agents include nitrogen-containing heterocyclic compounds, e.g., benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylmethylbenzimidazole, and hydroxyazaindolidine; mercapto-substituted heterocyclic compounds, e.g., 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzimidazole, and 2-mercaptobenzothiazole; and mercapto-substituted aromatic compounds (e.g., thiosalicylic acid). The anti-fogging agent may be dissolved from the color reversal photographic materials during processing and be accumulated in the developing solution.

The pH of the developing solution prepared as described above is selected so as to give the desired density and contrast, but it is preferred to be in a range of from about 8.5 to about 11.5.

In order to carry out sensitization processing with the black-and-white developing solution, the processing time is extended to at most about 3 times the standard processing time. In this case, when the processing temperature is raised, prolonged processing times for the sensitization processing can be shortened.

The reversal bath used after the black-and-white development in the present invention may contain known fogging agents, including stannous ion complex salts such as a stannous ion-organophosphoric acid complex salt (as described in U.S. Patent 3,617,282), a stannous ion-organic phosphonocarboxylic acid complex salt (as described in JP-B-56-32616), and a stannous ion-aminopolycarboxylic acid complex salt (as described in British Patent 1,209,050), and boron compounds such as boron hydride compounds (as described in U.S. Patent 2,984,567) and heterocyclic amine borane compounds (as described in British Patent 1,011,000).

The fogging bath (reversal bath) can vary in pH over a wide range from acid to alkaline, i.e., in a range of 2 to 12, preferably 2.5 to 10, more preferably 3 to 9.

Light reversal treatment may be employed in place of the reversal bath. Further, the reversal step can be omitted by adding a fogging agent to the color developing bath.

The pH of the color developing solution or the black-and-white developing solution is usually in a range from 9 to 12. Further, the amount of replenish ment for the developing solution can be varied depending on the color photographic light-sensitive materials to be processed, but is generally not more than 3 liters per square meter of the photographic light-sensitive material. The amount of replenishment can be reduced to not more than 500 ml by decreasing the bromide ion concentration in the replenisher. In reducing the amount of replenishment, it is preferred to prevent evaporation and aerial oxidation of the processing solution by means of reducing the area of the processing tank which is in contact with the air.

The contact area of the photographic processing solution with the air in the processing tank can be represented by the opening rate as defined below.

$$\text{Opening Rate} = \frac{\text{Contact area of processing solution with the air (cm}^2\text{)}}{\text{Volume of processing solution (cm}^3\text{)}}$$

The opening rate described above is preferably not more than 0.1, more preferably from 0.001 to 0.05. Means for reducing the opening rate include a method using a movable cover as described in JP-A-1-82033, a slit development processing method as described in JP-A-63-216050, and a method wherein a shelter such as a floating cover is provided on the surface of the photographic processing solution in the processing tank. It is preferred to apply the reduction of the opening rate not only to the steps of color development and black-and-white development but also to all other following steps, for example, bleaching, bleach-fixing, fixing, washing with water and stabilizing.

Further, the amount of replenishment can be reduced using a means which restrains accumulation of bromide ion in the developing solution.

The processing time of the color development is usually selected in a range from 2 minutes to 5 minutes. However, it is possible to further reduce the processing time by performing the color development at high temperature and high pH using a high concentration of color developing agent.

After color development, the photographic emulsion layers are usually subjected to bleach processing.

The bleach processing can be performed simultaneously with a fix processing (bleach-fix processing), or it can be performed independently from the fix processing. Further, for the purpose of rapid processing, a processing method wherein, after a bleach processing, a bleach-fix processing is conducted may be employed. Moreover, it may be appropriately practiced depending on the purpose to process using a continuous two tank bleach-fixing bath, to carry out fix processing before bleach-fix processing, or to conduct bleach processing after bleach-fix processing.

Examples of bleaching agents which can be employed in the bleach processing or bleach-fix processing include compounds of a multivalent metal such as iron(III); peracids; quinones; and nitro compounds. Representative examples of bleaching agents include organic complex salts of iron(III), for example, complex salts of aminopolycarboxylic acids (such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, or glycol ether diaminetetraacetic acid), or complex salts organic acids (such as citric acid, tartaric acid, or malic acid). Of these compounds, iron(III) complex salts of aminopolycarboxylic acids representatively illustrated by iron(III) complex salts of ethylenediaminetetraacetic acid and iron(III) complex salts of 1,3-diaminopropanetetraacetic acid are preferred in view of rapid processing and less environmental pollution. Furthermore, iron(III) complex salts of aminopolycarboxylic acids are particularly useful in both bleaching solutions and bleach-fixing solutions.

The pH of the bleaching solution or bleach-fixing solution containing an iron(III) complex salt of aminopolycarboxylic acid is usually in a range from 4.0 to 8. For the purpose of rapid processing, it is possible to process at pH lower than the above described range.

In the bleaching solution, the bleach-fixing solution or a prebath thereof, a bleach accelerating agent can be used, if desired. Specific examples of suitable bleach accelerating agents include compounds having a mercapto group or a disulfide bond as described, for example, in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and Research Disclosure, No. 17129 (July 1978); thiazolidine derivatives as described, for example, in JP-A-50-140129; thiourea derivatives as described, for example, in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561; iodides as described, for example, in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds as described, for example, in West German Patents 966,410 and 2,748,430; polyamine compounds as described, for example, in JP-B-45-8836; compounds as described, for example, in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and bromide ions. Of these compounds, the compounds having a mercapto group or a disulfide bond are preferred in view of their large bleach accelerating effects. Particularly, the compounds as described in US. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are preferred. Further, the compounds as described in U.S. Patent 4,552,834 are also preferred. These bleach accelerating agents may be incorporated into the color photographic light-sensitive material. These bleach accelerating agents are particularly effectively employed when color photographic light sensitive materials for photographing are subjected to bleach-fix processing.

To the bleaching solution or bleach-fixing solution, an organic acid is preferably incorporated for the purpose of preventing bleach staining. Particularly preferred organic acids are compounds having an acid dissociation constant (pKa) from 2 to 5 and include specifically, for example, acetic acid and propionic acid.

Fixing agents which can be employed in the fixing solution or bleach-fixing solution include thiosulfates, thiocyanates, thioether compounds, thioureas, or a large amount of iodide. Of these compounds, thiosulfates are generally employed. Particularly, ammonium thiosulfate is most widely employed. Combinations of thiosulfates with thiocyanates, thioether compounds or thioureas are also preferably employed. It is preferred to use sulfites, bisulfites, carbonylbisulfite adducts or sulfinic acid compounds as described in European Patent 294769A as preservatives in the fixing solution or bleach-fixing solution. Moreover, it is preferred to add various aminopolycarboxylic acids and organic phosphonic acids to the fixing or bleach-fixing solution for the purpose of stabilizing the solution.

Shorter total times for the desilvering step are preferable provided that inferior desilvering does not occur. Thus, the processing time for the desilvering step is preferably from 1 minute to 3 minutes, more preferably from 1 minute to 2 minutes. The processing temperature is from 25 to 50° C, preferably 35 to 45° C. In the preferred processing temperature range, the desilvering rate increases and the occurrence of staining after processing is effectively prevented.

In the desilvering step, it is preferred to perform stirring as vigorously as possible.

Specific examples of methods for improving stirring include a method wherein a jet of the processing solution is directed against the emulsion surface of the light-sensitive material as described in JP-A-62-183460 and JP-A-62-183461, a method for increasing the stirring effect using a rotating means as described in JP-A-62-183461, a method for increasing the stirring effect by transferring the light-sensitive material while bringing the emulsion surface thereof into contact with a wiper blade provided in the solution to form turbulent flow on the emulsion surface, and a method of increasing circulation flux of the total processing solution. These means for improving stirring are effective in any of the bleaching solution, the bleach-fixing solution and the fixing solution. It is believed that the intensification of stirring promotes the supply of bleaching agent and fixing agent to the emulsion layer, thereby increasing the desilvering rate.

Further, the above-described means for intensifying stirring are more effective where a bleach accelerating agent is used. They remarkably increase its accelerating effect and eliminate fixing hindrance arising from the use of the bleach accelerating agent.

Automatic developing machines for processing in the context of the present invention are preferably provided with a transportation means for the light-sensitive material as described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. As described in JP-A-60-191257, such a transportation means can greatly reduce the amount of processing solution carried over from the preceding bath to the subsequent bath and degradation of the processing solutions is effectively prevented. Such an effect is particularly useful for reducing the processing time at each step and reducing the replenishment amount of the processing solution at each step.

After the desilvering step, the silver halide color photographic material according to the present invention is generally subjected to a water washing step and/or a stabilizing step.

The amount of water required for the water washing step may be set in a wide range depending on the characteristics of the photographic light-sensitive materials (due to elements used therein, for example, couplers), uses thereof, the temperature of the washing water, the number of water washing tanks (stages), the replenishment system such as countercurrent or cocurrent, and other various conditions. The relationship between the number of water washing tanks and the amount of water in a multi-stage countercurrent system can be determined based on the method described in Journal of the Society of Mothion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May, 1955).

According to the multi-stage countercurrent system described in the above publication, the amount of water for washing can be significantly reduced. However, increasing the residence time of water in the tank causes propagation of bacteria and problems such as adhesion of floatage on the photographic materials occur. In the method of processing the silver halide color photographic material according to the present invention, a method for reducing the amounts of calcium ions and magnesium ions as described in JP-A-62-288838 can be particularly effectively employed to solve such problems. Further, sterilizers, for example, isothiazolone compounds as described in JP-A-57-8542, thiabendazoles, chlorine type sterilizers such as sodium chloroisocyanurate, benzotriazoles, sterilizers as described in Hiroshi Horiguchi, Bokin-Bobai No Kagaku (Sankyo Shuppan, 1986), Biseibutsu No Mekkin-, Sakkin-, Bobai-Gijutsu, edited by Eiseigijutsu Kai (Kogyogijutsu Kai 1982), and Bokin-Bobaizai Jiten, edited by Nippon Bokin-Bobai Gakkai (1986) can be employed.

The pH of the washing water used in the processing of the photographic light-sensitive materials according to the present invention is usually from 4 to 9, preferably from 5 to 8. The temperature of the washing water and the time for the water washing step can be variously set depending on the characteristics or uses of the photographic light-sensitive materials. However, it is typical to select a range of from 15°C to 45°C and a period from 20 sec. to 10 min. and preferably a range of from 25°C to 40°C and a period from 30 sec. to 5 min.

The photographic light-sensitive material of the present invention can also be directly processed with a stabilizing solution in place of the above-described water washing step. In such a stabilizing process, any of the known methods as described, for example, in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be employed.

Further, it is possible to conduct the stabilizing process subsequent to the above-described water washing process. One example thereof is a stabilizing bath containing a dye stabilizer and a surface active agent, which is employed as a final bath in the processing of color photographic light-sensitive materials for photographing. Examples of the dye stabilizers include aldehydes such as formalin or glutaraldehyde, N-methylol compounds, hexamethylenetetramine, and aldehyde sulfite adducts. To such a stabilizing bath, various chelating agents and antimolds may also be added.

Overflow solutions resulting from replenishment of the above-described washing water and/or stabilizing solution may be reused in other steps such as the desilvering step.

In processing using an automatic developing machine, concentration of the processing solution at each step tends to occur due to evaporation. To compensate for the concentration of the processing solution, it is preferred to replenish the appropriate amount of water.

For the purposes of simplifying and accelerating processing, a color developing agent may be incorporated into the silver halide color photographic material according to the present invention. In order to incorporate the color developing agent, it is preferred to employ various precursors of color developing agents. Suitable examples of precursors of developing agents include indoaniline type compounds as described in U.S. Patents 3,342,597, Schiff's base type compounds as described in U.S. Patent 3,342,599 and Research Disclosure, No. 14850 and ibid., No. 15159, aldol compounds as described in Research Disclosure, No. 13924, metal salt complexes as described in U.S. Patent 3,719,492, and urethane type compounds as described in JP-A-53-135628.

Further, the silver halide color photographic material according to the present invention may contain, if desired, various 1-phenyl-3-pyrazolidones for the purpose of accelerating color development. Typical examples of these compounds include those described, for example in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

In the present invention, various kinds of processing solutions can be employed at a temperature range from 10° C to 50° C. Although a standard temperature is from 33° C to 38° C, it is possible to carry out processing at higher temperatures to accelerate the processing whereby the processing time is shortened, or at lower temperatures to improve image quality and to maintain stability of the processing solutions.

Further, for the purpose of reducing the amount of silver employed in the color photographic light-sensitive material, the photographic processing may be conducted utilizing color intensification using cobalt or hydrogen peroxide as described in West German Patent 2,226,770 or U.S. Patent 3,674,499.

Moreover, the silver halide color photographic material of the present invention can be applied to heat-developable light-sensitive materials as described, for example, in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056 and European Patent 210660A2.

The present invention is illustrated in greater detail with reference to the following examples, but should not be construed as being limited thereto.

EXAMPLE 1

On a paper support, both surfaces of which were laminated with polyethylene, were coated layers as shown below to prepare a multilayer color printing paper which was designated Sample 101. The coating solutions were prepared in the following manner.

Preparation of Coating Solution for First Layer:

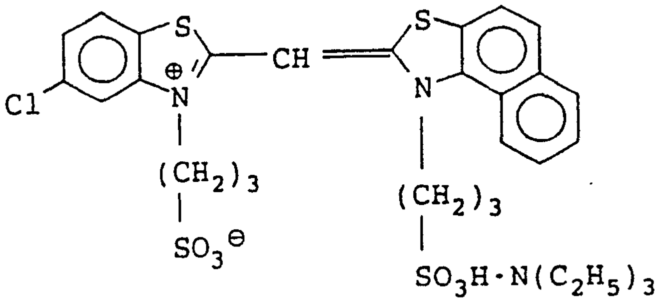
19.1 g of Yellow coupler (ExY), 4.4 g of Color image stabilizer (Cpd-1) and 0.7 g of Color image stabilizer (Cpd-7) were dissolved in a mixture of 27.2 ml of ethyl acetate and 8.2 g of Solvent (Solv-1) and the resulting solution was emulsified and dispersed in 185 ml of a 10% aqueous solution of gelatin containing 8 ml of a 10% aqueous solution of sodium dodecylbenzenesulfonate. Separately, to a silver chlorobromide emulsion (cubic grains, mixture of two emulsions having average grain size of 0.88 mμ and 0.70 mμ in 3:7 by molar ratio of silver, coefficient of variation of grain size: 0.08 and 0.10 respectively, 0.2 mol% silver bromide based on the whole of grains being localized at the surface of grains respectively) were added two blue-sensitive sensitizing dyes shown below in an amount of each 2.0×10^{-4} mol per mol of silver in the case of the larger grain size emulsion and in an amount of each 2.5×10^{-4} mol per mol of silver in the case of the smaller grain size emulsion, and the emulsion was then subjected to sulfur sensitization. The above described emulsified dispersion was mixed with the silver chlorobromide emulsion, with the concentration of the resulting mixture being controlled to form the composition shown below, whereby the coating solution for the first layer was prepared.

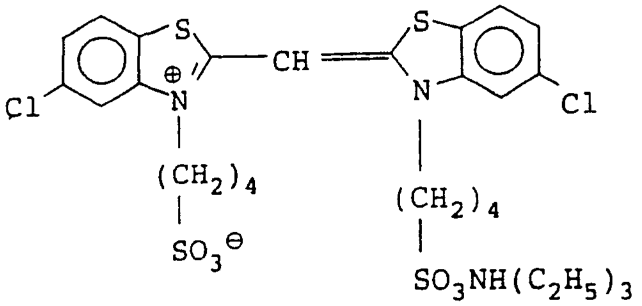
Coating solutions for the second layer to the seventh layer were prepared in a similar manner as described for the coating solution for the first layer.

1-Oxy-3,5-dichloro-s-triazine sodium salt was used as a gelatin hardener in each layer.

The following spectral sensitizing dyes were employed in the emulsion layers, respectively.

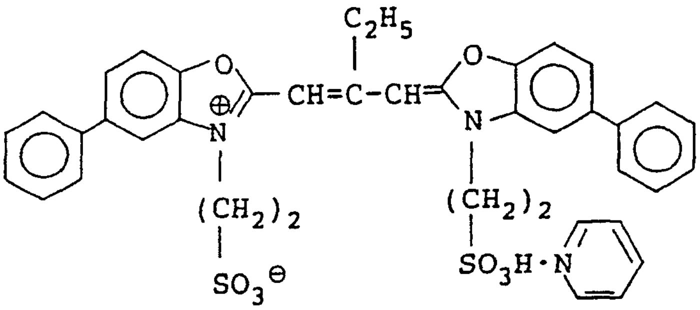
Blue-Sensitive Emulsion Layer:



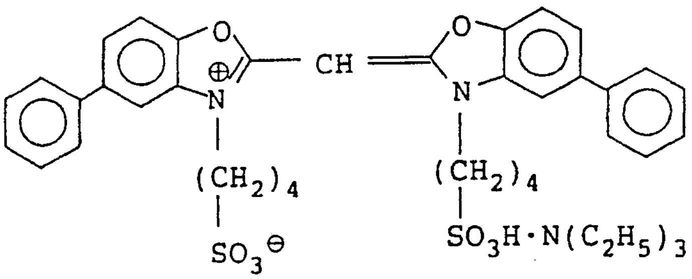


(Amount added: each 2.0×10^{-4} mol per mol of silver halide in the larger grain size emulsion and each 2.5×10^{-4} mol per mol of silver halide in the smaller grain size emulsion)

Green-Sensitive Emulsion Layer:

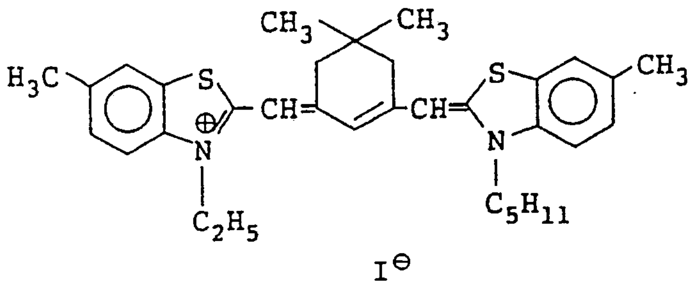


(Amount added: 4.0×10^{-4} mol per mol of silver halide in the larger grain size emulsion and 5.6×10^{-4} mol per mol of silver halide in the smaller grain size emulsion) and



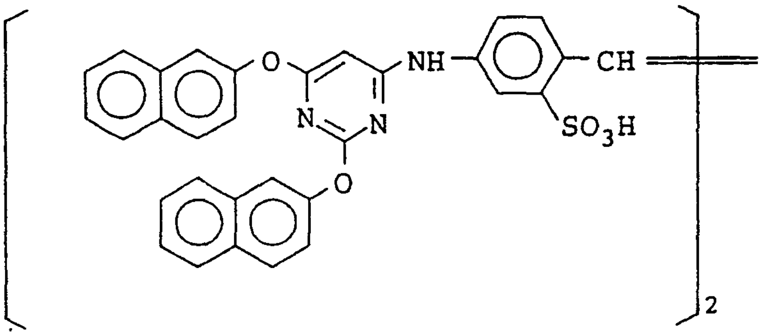
(Amount added: 7.0×10^{-5} mol per mol of silver halide in the larger grain size emulsion and 1.0×10^{-5} mol per mol of silver halide in the smaller grain size emulsion)

Red Sensitive Emulsion Layer:



(Amount added: 0.9×10^{-4} mol per mol of silver halide in the larger grain size emulsion and 1.1×10^{-4} mol per mol of silver halide in the smaller grain size emulsion)

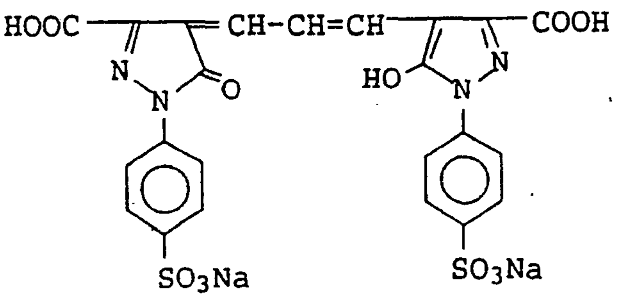
The compound shown below was added to the red-sensitive emulsion layer in an amount of 2.6×10^{-3} mol per mol of silver halide.



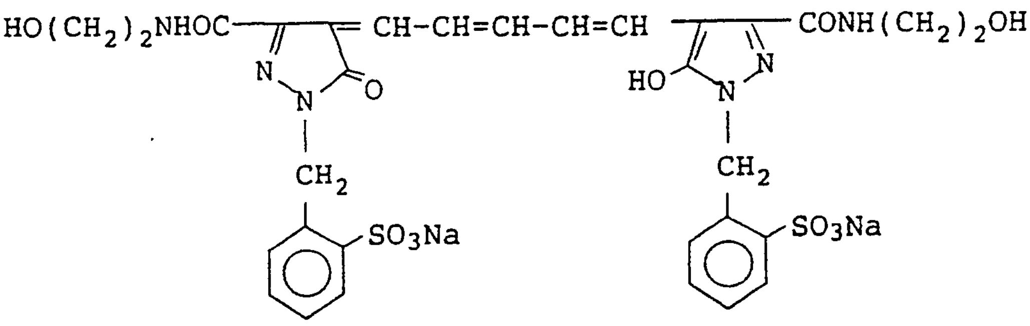
To the blue-sensitive emulsion layer, green-sensitive emulsion layer and red-sensitive emulsion layer, 1-(5-methylureidophenyl)-5-mercaptotetrazole was added in amounts of 8.5×10^{-5} mol, 7.7×10^{-4} mol and 2.5×10^{-4} mol per mol of silver halide, respectively.

Further, to the blue-sensitive emulsion layer and green-sensitive emulsion layer, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added in amounts of 1×10^{-4} mol and 2×10^{-4} mol per mol of silver halide, respectively.

Moreover, to prevent irradiation, the following dyes were added to the emulsion layers.



and



Layer Construction

The composition of each layer is shown below. The numerical values denote the coating amounts of components in the units of g/m^2. The coating amount of the silver halide emulsion is indicated in terms of silver coating amount.

Support

Polyethylene laminated paper (the polyethylene coating containing a white pigment (TiO_2) and a bluish dye (ultramarine) on the first layer side)

First Layer (Blue-sensitive layer)	
Silver chlorobromide emulsion described above	0.30
Gelatin	1.86
Yellow coupler (ExY)	0.82
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35
Color image stabilizer (Cpd-7)	0.06

Second Layer (Color mixing preventing layer)	
Gelatin	0.99
Color mixing preventing agent (Cpd-5)	0.08
Solvent (Solv-1)	0.16
Solvent (Solv-4)	0.08

Third Layer (Green-Sensitive layer)

Silver chlorobromide emulsion (cubic grains, mixture of two emulsions having average grain size of 0.55 µm and 0.39 µm in 1:3 by molar ratio of silver, coefficient of variation of grain size: 0.10 and 0.08 respectively, 0.8 mol% silver bromide based on the whole of grains being localized at the surface of grains respectively)	0.12
Gelatin	1.24
Magenta coupler (ExM)	0.20
Color image stabilizer (Cpd-2)	0.03
Color image stabilizer (Cpd-3)	0.15
Color image stabilizer (Cpd-4)	0.02
Color image stabilizer (Cpd-9)	0.02
Organic solvent having a high boiling point (S-3)	0.40

Fourth Layer (Ultraviolet light absorbing layer)	
Gelatin	1.58
Ultraviolet light absorbing agent (UV-1)	0.47
Color mixing preventing agent (Cpd-5)	0.05
Solvent (Solv-5)	0.24

Fifth Layer (Red-sensitive layer)	
Silver chlorobromide emulsion (cubic grains, mixture of two emulsions having average grain size of 0.58 μm and 0.45 μm in 1:4 by molar ratio of silver, coefficient of variation of grain size: 0.09 and 0.11 respectively, 0.6 mol% silver bromide based on the whole of grains being localized at a part of the surface of grains)	0.23
Gelatin	1.34
Cyan coupler (ExC)	0.32
Color image stabilizer (Cpd-6)	0.17
Color image stabilizer (Cpd-7)	0.40
Color image stabilizer (Cpd-8)	0.04
Solvent (Solv-6)	0.15

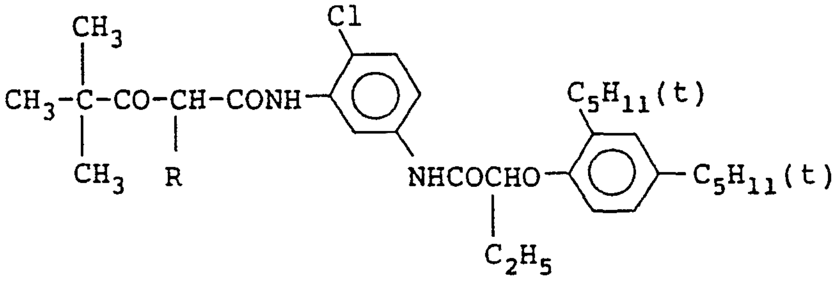
Sixth Layer (Ultraviolet light absorbing layer)	
Gelatin	0.53
Ultraviolet light absorbing agent (UV-1)	0.16
Color mixing preventing agent (Cpd-5)	0.02
Solvent (Solv-5).	0.08

Seventh Layer (Protective layer)	
Gelatin	1.33
Acryl-modified polyvinyl alcohol copolymer (Degree of modification: 17%)	0.17
Liquid paraffin	0.03

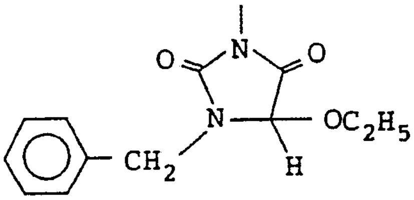
The compounds used in the above-described layers have the chemical structures shown below respectively.

Yellow coupler (ExY)

A mixture of

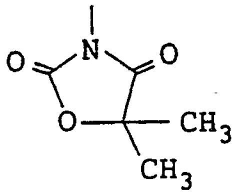


R=



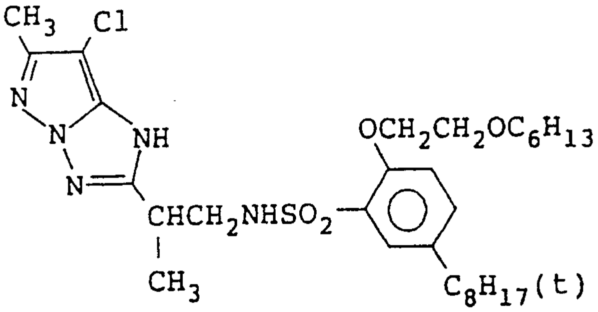
and

R=



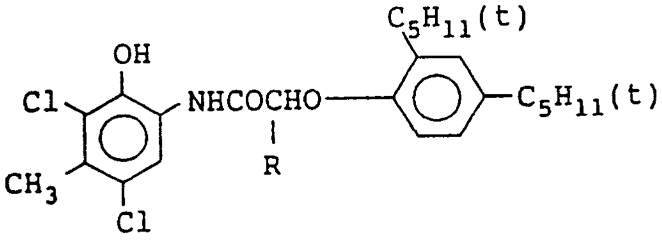
in a molar ratio of 1:1.

Magenta coupler (ExM)



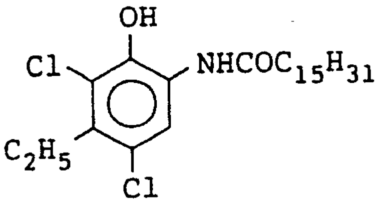
Cyan coupler (ExC)

A mixture of



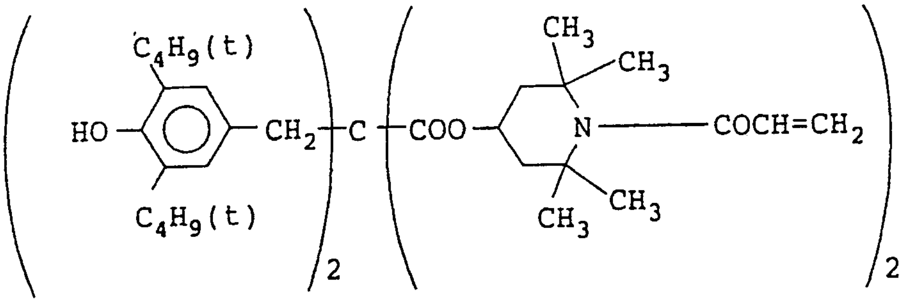
R=C_2H_5, C_4H_9

and

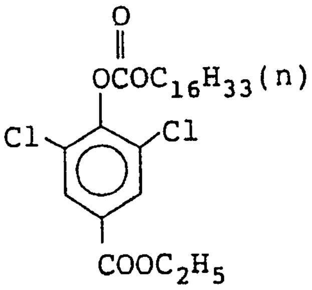


in a weight ratio of 2:4:4.

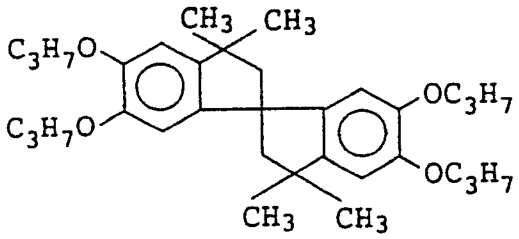
Color image stabilizer (Cpd-1)



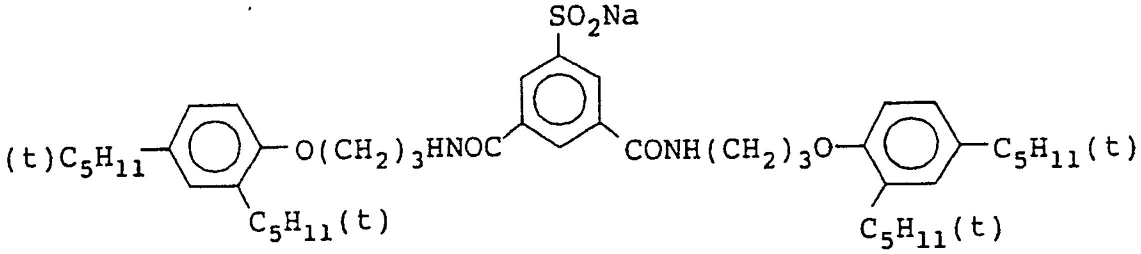
Color image stabilizer (Cpd-2)



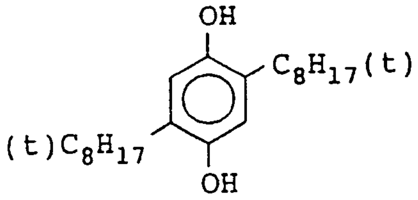
Color image stabilizer (Cpd-3)



Color image stabilizer (Cpd-4)

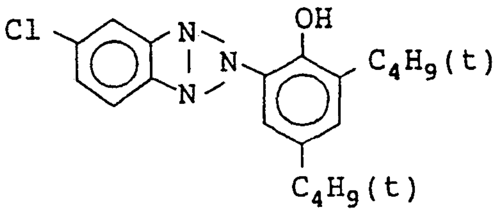


Color mixing preventing agent (Cpd-5)

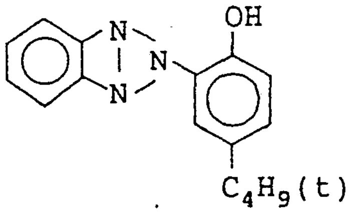


Color image stabilizer (Cpd-6)

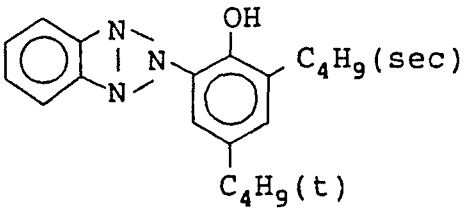
A mixture of



,

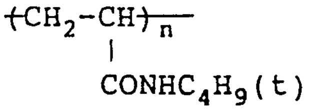


and



in a weight ratio of 2:4:4.

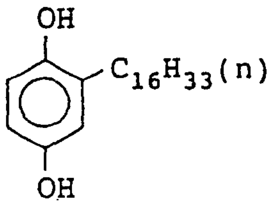
Color image stabilizer (Cpd-7)



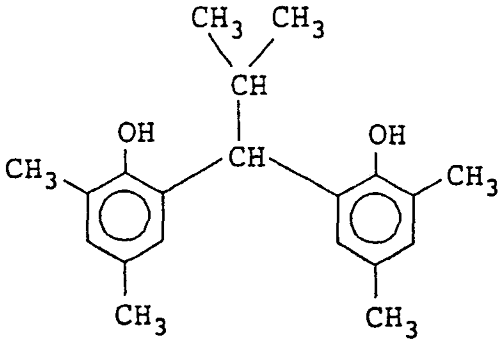
$$-\!\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{CH}\right)_{\!n}\!-$$

(average molecular weight: 60,000)

Color image stabilizer (Cpd-8)

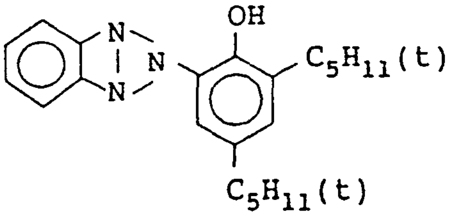


Color image stabilizer (Cpd-9)



Ultraviolet light absorbing agent (UV-1)

A mixture of



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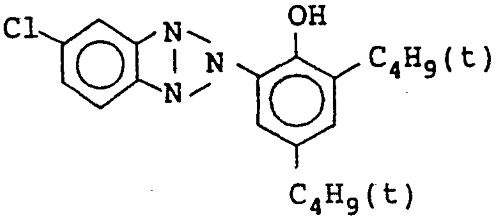
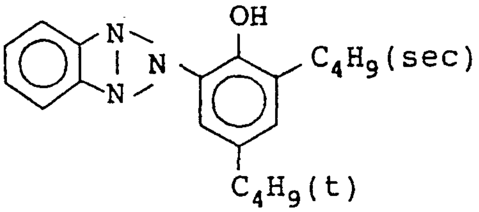
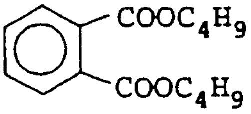


and

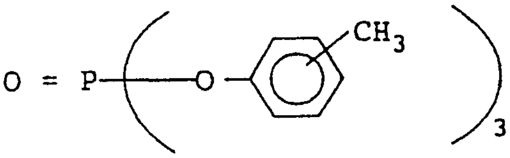


in a weight ratio of 4:2:4.

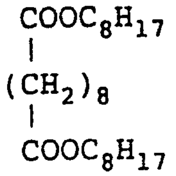
Solvent (Solv-1)



Solvent (Solv-4)

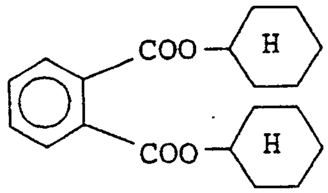


Solvent (Solv-5)



$$\begin{array}{c} \mathrm{COOC_8H_{17}} \\ | \\ \mathrm{(CH_2)_8} \\ | \\ \mathrm{COOC_8H_{17}} \end{array}$$

Solvent (Solv-6)



Samples 102 to 105 were prepared in the same manner as described for Sample 101, except that the amount of organic solvent having a high boiling point (S-3) added to the third layer of Sample 101 was changed to 0.5 times, 0.2 times, and 0.1 times the amount added to Sample 101, and 0, respectively.

Samples 106 to 110 were prepared in the same manner as described for Samples 101 to 105, except that Magenta coupler ExM was replaced with an equimolar amount of Coupler M-6 according to the present invention in the third layer and the amount of the organic solvent having a high boiling point was adjusted to 2 times, 1 time, 0.4 times, 0.2 times and 0 times the amount of the coupler, respectively. Such adjustment of the weight ratio was also made in the following examples.

Samples 111 to 120 were prepared in the same manner as described for Samples 101 to 105 except that Magenta coupler ExM was replaced with an equimolar amount of Coupler M-12 or Coupler M-24 and the amount of the organic solvent having a high boiling point was adjusted as described above in the third layer, respectively.

Sample 101 thus prepared was exposed in an average manner, and then subjected to continuous processing according to Processing Step (I) shown below until the amount of replenisher added to the color developing solution reached twice the volume of the tank for color development.

Then, each of Samples 101 to 120 was exposed wedgewise through a green filter and processed according to Processing Step (I) using the processing solutions after the continuous processing.

The hue of the magenta color obtained in each sample was measured by a reflective type spectrophotometer at the area having an optical density of 1.5. The results obtained are shown in Fig. 1.

As is apparent from the results shown in Fig. 1, where a coupler other than those of the present invention was used, aggregation of dyes occurred and a large subsidiary absorption appeared on the short wavelength side, resulting in a shift of the magenta color to red, when the amount of the solvent was reduced to 1/2 or less of the coupler by weight. On the contrary, with the couplers according to the present invention, the formation of aggregation was restrained and the color reproducibility was not affected even if the amount of solvent was reduced.

Then, the samples obtained were irradiated intermittently with xenon light for 10 days and the light-fastness of the magenta image was evaluated. The results are shown in Table 1 below. It is apparent that where a coupler according to the present invention was used, degradation of light-fastness was minimal and excellent color image preservability was maintained when the amount of solvent was reduced.

Further, development processing was conducted, except that the amount of replenisher for Rinse (3) was reduced from 350 ml in Processing Step (I) to 200 ml. This was designated Processing Step (II). The amount of rinse solution carried out by the light-sensitive material was 30 ml per square meter.

To evaluate the occurrence of staining in the samples obtained by the above described processing, each of the samples was stored for 10 days under conditions of 80° C and 70% RH and the magenta density of the samples was measured using a color densitometer manufactured by Macbeth Co. The results are also shown in Table 1 below. From these results it can be seen that in the samples containing the coupler and organic solvent having a high boiling point according to the present invention the occurrence of magenta staining was minimal even where the amount of replenisher for the rinse solution was reduced.

Moreover, it is apparent that the effect of the present invention increases as the amount of organic solvent having a high boiling point used is reduced.

Furthermore, samples were prepared in the same manner as described for Samples 101 to 104, except that the coupler in the third layer was changed to Coupler M-42. The samples were subjected to Processing Step (I). The spectral absorption properties and light-fastness of the magenta images obtained were determined. As a result, it was seen that while the spectral absorption property was maintained in a satisfactory manner, the amount of fading due to light was large compared with the samples using Couplers M-6, M-12 and M-24, when the amount of organic solvent having a high boiling point was reduced.

Processing Step (I):

Processing Step	Temperature	Time	Amount of * Replenishment	Tank Capacity
	(°C)	(sec)	(ml)	(ℓ)
Color Development	35	45	161	17
Bleach-Fixing	30-35	45	215	17
Rinse (1)	30-35	20	-	10
Rinse (2)	30-35	20	-	10
Rinse (3)	30-35	20	350	10
Drying	70-80	60		

* The amount of replenishment per m^2 of photographic light-sensitive material.

The rinse steps were conducted using a three-tank countercurrent system from Rinse (3) to Rinse (1). The composition of each processing solution used is illustrated below.

Color Developing Solution:	Tank Solution	Replenisher
Water	800 ml	800 ml
Ethylenediamine-N,N,N,N-tetramethylenephosphonic acid	1.5 g	2.0 g
Potassium bromide	0.015 g	-
Triethanolamine	8.0 g	12.0 g
Sodium chloride	1.4 g	-
Potassium carbonate	25 g	25 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	7.0 g
N,N-Bis(carboxymethyl)hydrazine	5.5 g	7.0 g
Fluorescent brightening agent (WHITEX 4B manufactured by Sumitomo Chemical Co., Ltd.)	1.0 g	2.0 g
Water to make	1000 ml	1000 ml
pH (at 25°C)	10.05	10.45

Bleach-Fixing Solution: (both tank solution and replenisher)	
Water	400 ml
Ammonium thiosulfate (70%)	100 ml
Sodium sulfite	17 g
Ammonium iron (III) ethylenediaminetetraacetate	55 g
Disodium ethylenediaminetetraacetate	5 g
Ammonium bromide	40 g
Water to make	1000 ml
pH (at 25°C)	6.0

Rinse Solution: (both tank solution and replenisher)

Ion-exchanged water (calcium and magnesium contents: not more than 3 ppm respectively)

TABLE 1

Sample No.	Coupler in Third Layer	Solvent/ Coupler Ratio	Light* Fading Rate (%)	Magenta Stain Processing Step (I)	Magenta Stain Processing Step (II)
101 (Comparison)	ExM	2	5	0.18	0.25
102 (")	"	1	15	0.15	0.19
103 (")	"	0.4	40	0.11	0.15
104 (")	"	0.2	53	0.08	0.11
105 (")	"	0	68	0.07	0.09
106 (")	M-6	2	1	0.05	0.07
107 (Present Invention)	"	1	2	0.03	0.05
108 (")	"	0.4	5	0.02	0.03
109 (")	"	0.2	8	0.02	0.02
110 (")	"	0	11	0.01	0.01
111 (Comparison)	M-12	2	1	0.03	0.06
112 (Present Invention)	"	1	2	0.02	0.05
113 (")	"	0.4	5	0.01	0.02
114 (")	"	0.2	9	0.01	0.02

TABLE 1 (cont'd)

Sample No.	Coupler in Third Layer	Solvent/ Coupler Ratio	Light* Fading Rate (%)	Magenta Stain	
				Processing Step (I)	Processing Step (II)
115 (Present Invention)	M-12	0	13	0.01	0.01
116 (Comparison)	M-24	2	1.5	0.04	0.06
117 (Present Invention)	"	1	3	0.03	0.04
118 (")	"	0.4	6.5	0.02	0.03
119 (")	"	0.2	12	0.01	0.02
120 (")	"	0	16	0.01	0.01

* At the area having an optical density of 1.0.

EXAMPLE 2

A cellulose triacetate film support (thickness: 127 μ) having a subbing layer was coated to prepare a multilayer color photographic light-sensitive material, each layer having the composition set forth below. This photographic material was designated Sample 201. The numerical values indicate amounts added per m^2. It should be noted that the effects of the compounds added are not limited to the uses described.

First Layer: Antihalation Layer	
Black colloidal silver	0.25 g
Gelatin	1.9 g
Ultraviolet light absorbing agent U-1	0.04 g
Ultraviolet light absorbing agent U-2	0.1 g
Ultraviolet light absorbing agent U-3	0.1 g
Ultraviolet light absorbing agent U-6	0.1 g
Organic solvent having a high boiling point S-1	0.1 g

Second Layer: Intermediate Layer	
Gelatin	0.40 g
Compound Cpd-D	10 mg
Organic solvent having a high boiling point Oil-3	40 mg

Third Layer: Intermediate Layer	
Fogged fine grain silver iodobromide emulsion (average grain size: 0.06 μm, AgI content: 1 mol%)	0.05 g (in terms of silver)
Gelatin	0.4 g

Fourth Layer: Low-Speed Red-Sensitive Emulsion Layer

Silver iodobromide emulsion [a 1:1 mixture of a monodispersed cubic emulsion (average grain size: 0.4 μm, AgI content: 4.5 mol%) and a monodispersed cubic emulsion (average grain size: 0.3 μm, AgI content: 4.5 mol%)] spectrally sensitized with Sensitizing Dyes ES-1 and ES-2	0.4 g (in terms of Ag)
Gelatin	0.8 g
Coupler C-1	0.20 g
Compound Cpd-D	5.0 mg
Organic solvent having a high boiling point S-1	0.20 g

Fifth Layer: Medium-Speed Red-Sensitive Emulsion Layer	
Silver iodobromide emulsion (monodispersed cubic grain, average grain size: 0.5 μm, AgI content: 4 mol%) spectrally sensitized with Sensitizing Dyes ES-1 and ES-2	0.4 g (in terms of silver)
Gelatin	0.8 g
Coupler C-1	0.2 g
Coupler C-2	0.2 g
Organic solvent having a high boiling point S-1	0.4 g

Sixth Layer: High-Speed Red-Sensitive Emulsion Layer	
Silver iodobromide emulsion (monodispersed twin grains, average grain size: 0.7 µm, AgI content: 2 mol%) spectrally sensitized with Sensitizing Dyes ES-1 and ES-2	0.4 g (in terms of silver)
Gelatin	1.1 g
Coupler C-3	1.0 g
Organic solvent having a high boiling point S-1	1.1 g

Seventh Layer: Intermediate Layer	
Gelatin	0.6 g
Dye D-1	0.02 g

Eighth Layer: Intermediate Layer	
Fogged silver iodobromide emulsion (average grain size: 0.06 µm, AgI content: 0.3 mol%)	
Gelatin	1.0 g
Color mixing preventing agent Cpd-A	0.2 g

Ninth Layer: Low-Speed Green-Sensitive Emulsion Layer

Silver iodobromide emulsion [a 1:1 mixture of a first emulsion (monodispersed cubic grain, average grain size: 0.4 µm, AgI content: 4.5 mol%) and a second emulsion (monodispersed cubic grain, average grain size: 0.2 µm, AgI content: 4.5 mol%)] spectrally sensitized with Sensitizing Dyes ES-3 and ES-4	0.5 g (in terms of silver)
Gelatin	0.5 g
Coupler C-8	0.15 g
Compound Cpd-D	5.0 mg
Compound Cpd-B	0.01 g
Compound Cpd-E	0.01 g
Compound Cpd-F	0.01 g
Compound Cpd-G	0.01 g
Compound Cpd-H	0.01 g
Organic solvent having a high boiling point S-1	0.3 g

Tenth Layer: Medium-Speed Green-Sensitive Emulsion Layer	
Silver iodobromide emulsion (monodispersed cubic grain, average grain size: 0.5 µm, AgI content: 3 mol%) spectrally sensitized with Sensitizing Dyes ES-3 and ES-4	0.4 g (in terms of silver)
Gelatin	0.6 g
Coupler C-8	0.2 g
Compound Cpd-B	0.03 g
Compound Cpd-E	0.01 g
Compound Cpd-F	0.01 g
Compound Cpd-G	0.01 g
Compound Cpd-H	0.01 g
Organic solvent having a high boiling point S-1	0.4 g

Eleventh Layer: High-Speed Green-Sensitive Emulsion Layer

Silver iodobromide emulsion [monodispersed tabular grain, average value of diameter/thickness of 7, average grain size (in terms of sphere): 0.6 μm, AgI content: 1.3 mol%] spectrally sensitized with Sensitizing Dyes ES-3 and ES-4	0.5 g (in terms of silver)
Gelatin	1.0 g
Coupler C-8	0.6 g
Compound Cpd-B	0.01 g
Compound Cpd-E	0.01 g
Compound Cpd-F	0.01 g
Compound Cpd-G	0.01 g
Compound Cpd-H	0.01 g
Organic solvent having a high-boiling point S-1	1.2 g

Twelfth Layer: Intermediate Layer	
Gelatin	0.6 g
Dye D-2	0.05 g

Thirteenth Layer: Yellow Filter Layer	
Yellow colloidal silver	0.1 g (in terms of silver)
Gelatin	1.1 g
Color mixing preventing agent Cpd-A	0.01 g

Fourteenth Layer: Intermediate Layer	
Gelatin	0.6 g

Fifteenth Layer: Low-Speed Blue-Sensitive Emulsion Layer

Silver iodobromide emulsion [a 1:1 mixture of a first monodispersed cubic emulsion (average grain size: 0.4 μm, AgI content: 3 mol%) and a second monodispersed cubic emulsion (average grain size: 0.2 μm, AgI content: 3 mol%)] sensitized with Sensitizing Dyes ES-5 and ES-6	0.6 g (in terms of silver)
Gelatin	0.8 g
Coupler C-5	0.6 g

Sixteenth Layer: Medium-Speed Blue-Sensitive Emulsion Layer

Silver iodobromide emulsion (monodispersed cubic grain, average grain size: 0.5 μm, AgI content: 2 mol%) sensitized with Sensitizing Dyes ES-5 and ES-6	0.4 g (in terms of silver)
Gelatin	0.9 g
Coupler C-5	0.3 g
Coupler C-6	0.3 g

Seventeenth Layer: High-Speed Blue-Sensitive Emulsion Layer

Silver iodobromide emulsion (tabular grains, average value of diameter/thickness of 7, average grain size of 0.7 μm in terms of sphere, AgI content: 1.5 mol%) sensitized with Sensitizing Dyes ES-5 and ES-6	0.4 g (in terms of silver)
Gelatin	1.2 g
Coupler C-6	0.7 g

Eighteenth Layer: First Protective Layer

Gelatin	0.7 g
Ultraviolet light absorbing agent U-1	0.04 g
Ultraviolet light absorbing agent U-3	0.03 g
Ultraviolet light absorbing agent U-4	0.03 g
Ultraviolet light absorbing agent U-5	0.05 g
Ultraviolet light absorbing agent U-6	0.05 g
Formalin scavenger Cpd-C	0.8 g
Dye D-3	0.05 g

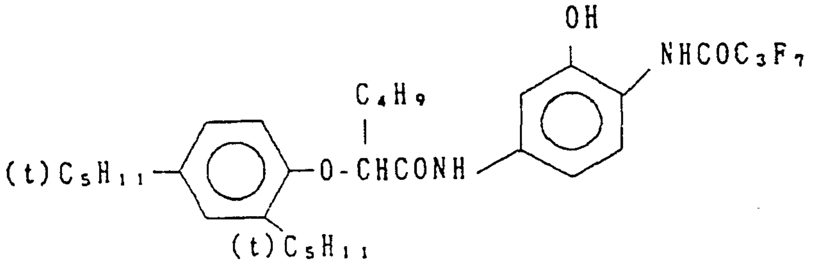
Nineteenth Layer: Second Protective Layer	
Fogged fine grain silver iodobromide emulsion (average grain size: 0.06 μm, AgI content: 1 mol%)	0.1 g (in terms of silver)
Gelatin	0.4 g

Twentieth Layer: Third Protective Layer	
Gelatin	0.4 g
Polymethyl methacrylate (average particle size: 1.5 μm)	0.1 g
Methyl methacrylate-acrylic acid (4:6) copolymer (average particle size: 1.5 μm)	0.1 g
Silicone oil	0.03 g
Surfactant W-1	3.0 mg

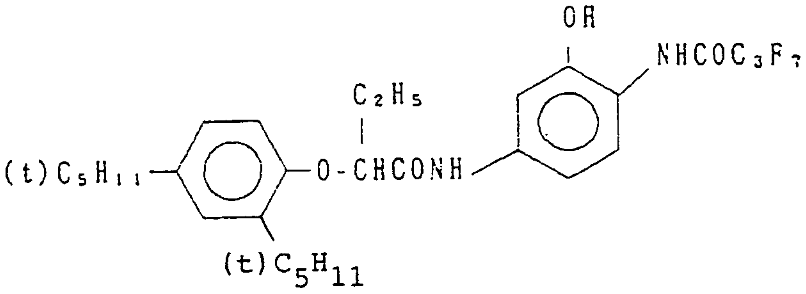
In addition to the above-described composition, Gelatin hardener H-1 and surfactants for coating and emulsification were added to each layer.

The compounds used in the above-described layers are shown below.

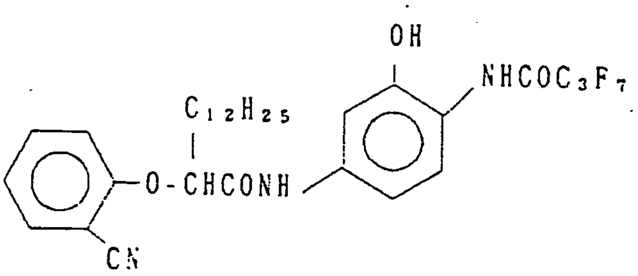
C - 1



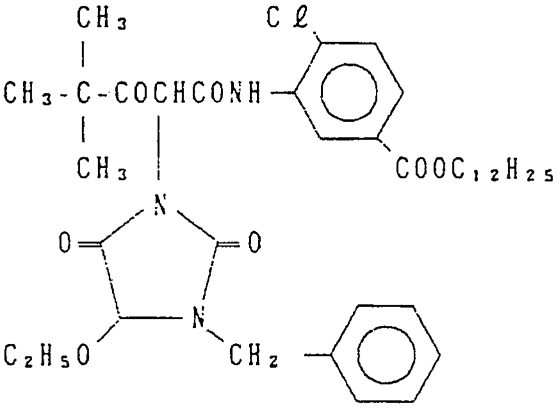
C - 2



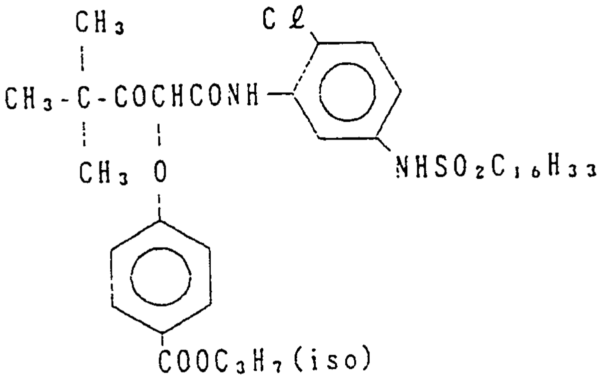
C - 3


OH
NHCOC3F7
C12H25
O-CHCONH
CN

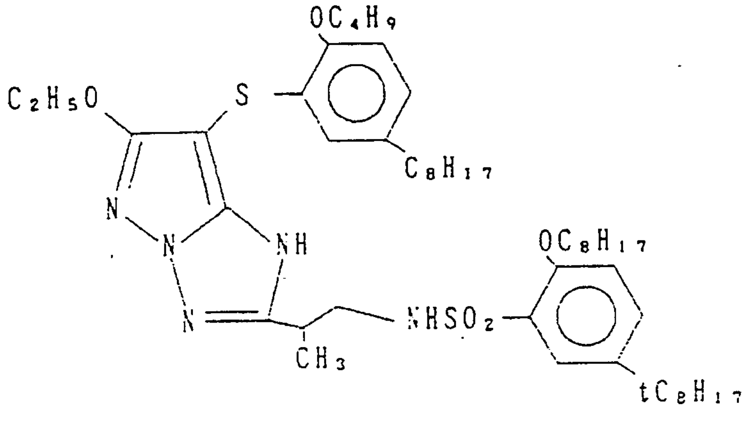
C - 5


CH3
Cℓ
CH3-C-COCHCONH
CH3
COOC12H25
N
O
O
C2H5O
N
CH2

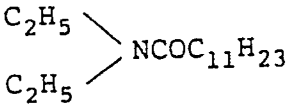
C - 6


CH3
Cℓ
CH3-C-COCHCONH
CH3
O
NHSO2C16H33
COOC3H7(iso)

Coupler C-8

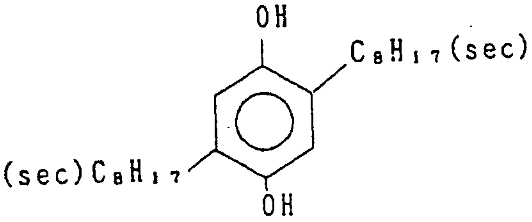


Oil-3

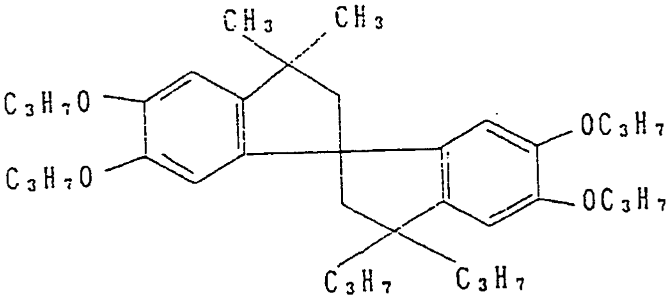


$(C_2H_5)_2NCOC_{11}H_{23}$

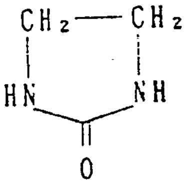
Cpd−A



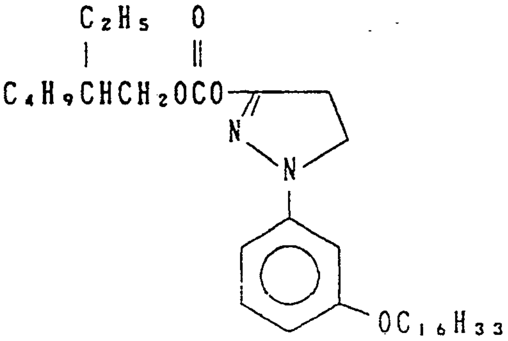
Cpd−B



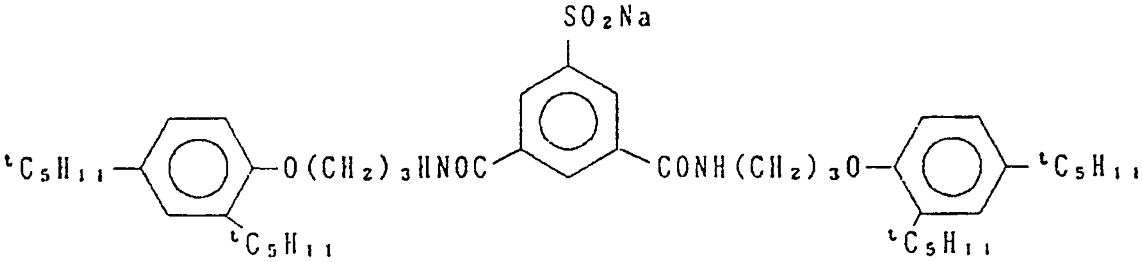
Cpd−C



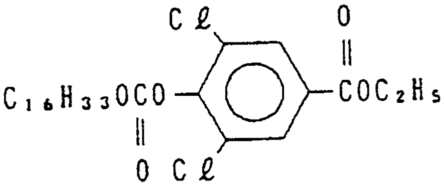
Cpd－E


C₂H₅
O
C₄H₉CHCH₂OCO
N
N
OC₁₆H₃₃

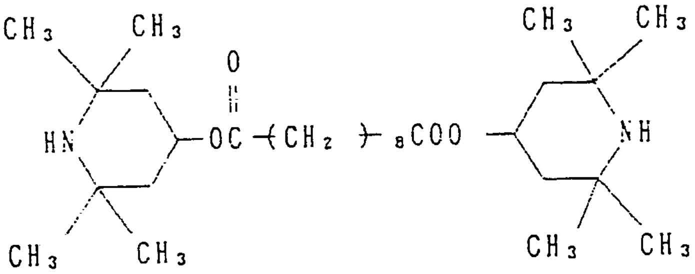
Cpd－F


SO₂Na
ᵗC₅H₁₁
O(CH₂)₃HNOC
CONH(CH₂)₃O
ᵗC₅H₁₁
ᵗC₅H₁₁
ᵗC₅H₁₁

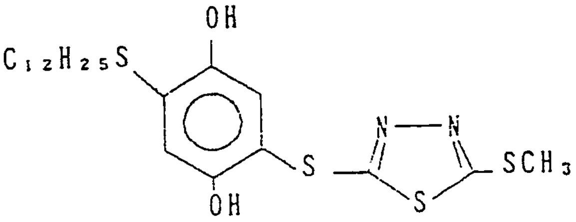
Cpd-G



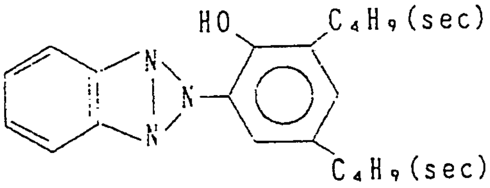
Cpd-H



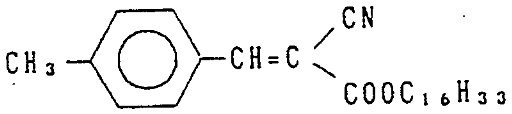
Cpd-D



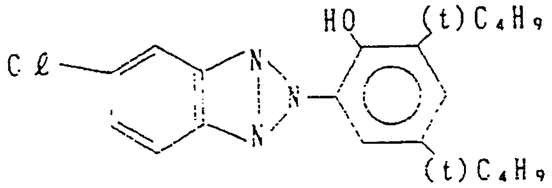
U-1



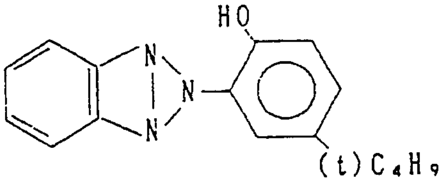
U - 2



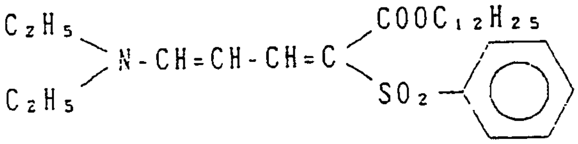
U - 3



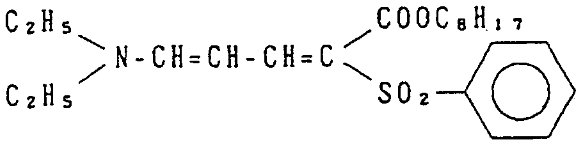
U - 4



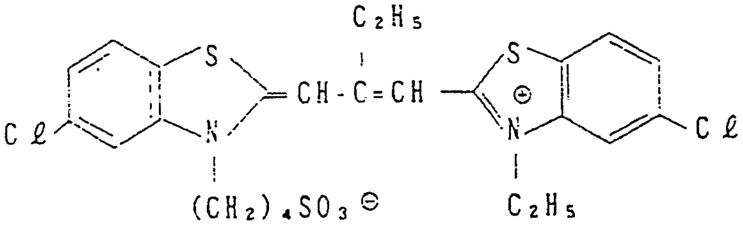
U - 5



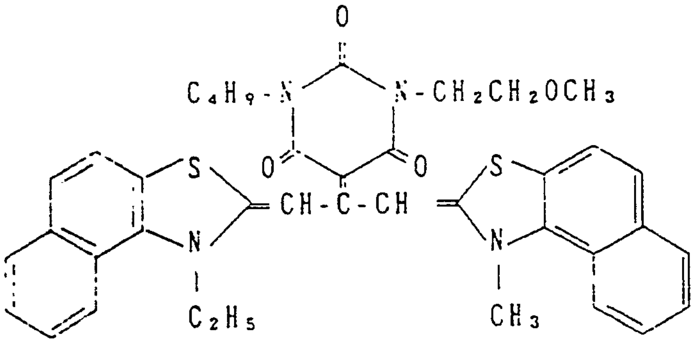
U - 6



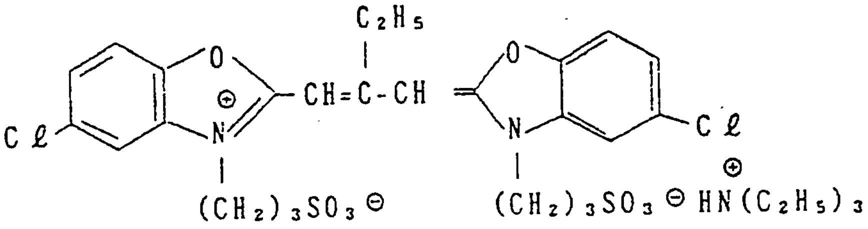
ES - 1



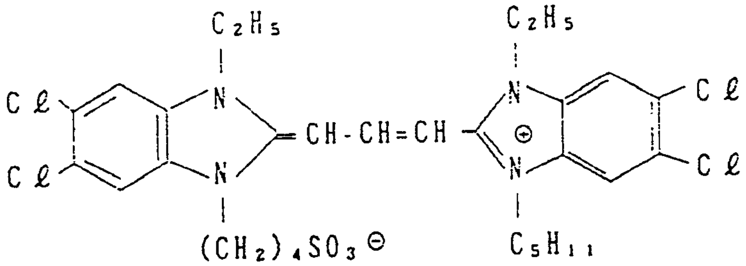
ES - 2



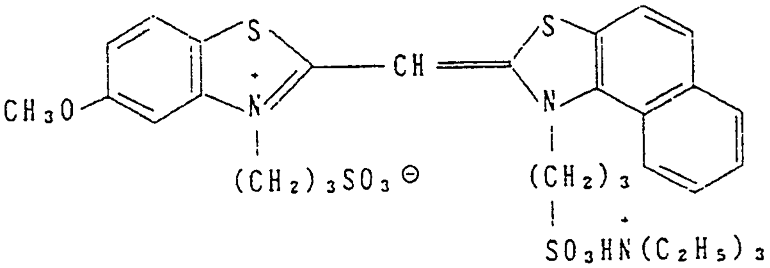
ES − 3


C₂H₅
O
CH=C-CH
O
Cℓ
N
N
Cℓ
(CH₂)₃SO₃⊖
(CH₂)₃SO₃⊖ HN(C₂H₅)₃

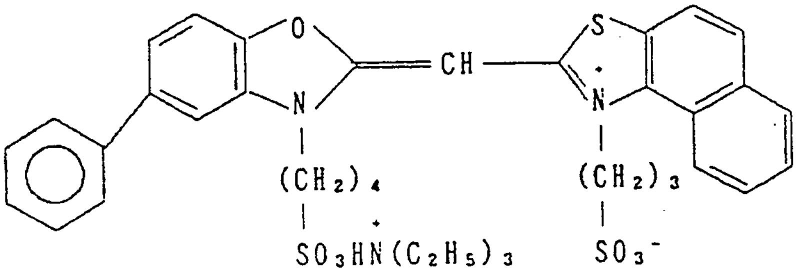
ES − 4


C₂H₅
C₂H₅
Cℓ
N
N
Cℓ
CH-CH=CH
Cℓ
N
N
Cℓ
(CH₂)₄SO₃⊖
C₅H₁₁

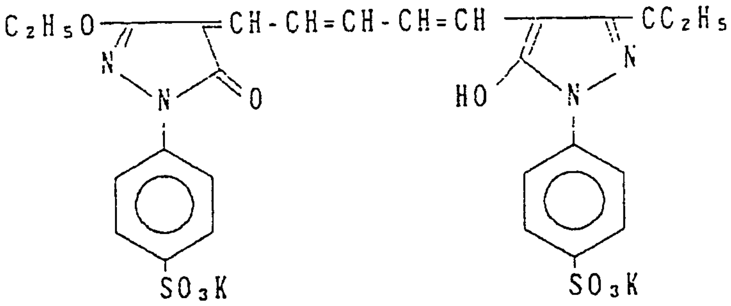
ES − 5


S
CH
S
CH₃O
N
N
(CH₂)₃SO₃⊖
(CH₂)₃
SO₃HN(C₂H₅)₃

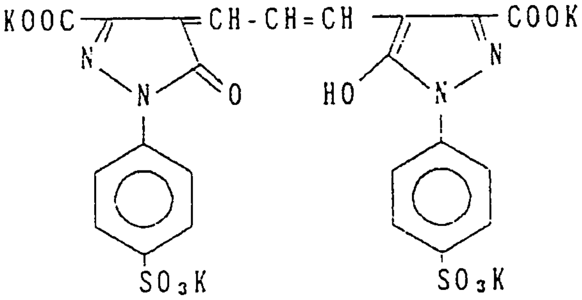
ES − 6


O
N
CH
S
N
(CH₂)₄
SO₃HN(C₂H₅)₃
(CH₂)₃
SO₃⁻

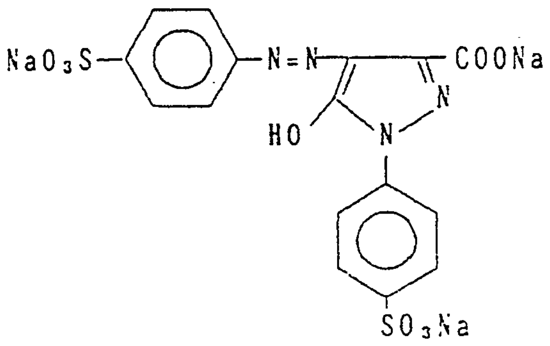
D − 1


C₂H₅O
CH-CH=CH-CH=CH
CC₂H₅
N
N
O
HO
N
N
SO₃K
SO₃K

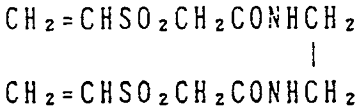
D − 2


KOOC
CH-CH=CH
COOK
N
N
O
HO
N
N
SO₃K
SO₃K

D - 3

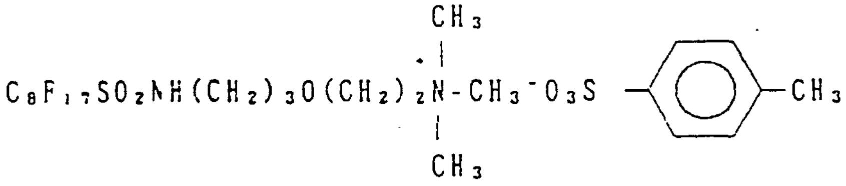


H - 1



$$\begin{array}{r} CH_2=CHSO_2CH_2CONHCH_2 \\ | \\ CH_2=CHSO_2CH_2CONHCH_2 \end{array}$$

W - 1



Samples 202 was prepared in the same manner as described for Sample 201, except that the amount of organic solvent having a high boiling point S-1 used in the ninth, tenth and eleventh layers of Sample 201 was changed to 0.5 times the respective amounts used in Sample 201.

Samples 203 was prepared in the same manner as described for Sample 201, except that the amount of organic solvent having a high boiling point S-1 used in the ninth, tenth and eleventh layers of Sample 201 was changed to 0.1 times the respective amounts used in Sample 201.

Sample 204 to 206 were prepared in the same manner as described for Samples 201 to 203, except that Coupler C-8 added to the ninth, tenth and eleventh layers of Samples 201 to 203 was replaced with the equimolar amount of Coupler M-1 according to the present invention and the amount of the organic solvent was adjusted to maintain the same weight ratio of organic solvent to coupler, respectively.

Samples 207 to 212 were prepared in the same manner as described for Samples 201 to 203, except that Coupler C-8 added to the ninth, tenth and eleventh layers of Samples 201 to 203 was replaced with the equimolar amount of Coupler M-14 or Coupler M-20 and the amount of the organic solvent was adjusted as described above, respectively.

The magenta coupler and the weight ratio of organic solvent to coupler used in the ninth, tenth and eleventh layers of Samplers 201 to 212 are summarized in Table 2 below.

TABLE 2

Sample No.	Coupler	Ratio of Organic Solvent to Coupler
201 (Comparison)	C-8	2
202 (Comparison)	C-8	1
203 (Comparison)	C-8	0.2
204 (Comparison)	M-1	2
205 (Present Invention)	M-1	1
206 (Present Invention)	M-1	0.2
207 (Comparison)	M-13	2
208 (Present Invention)	M-13	1
209 (Present Invention)	M-13	0.2
210 (Comparison)	M-20	2
211 (Present Invention)	M-20	1
212 (Present Invention)	M-20	0.2

Samples 201 to 212 were exposed uniformly through a red filter and a blue filter and further exposed wedgewise through a green filter, and then subjected to development processing according to Processing Step (II) described below.

The visible absorption spectrum of each sample was measured by a spectrophotometer. The results obtained are shown in Fig. 2.

As is apparent from the results shown in Fig. 2, where a comparative coupler other than those of the present invention was used, aggregation of dyes occurred, when the amount of the solvent having a high boiling point was reduced. On the contrary, with the couplers according to the present invention, the formation of aggregation was almost not observed even where the amount of organic solvent having a high boiling point was reduced.

Further, these samples were cut into a 35 mm width strip, loaded into a camera, used to photograph usual subjects and processed. With these samples, the color reproducibility of the red series color was particularly observed. The samples according to the present invention exhibited only minimal changes in hue from low density areas to high density areas. They also exhibited high saturation and excellent color reproducibility.

Processing Step (II):

Processing Step	Time	Temperature (°C)	Tank Capacity (ℓ)	Amount of Replenishment (ℓ/m²)
Black-and-White Development	6 min.	38	12	2.2
First Washing with Water	2 min.	38	4	7.5
Reversal	2 min.	38	4	1.1
Color Development	6 min.	38	12	2.2
Conditioning	2 min.	38	4	1.1
Bleaching	6 min.	38	12	0.22
Fixing	4 min.	38	8	1.1
Second Washing with Water	4 min.	38	8	7.5
Stabilizing	1 min.	25	2	1.1

Each processing solution has the following composition.

Black-and-White Development Solution:	Tank Solution	Replenisher
Pentasodium salt of nitrilo-N,N,N-trimethylenephosphonic acid	2.0 g	2.0 g
Sodium sulfite	30 g	30 g
Potassium hydroquinonemonosulfonate	20 g	20 g
Potassium carbonate	33 g	33 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2.0 g	2.0 g
Potassium bromide	2.5	1.4 g
Potassium thiocyanate	1.2 g	1.2 g
Potassium iodide	2.0 mg	-
Water to make	1000 ml	1000 ml
pH	9.60	9.60

The pH was adjusted with hydrochloric acid or potassium hydroxide.

Reversal Solution: (both tank solution and replenisher)	
Pentasodium salt of nitrilo-N,N,N-trimethylenephosphonic acid	3.0 g
Stannous chloride (dihydrate)	1.0 g
p-Aminophenol	0.1 g
Sodium hydroxide	8 g
Glacial acetic acid	15 ml
Water to make	1000 ml
pH	6.00

The pH was adjusted with hydrochloric acid or sodium hydroxide.

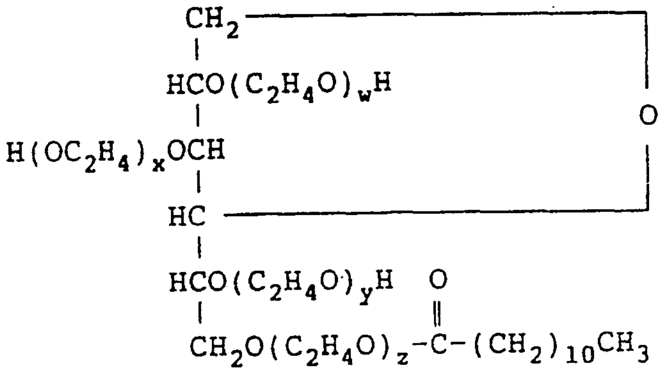
Color developing Solution:	Tank Solution	Replenisher
Pentasodium salt of nitrilo-N,N,N-trimethylenephosphonic acid	2.0 g	2.0 g
Sodium sulfite	7.0 g	7.0 g
Sodium tertiary phosphate (dodecahydrate)	36 g	36 g
Potassium bromide	1.0	-
Potassium iodide	90 mg	-
Sodium hydroxide	3.0 g	3.0 g
Citrazinic acid	1.5 g	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g	11 g
3,6-Dithiaoctane-1,8-diol	1.0 g	1.0 g
Water to make	1000 ml	1000 ml
pH	11.80	12.00

The pH was adjusted with hydrochloric acid or potassium hydroxide.

Conditioning Solution: (both tank solution and replenisher)	
Disodium ethylenediaminetetraacetate (dihydrate)	8.0 g
Sodium sulfite	12 g
1-Thioglycerin	0.4 ml
Sorbitan ester*	0:1 g
Water to make	1000 ml
pH	6.20

The pH was adjusted with hydrochloric acid or sodium hydroxide.

Sorbitan ester:



(w+x+y+z=20)

Bleaching Solution:	Tank Solution	Replenisher
Sodium ethylenediaminetetraacetate (dihydrate)	2.0 g	4.0 g
Ammonium iron(III) ethylenediaminetetraacetate (dihydrate)	120 g	240 g
Potassium bromide	100 g	200 g
Ammonium nitrate	10 g	20 g
Water to make	1000 ml	1000 ml
pH	5.70	5.50

The pH was adjusted with hydrochloric acid or sodium hydroxide.

Fixing Solution: (both tank solution and replenisher)	
Ammonium thiosulfate	8.0 g
Sodium sulfite	5.0 g
Sodium bisulfite	5.0 g
Water to make	1000 ml
pH	6.60

The pH was adjusted with hydrochloric acid or aqueous ammonia.

Stabilizing Solution: (both tank solution and replenisher)	
Formalin (37%)	5.0 ml
Polyoxyethylene-p-monononylphenyl ether (average degree of polymerization)	0.5 ml
Water to make	1000 ml
pH	not adjusted

EXAMPLE 3

On a cellulose triacetate film support provided with a subbing layer was coated each layer having the composition set forth below to prepare a multilayer color photographic light-sensitive material which was designated Sample 301.

With respect to the compositions of the layers, coating amounts of silver halide and colloidal silver are shown by g/m^2 units in terms of silver, the coating amounts of couplers, additives and gelatin are shown by g/m^2 units, and the coating amounts of sensitizing dyes are shown by mol number per mol of silver halide present in the same layer.

The symbols which denote additives used in this Example have the meanings described below. When the additive has two or more functions, one of them is indicated as representative.

UV: Ultraviolet light absorbing agent
Solv: Organic solvent having a high boiling point
ExF: Dye
ExS: Sensitizing dye
ExC: Cyan coupler
ExM: Magenta coupler
ExY: Yellow coupler
Cpd: Additive

First Layer: Antihalation Layer	
Black colloidal silver	0.15
Gelatin	2.0
ExM-6	0.2
UV-1	0.03
UV-2	0.06
UV-3	0.07
S-1	0.3
Solv-2	0.08
ExF-1	0.01
ExF-2	0.01
ExF-3	0.005
Cpd-6	0.001

Second Layer: Low-Speed Red-Sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 4 mol%, uniform AgI type, diameter corresponding to sphere: 0.4 µm, coefficient of variation of diameter corresponding to sphere: 30%, tabular grain, diameter/thickness ratio: 3.0)	0.37 (as silver)
Silver iodobromide emulsion (AgI: 6 mol%, internal high AgI type, with core/shell ratio of 2:1, diameter corresponding to sphere: 0.45 µm, coefficient of variation of diameter corresponding to sphere: 23%, tabular grain, diameter/thickness ratio: 2.0)	0.19 (as silver)
Gelatin	0.8
ExS-1	2.3×10^{-4}
ExS-2	1.4×10^{-4}
ExS-5	2.3×10^{-4}
ExS-7	4.2×10^{-6}
ExC-1	0.17
ExC-2	0.03
ExC-3	0.009

Third Layer: Medium-Speed Red-Sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 6 mol%, internal high AgI type, with core/shell ratio of 2:1, diameter corresponding to sphere: 0.65 μm, coefficient of variation of diameter corresponding to sphere: 23%, tabular grain, diameter/thickness ratio: 2.0)	0.65 (as silver)
Gelatin	1.0
ExS-1	2.3×10^{-4}
ExS-2	1.4×10^{-4}
ExS-5	2.3×10^{-4}
ExS-7	4.2×10^{-6}
ExC-1	0.31
ExC-2	0.01
ExC-3	0.10

Fourth Layer: High-Speed Red-sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 6 mol%, multilayer structure grain having silver amount of 3:4:2, AgI content: 24 mol, 0 mol, 6 mol from inside, diameter corresponding to sphere: 0.75 µm, coefficient of variation of diameter corresponding to sphere: 23%, tabular grain, diameter/thickness ratio: 2.5)	1.5 (as silver)
Gelatin	1.4
ExS-1	1.9×10^{-4}
ExS-2	1.2×10^{-4}
ExS-5	1.9×10^{-4}
ExS-7	8.0×10^{-6}
ExC-1	0.08
ExC-4	0.09
S-1	0.08
Solv-2	0.20
Cpd-7	4.6×10^{-4}

Fifth Layer: Intermediate Layer	
Gelatin	0.6
Cpd-1	0.1
Polyethyl acrylate latex	0.08
S-1	0.08

Sixth Layer: Low-Speed Green-Sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 4 mol%, uniform AgI type, diameter corresponding to sphere: 0.33 μm, coefficient of variation of diameter corresponding to sphere: 37%, tabular grain, diameter/thickness ratio: 2.0)	0.18 (as silver)
Gelatin	0.4
ExS-3	1.6×10^{-4}
ExS-4	4.8×10^{-4}
ExS-5	1×10^{-4}
ExM-5	0.10
ExM-7	0.03
ExY-8	0.01
S-1	0.15

Seventh Layer: Medium-Speed Green-Sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 4 mol%, uniform AgI type, diameter corresponding to sphere: 0.55 μm, coefficient of variation of diameter corresponding to sphere: 15%, tabular grain, diameter/thickness ratio: 4.0)	0.27 (as silver)
Gelatin	0.6
ExS-3	2×10^{-4}
ExS-4	7×10^{-4}
ExS-5	1.4×10^{-4}
ExM-5	0.17
ExM-7	0.04
ExY-8	0.02
S-1	0.25

Eighth Layer: High-Speed Green-Sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 8.8 mol%, multi-layer structure grain having silver amount of 3:4:2, AgI content: 24 mol, 0 mol, 3 mol from inside, diameter corresponding to sphere: 0.75 µm, coefficient of variation of diameter corresponidng to sphere 23%, tabular grain, diameter/thickness ratio: 1.6)	0.5 (as silver)
Gelatin	0.6
ExS-4	5.2×10^{-4}
ExS-5	1×10^{-4}
ExS-8	0.3×10^{-4}
ExM-5	0.08
ExM-6	0.03
ExY-8	0.02
ExC-1	0.01
ExC-4	0.01
S-1	0.15
Solv-2	0.05
Cpd-7	1×10^{-4}
Cpd-8	0.01

Ninth Layer: Intermediate Layer	
Gelatin	0.6
Cpd-1	0.04
Polyethyl acrylate latex	0.05
S-1	0.02
UV-4	0.03
UV-5	0.04

Tenth Layer: Donor Layer of Interimage Effect to Red-Sensitive Layer

Silver iodobromide emulsion (AgI: 8 mol%, internal high AgI type, with core/shell ratio of 2:1, diameter corresponding to sphere: 0.65 μm, coefficient of variation of diameter corresponding to sphere: 25%, tabular grain, diameter/thickness ratio: 2.0)	0.72 (as silver)
Silver iodobromide emulsion (AgI: 4 mol%, uniform AgI type, diameter corresponding to sphere: 0.4 μm, coefficient of variation of diameter corresponding to sphere: 30%, tabular grain, diameter/thickness ratio: 3.0)	0.21 (as silver)
Gelatin	1.0
ExS-3	6×10^{-4}
ExM-10	0.19
S-1	0.30
Solv-6	0.03

Eleventh Layer: Yellow Filter Layer	
Yellow colloidal silver	0.06
Gelatin	0.8
Cpd-2	0.13
S-1	0.13
Cpd-1	0.07
Cpd-6	0.002
H-1	0.13

Twelfth Layer: Low-Speed Blue-sensitive Emulsion Layer

Silver iodobromide emulsion (AgI: 4.5 mol%, uniform AgI type, diameter corresponding to sphere: 0.7 µm, coefficient of variation of diameter corresponding to sphere: 15%, tabular grain, diameter/thickness ratio: 7.0)	0.45 (as silver)
Silver iodobromide emulsion (AgI: 3 mol%, uniform AgI type, diameter corresponding to sphere: 0.3 µm, coefficient of variation of diameter corresponding to sphere: 30%, tabular grain, diameter/thickness ratio: 7.0)	0.25 (as silver)
Gelatin	2.1
ExS-6	9×10^{-4}
ExC-1	0.13
ExC-4	0.03
ExY-9	0.16
ExY-11	1.04
S-1	0.51

Thirteenth Layer: Intermediate Layer

Gelatin	0.4
ExY-12	0.20
S-1	0.19

Fourteenth Layer: High-Speed Blue-sensitive Emulsion Layer	
Silver iodobromide emulsion (AgI: 10 mol%, internal high AgI type, diameter corresponding to sphere: 1.0 µm, coefficient of variation of diameter corresponding to sphere: 25%, multiple twin tabular grain, diameter/thickness ratio: 2.0)	0.4 (as silver)
Gelatin	0.5
ExS-6	1×10^{-4}
ExY-9	0.01
ExY-11	0.20
ExC-1	0.01
S-1	0.10

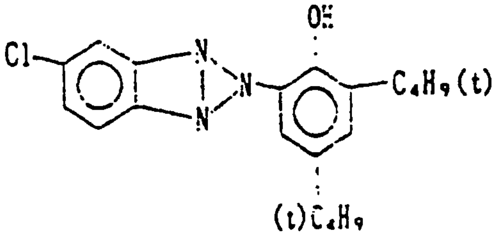
Fifteenth Layer: First Protective Layer	
Fine grain silver iodobromide emulsion (AgI: 2 mol%, uniform AgI type, diameter corresponding to sphere: 0.07 µm)	0.12 (as silver)
Gelatin	0.7
UV-4	0.11
UV-5	0.16
Solv-5	0.02
H-1	0.13
Cpd-5	0.10
Polyethyl acrylate latex	0.09

Sixteenth Layer: Second Protective Layer	
Fine grain silver iodobromide emulsion (AgI: 2 mol%, uniform AgI type, diameter corresponding to sphere: 0.07 µm)	0.36 (as silver)
Gelatin	0.85
Polymethyl methacrylate particle (diameter: 1.5 µm)	0.2
Cpd-4	0.04
W-4	0.02
H-1	0.17

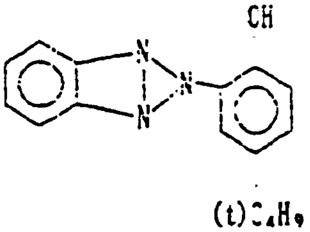
Each layer described above further contained a stabilizer for the emulsion (Cpd-3: 0.07 g/m^2) and surface active agents (W-1: 0.006 g/m^2, W-2: 0.33 g/m^2, W-3: 0.10 g/m^2) as coating aids or emulsifying or dispersing agents in addition to the above-described compounds.

The compounds used for the preparation of the light-sensitive material are illustrated below.

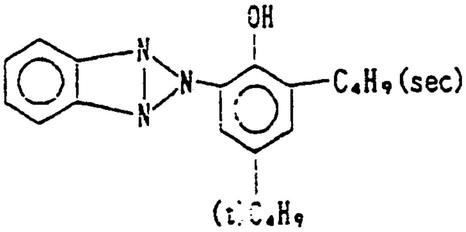
UV-1



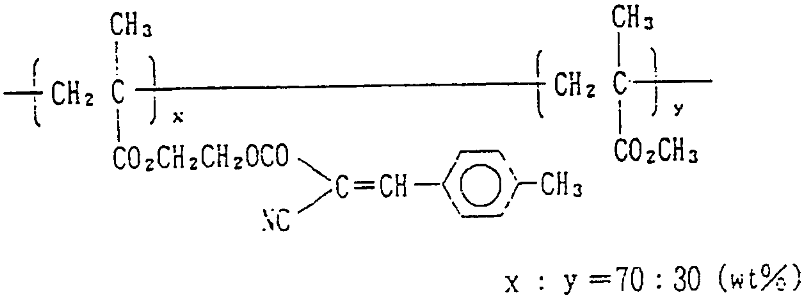
UV-2



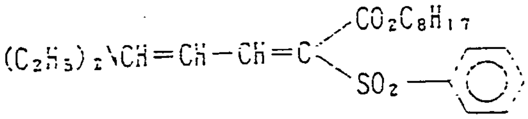
UV-3



UV-4



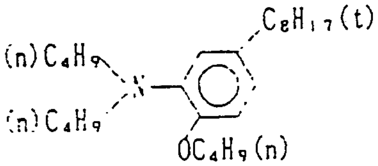
UV-5



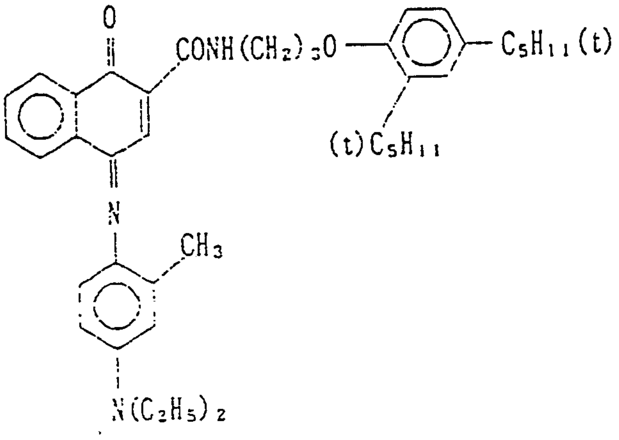
Solv-2 Dibutyl phthalate

Solv-5 Tricresyl phosphate

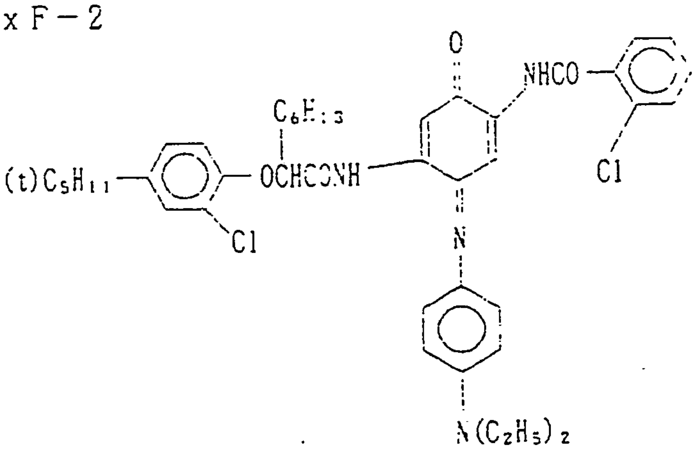
Solv-6



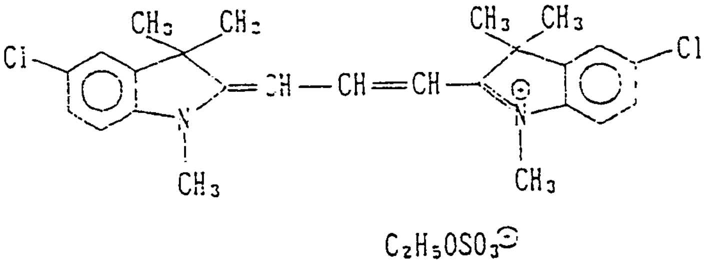
ExF-1



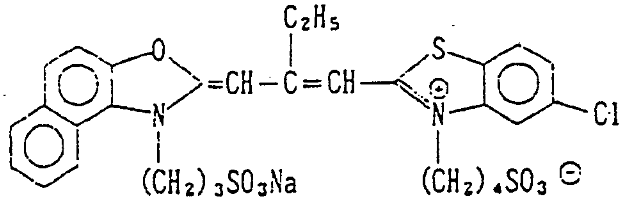
ExF-2



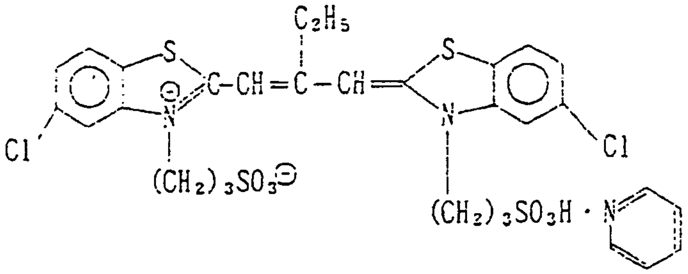
ExF-3



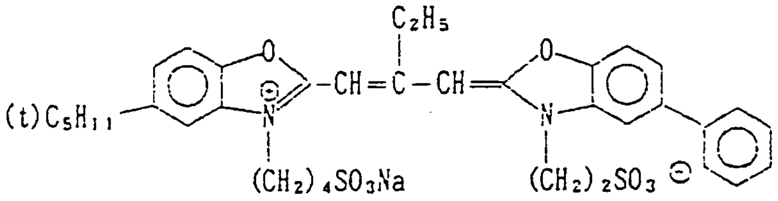
ExS-1



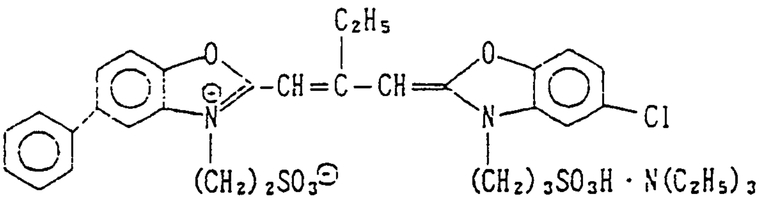
ExS-2



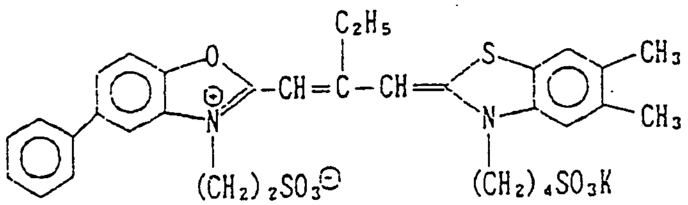
ExS-3



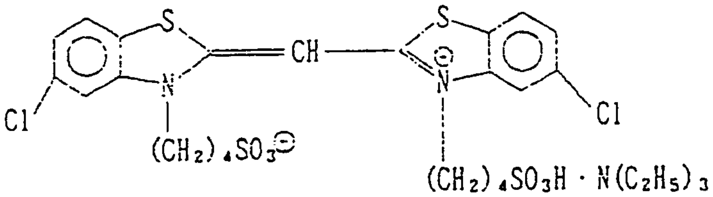
ExS-4



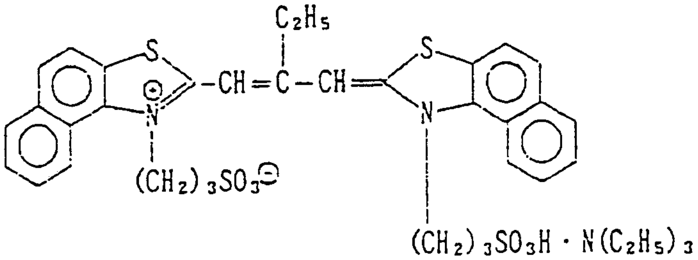
ExS−5



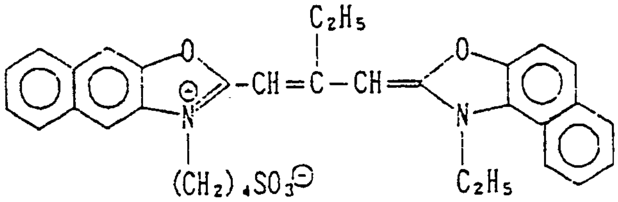
ExS−6



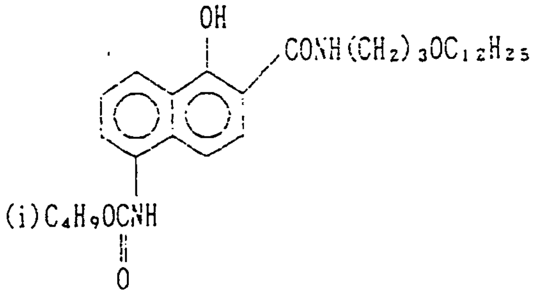
ExS−7



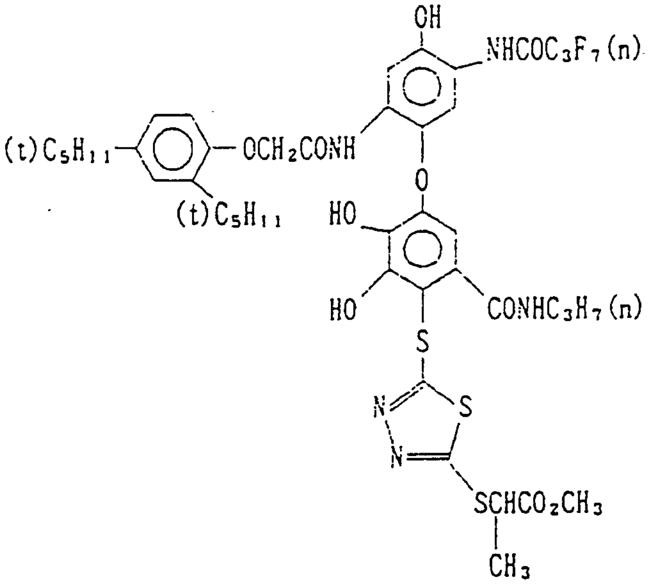
ExS−8



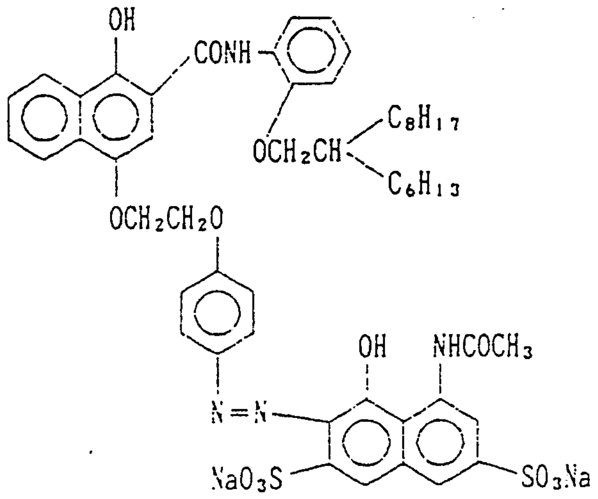
ExC−1



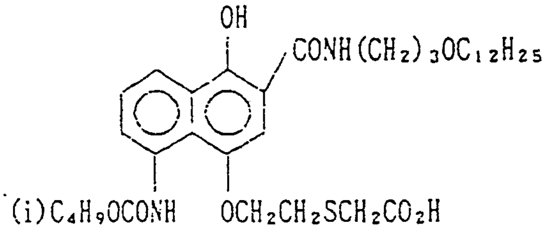
ExC−2



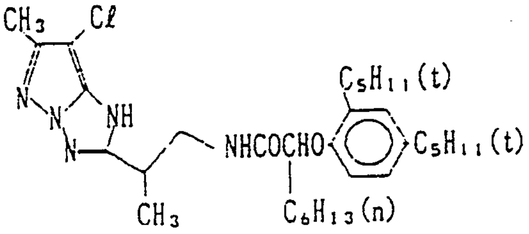
ExC−3


OH
CONH
OCH₂CH
C₈H₁₇
C₆H₁₃
OCH₂CH₂O
OH
NHCOCH₃
N=N
NaO₃S
SO₃Na

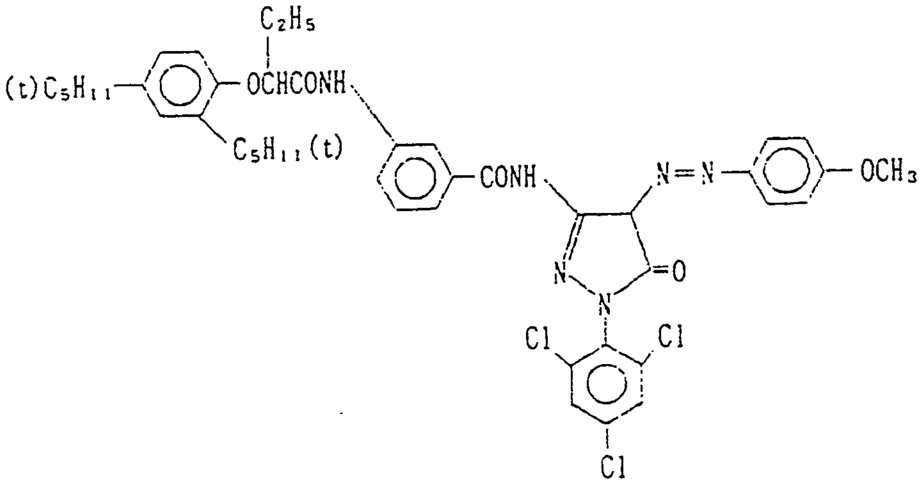
ExC−4


OH
CONH(CH₂)₃OC₁₂H₂₅
(i)C₄H₉OCONH
OCH₂CH₂SCH₂CO₂H

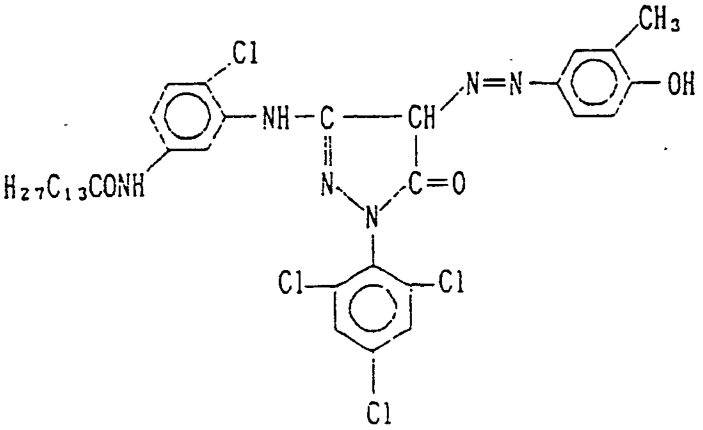
ExM-5


CH3
Cℓ
N
N
NH
N
NHCOCHO
C5H11(t)
C5H11(t)
C6H13(n)
CH3

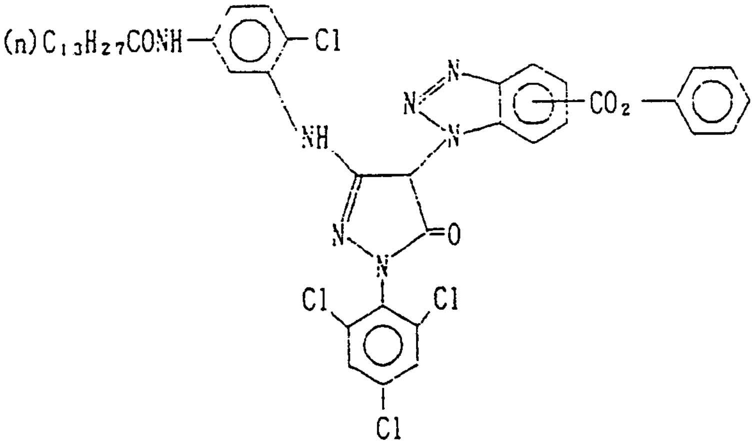
ExM-6


C2H5
(t)C5H11
OCHCONH
C5H11(t)
CONH
N=N
OCH3
N
N
=O
Cl
Cl
Cl

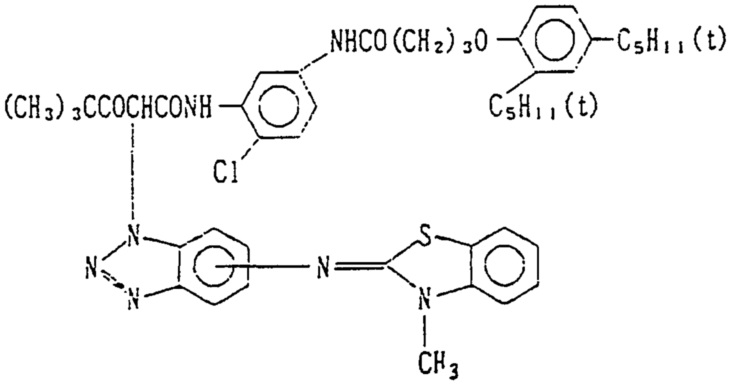
ExM-7



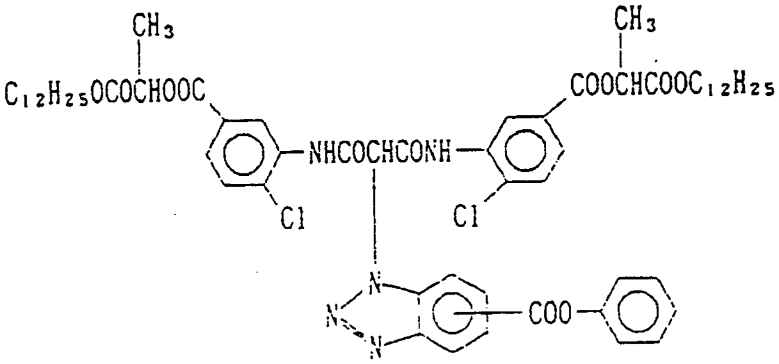
ExM-10



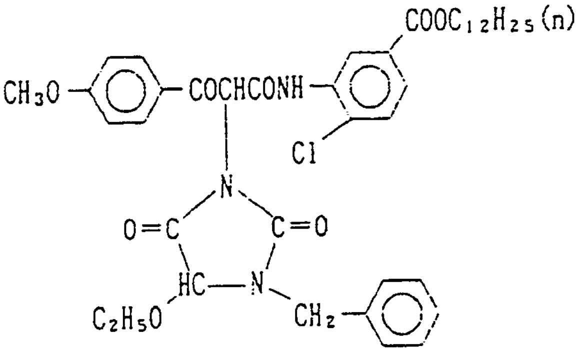
ExY-8



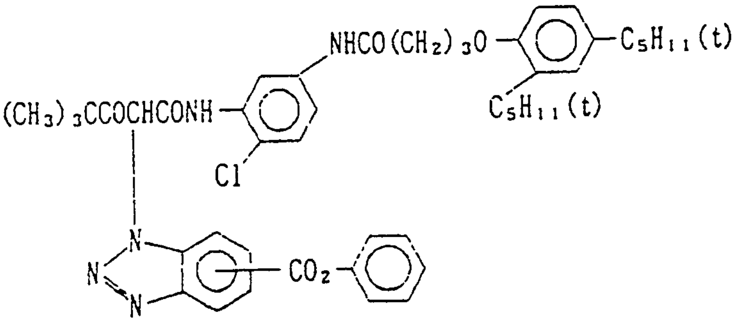
ExY-9



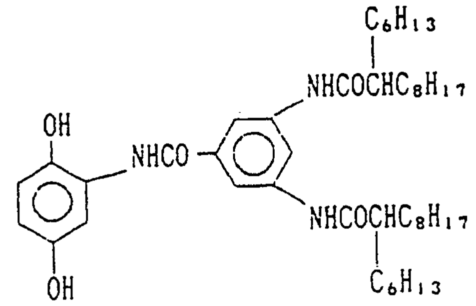
ExY-11



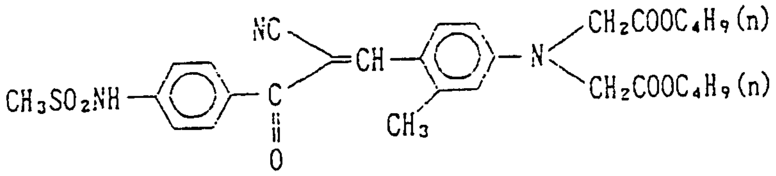
ExY-12



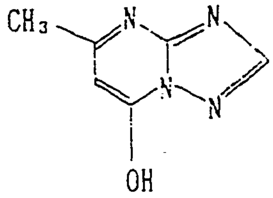
Cpd－1



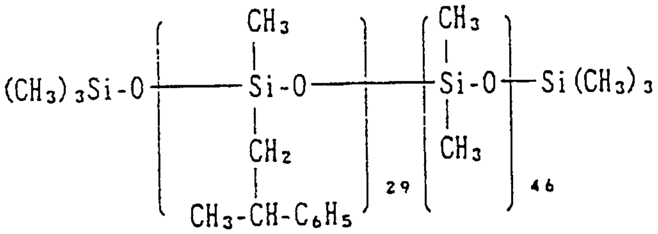
Cpd－2



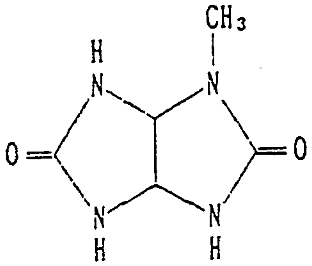
Cpd－3



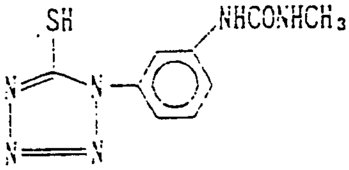
Cpd－4



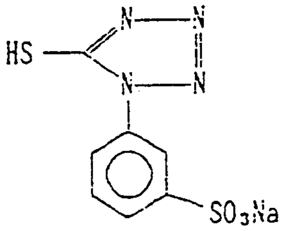
Cpd-5



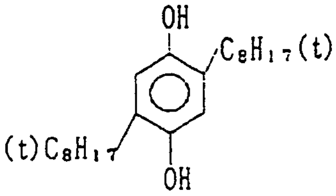
Cpd-6



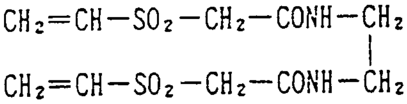
Cpd-7



Cpd-8

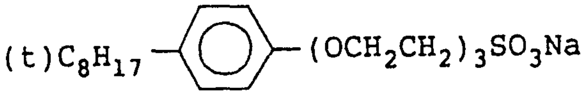


H-1

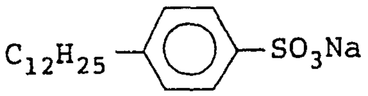


$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \\ \hphantom{CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}}| \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

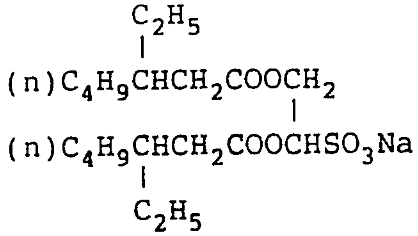
W-1



W-2



W-3



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

W-4 $C_8F_{17}SO_2N(C_3H_7)CH_2COOK$

Samples 302 to 303 were prepared in the same manner as described for Sample 301, except that the amount of organic solvent having a high boiling point (S-1) added to the sixth, seventh and eighth layers of Sample 301 was changed to 2 3 times and 1 10 times the amount used in Sample 301, respectively. The ratio of oil-soluble components to gelatin used was maintained constant. "Oil-soluble components" means all compounds present in the oil droplets.

Samples 304 to 306 were prepared in the same manner as described for Samples 301 to 303, except that Magenta coupler ExM-5 used in the sixth, seventh and eighth layers was replaced with an equimolar amount of Coupler M-6 according to the present invention and the amount of the organic solvent having a high boiling point was adjusted to maintain the weight ratio of organic solvent to coupler the same as in Samples 301 to 303, respectively.

Samples 307 to 309 were prepared in the same manner as described for Samples 304 to 306, except that Coupler M-6 was replaced with an equimolar amount of Coupler M-14 and the amount of the organic solvent having a high boiling point was adjusted to maintain the same weight ratio of organic solvent to coupler.

Samples 301 to 309 thus prepared were exposed in a conventional manner and subjected to development processing according to Processing Step (III) described below. Then, the transmitant spectral absorption curve of each sample was measured. The results showed that with the samples other than those of the present invention, the subsidiary absorption on the short wavelength side became large and the forms of the absorption curves at low density and high density were changed when the amount of organic solvent having a high boiling point was reduced.

Further, these samples were photographed in practice in different exposure amounts. From under exposed negatives and over exposed negatives, prints were prepared using an automatic printer manufactured by Fuji Photo Film Co., Ltd. In the over exposed samples, the color was greenish.

Moreover, to evaluate sharpness, MTF of each sample was measured. The results are shown in Table 3 below. The results indicate that sharpness is good when the content of oil-soluble components is low. These results support conventional knowledge that good sharpness is obtained when the dry layer thickness is small.

From these results it is apparent that only the combination of couplers with organic solvents having a high boiling point according to the present invention results in only minimal changes in color and excellent sharpness where pyrazolotriazole couplers are used. This fact can not be expected from known techniques.

Processing Step (III):

Processing Step	Processing Temperature (°C)	Processing Time	Amount of * Replenishment (ml)	Capacity of Tank (ℓ)
Color Development	37.8	3 min. 15 sec.	21	5
Bleaching	38.0	45 sec.	45	2
Fixing (1)	38.0	45 sec.	Two-tank countercurrent system	2
Fixing (2)	38.0	45 sec.	30	2
Stabilizing (1)	38.0	20 sec.	Three-tank countercurrent system	1
Stabilizing (2)	38.0	20 sec.		1
Stabilizing (3)	38.0	20 sec.	35	1
Drying	55	1 min. 00 sec.		

* Amounts of replenishment per 1 meter of 35 mm width strip.

The fixing tank of the automatic developing machine was equipped with a jet stirrer as described in JP-A-62-183460, page 3, and the light-sensitive material was processed in such a manner that a jet of the fixing solution was directed against the surface of the light-sensitive material.

The composition of each processing solution used is illustrated below.

Color Developing Solution:	Tank Solution	Replenisher
Hydroxyethyliminodiacetic acid	5.0 g	6.0 g
Sodium sulfite	4.0 g	5.0 g
Potassium carbonate	30.0 g	37.0 g
Potassium bromide	1.3 g	0.5 g
Potassium iodide	1.2 mg	-
Hydroxylamine sulfate	2.0 g	3.6 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	1.0×10^{-2} mol	1.3×10^{-2} mol
Water to make	1.0 ℓ	1.0 ℓ
pH	10.00	10.15

Bleaching Solution:	Tank Solution	Replenisher
Ferric complex of 1,3-diaminopropanetetraacetic acid	130 g	190 g
1,3-Diaminopropanetetraacetic acid	3.0 g	4.0 g
Ammonium bromide	85 g	120 g
Acetic acid	50 ml	70 ml
Ammonium nitrate	30 g	40 g
Water to make	1.0 ℓ	1.0 ℓ
pH	4.3	3.5

The pH was adjusted with acetic acid and aqueous ammonia.

Fixing Solution:	Tank Solution	Replenisher
1-Hydroxyethylidene-1,1-diphosphoric acid	5.0 g	7.0 g
Disodium ethylenediaminetetraacetate	0.5 g	0.7 g
Sodium sulfite	10.0 g	12.0 g
Sodium bisulfite	8.0 g	10.0 g
Aqueous solution of ammonium Thiosulfate (700 g/ℓ)	170.0 ml	200.0 ml
Ammonium thiocyanate	100.0 g	150.0 g
Thiourea	3.0 g	5.0 g
3,6-Dithia-1,8-octanediol	3.0 g	5.0 g
Water to make	1.0 ℓ	1.0ℓ
pH	6.5	6.7

The pH was adjusted with ammonium acetate.

Stabilizing Solution: (both mother solution and replenisher)	
Formalin (37%)	1.2 ml
5-Chloro-2-methyl-4-isothiazolin-3-one	6.0 mg
2-Methyl-4-isothiazolin-3-one	3.0 mg
Surface active agent $C_{10}H_{21}$-O$\leftarrow$CH$_2$CH$_2$O$\rightarrow_{10}$H	0.4 g
Ethylene glycol	1.0 g
Water to make	1.0 ℓ
pH	5.0 to 7.0

TABLE 3

Sample No.	Magenta Coupler in 6th, 7th and 8th Layers	Weight Ratio of Organic Solvent to Magenta Coupler	MTF (20 cycles/mm)
301 (Comparison)	ExM-5	1.5	0.61
302 (Comparison)	ExM-5	1.0	0.64
303 (Comparison)	ExM-5	0.1	0.72
304 (Comparison)	M-6	1.5	0.60
305 (Present Invention)	M-6	1.0	0.64
306 (Present Invention)	M-6	0.1	0.72
307 (Comparison)	M-14	1.5	0.61
308 (Present Invention)	M-14	1.0	0.65
309 (Present Invention)	M-14	0.1	0.74

EXAMPLE 4

Samples 213 to 221 were prepared in the same manner as described for Samples 204 to 212 of Example 2, except that the organic solvent having a high boiling point (S-1) added to the ninth, tenth and eleventh layers according to the present invention was replaced with the same weight of an organic solvent having a high boiling point (S-6), respectively.

In the same manner as above, Samples 222 to 230 were prepared using the same weight of (S-4) in place of (S-1), respectively.

Samples 204 to 230 were exposed wedgewise to white light, and processed in the same manner as in Example 2. The results showed that higher maximum density and higher gamma are obtained when the dielectric constant of the organic solvent having a high boiling point employed is higher. In the samples using the organic solvent having a high boiling point (S-4), the gradation was soft and D_{max} was somewhat low.

EXAMPLE 5

The following First to Fourteenth layers were coated on the front side of a paper support (having a thickness of 100 μm). both surfaces of which were laminated with polyethylene, and the following Fifteenth to Sixteenth layers were coated on the back side of the paper support to prepare a color photographic light sensitive material which was designated Sample 501. The polyethylene laminated on the First layer side of the support contained titanium dioxide (4 g/m^2) as a white pigment and a slight amount (0.003 g/m^2) of ultramarine as a bluish dye (chromaticity of the surface of the support was 88.0, -0.20 and -0.75 in an L*, a* and b* system).

Construction of Layers

The composition of each layer is shown below. The coating amounts of the components are described in the units of g/m^2. With respect to silver halide, the coating amount is indicated in terms of the silver coating amount. The emulsion used in each layer was prepared according to the method for preparation of Emulsion EM-1. The emulsion used in the Fourteenth layer was a Lippmann emulsion not being chemically sensitized on the surfaces of grains.

First Layer: Antihalation Layer	
Black colloidal silver	0.10
Gelatin	0.70

Second Layer: Intermediate Layer	
Gelatin	0.70

Third Layer: Low-Speed Red-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (average grain size: 0.25 µm, size distribution (coefficient of variation): 8%, octahedral)	0.04
Silver chlorobromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (silver chloride: 5 mol%, average grain size: 0.40 µm, size distribution: 10%, octahedral)	0.08
Gelatin	1.00
Cyan coupler (ExC-1, 2, 3, mixing ratio: 1/1/0.2 by weight)	0.30
Color fading preventing agent (Cpd-1, 2, 3, 4, mixing ratio: 1/1/1/1 by weight)	0.18
Stain preventing agent (Cpd-5)	0.003
Coupler dispersing medium (Cpd-6)	0.03
Coupler solvent (Solv-1, 2, 3, mixing ratio: 1/1/1 by weight)	0.12

Fourth Layer: High-Speed Red-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (average grain size: 0.60 µm, size distribution: 15%, octahedral)	0.14
Gelatin	1.00
Cyan coupler (ExC-1, 2, 3 mixing ratio: 1/1/0.2 by weight)	0.30
Color fading preventing agent (Cpd-1, 2, 3, 4, mixing ratio: 1/1/1/1 by weight)	0.18
Coupler dispersing medium (Cpd-6)	0.03
Coupler solvent (Solv-1, 2, 3, mixing ratio: 1/1/1 by weight)	0.12

Fifth Layer: Intermediate Layer	
Gelatin	1.00
Color mixing preventing agent (Cpd-7)	0.08
Color mixing preventing agent solvent (Solv-4, 5, mixing ratio: 1.1 by weight)	0.16
Polymer latex (Cpd-8)	0.10

Six Layer: Low-Speed Green-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (average grain size: 0.25 µm, size distribution: 8% octahedral)	0.04
Silver chlorobromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (silver chloride: 5 mol%, average grain size: 0.40 µm, size distribution: 10%, octahedral)	0.06
Gelatin	0.80
Magenta coupler (ExM-1)	0.11
Color fading preventing agent (Cpd-9, 26, mixing ratio: 1/1 by weight)	0.15
Stain preventing agent (Cpd-10, 11, 12, 13, mixing ratio: 10/7/7/1 by weight)	0.025
Coupler solvent (Solv-4, 6, mixing ratio: 1/1 by weight)	0.15

Seventh Layer: High-Speed Green-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (average grain size: 0.65 µm, size distribution: 16%, octahedral)	0.10
Gelatin	0.80
Magenta coupler (ExM-1)	0.11
Color fading preventing agent (Cpd-9, 26, mixing ratio: 1/1 by weight)	0.15
Stain preventing agent (Cpd-10, 11, 12, 13, mixing ratio: 10/7/7/1 by weight)	0.025
Coupler solvent (Solv-4)	0.15

Eighth Layer: Intermediate Layer

Same as Fifth Layer

Ninth Layer: Yellow Filter Layer	
Yellow colloidal silver (average grain size: 100Å)	0.12
Gelatin	0.70
Color mixing preventing agent (Cpd-7)	0.03
Color mixing preventing agent solvent (Solv-4, 5, mixing ratio: 1/1 by weight)	0.10
Polymer latex (Cpd-8)	0.07

Tenth Layer: Intermediate Layer

Same as Fifth Layer

Eleventh Layer: Low-Speed Blue-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (average grain size: 0.40 µm, size distribution: 8%, octahedral)	0.07
Silver chlorobromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (silver chloride: 8 mol%, average grain size: 0.60 µm, size distribution: 11%, octahedral)	0.14
Gelatin	0.80
Yellow coupler (ExY-1, 2, mixing ratio: 1/1 by weight)	0.35
Color fading preventing agent (Cpd-14)	0.10
Stain preventing agent (Cpd-5, 15, mixing ratio: 1/5 by weight)	0.007
Coupler dispersing medium (Cpd-6)	0.05
Coupler solvent (Solv-2)	0.10

Twelfth Layer: High-Speed Blue-Sensitive Layer	
Silver bromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (average grain size: 0.85 µm, size distribution: 18%, octahedral)	0.15
Gelatin	0.60
Yellow coupler (ExY-1, 2: mixing ratio: 1/1 by weight)	0.30
Color fading preventing agent (Cpd-14)	0.10
Stain preventing agent (Cpd-5, 15, mixing ratio: 1/5 by weight)	0.007
Coupler dispersing medium (Cpd-6)	0.05
Coupler solvent (Solv-2)	0.10

Thirteenth Layer: Ultraviolet Light Absorbing Layer	
Gelatin	1.00
Ultraviolet light absorbing agent (Cpd-2, 4, 16, mixing ratio: 1/1/1 by weight)	0.50
Color mixing preventing agent (Cpd-7, 17, mixing ratio: 1/1 by weight)	0.03
Dispersing medium (Cpd-6)	0.02
Ultraviolet light absorbing agent solvent (Solv-2, 7 mixing ratio: 1/1 by weight)	0.08
Irradiation preventing dye (Cpd-18, 19, 20, 21, 27, mixing ratio: 10/10/13/15/20 by weight)	0.05

Fourteenth Layer: Protective Layer	
Silver chlorobromide fine particles (silver chloride: 97 mol%, average grain size: 0.1 µm)	0.03
Acryl-modified copolymer of polyvinyl-alcohol (average molecular weight: 50,000)	0.01
Polymethyl methacrylate particles (average particle size: 2.4 µm) and silicon oxide (average particle size: 5 µm, mixing ratio: 1/1 by weight)	0.05
Gelatin	1.80
Gelatin hardener (H-1, 2: mixing ratio: 1/1 by weight)	0.18

Fifteenth Layer: Back Layer	
Gelatin	2.50
Ultraviolet light absorbing agent (Cpd-2, 4, 16, mixing ratio: 1/1/1 by weight)	0.50
Dye (Cpd-18, 19, 20, 21, 27 mixing ratio: 1/1/1/1/1 by weight)	0.06

Sixteenth Layer: Back Protective Layer	
Polymethyl methacrylate particles (average particle size: 2.4 µm) and silicon oxide (average particle size: 5 µm), mixing ratio: 1/1 by weight	0.05
Gelatin	2.00
Gelatin hardener (H-1, 2, mixing ratio: 1/1 by weight)	0.14

Preparation of Emulsion EM-1

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were added simultaneously to an aqueous gelatin solution at 75° C over a period of 15 minutes while vigorously stirring, to obtain an octahedral silver bromide emulsion having an average grain diameter of 0.35 µm. At that time, 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thione per mol of silver was added. Then, 6 mg of sodium thiosulfate and 7 mg of chloroauric acid (tetrahydrate) were added to the emulsion per mol of silver in order and the emulsion was heated to 75° C for 80 minutes to be chemically sensitized. The thus-prepared silver bromide grains were used as cores and were further grown under the same precipitation conditions as above to obtain finally a monodispersed octahedral core/shell type silver bromide emulsion having an average grain diameter of 0.7 µm. The coefficient of variation of the grain size was about 10%.

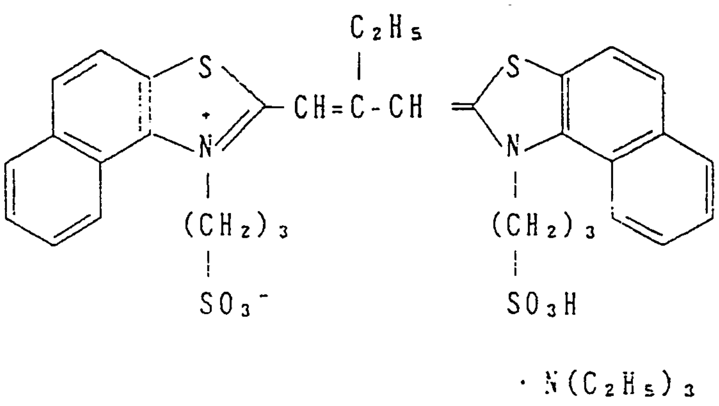
1.5 mg of sodium thiosulfate and 1.5 mg of chloroauric acid (tetrahydrate) were added to the emulsion per mol of silver, and the emulsion was heated to 60° C for 60 minutes to be chemically sensitized, thus an internal latent image type silver halide emulsion was obtained.

To each light-sensitive layer, ExZK-1 in an amount of 10^{-3} % by weight, and ExZK-2 in an amount of 10^{-2} % by weight, based on silver halide, were added as nucleating agents, and Cpd-22 was added as a nucleation accelerating agent in an amount of 10^{-2} % by weight based on silver halide.

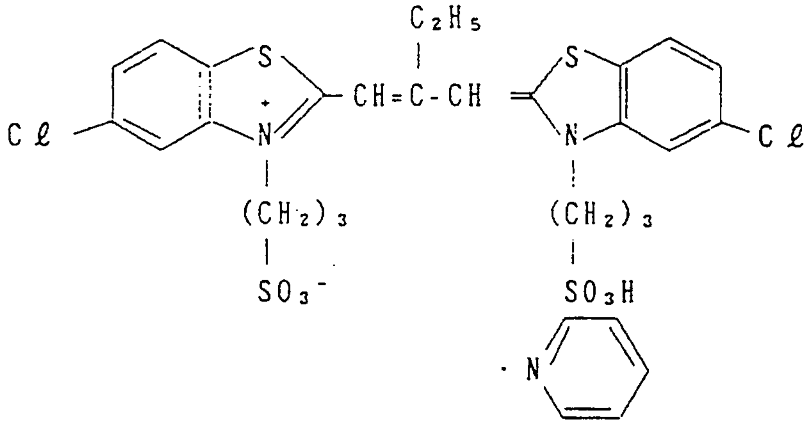
Also, to each layer, as emulsifying and dispersing aids, Alkanol XC (manufactured by Du Pont) and sodium alkylbenzenesulfonate, and as coating aids, succinic acid ester and Megafac F-120 (manufactured by Dai Nippon Ink and Chemical Co, Ltd.) were added. Furthermore, to the layers containing silver halide or colloidal silver, as stabilizers, Cpd-23, 24, and 25 were added.

The compounds used in this example are illustrated below.

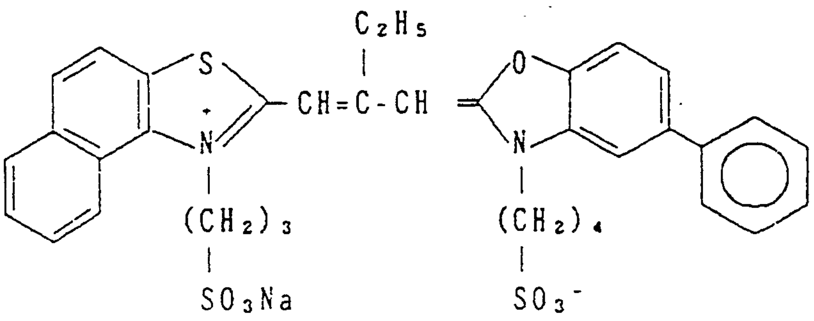
ExS-1



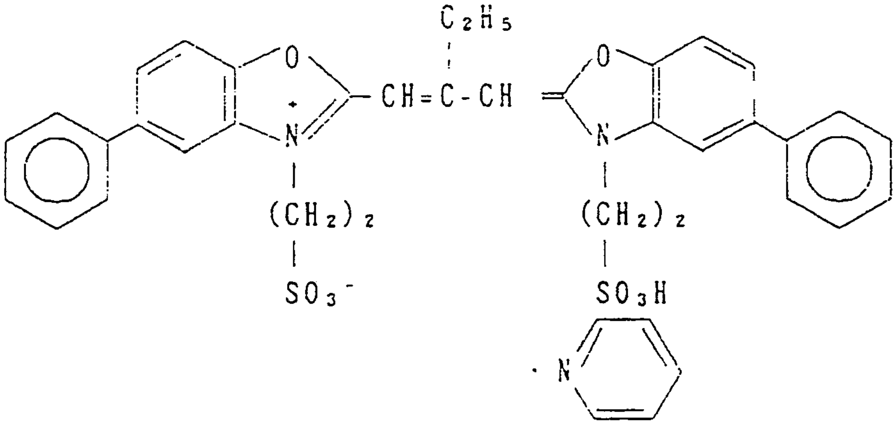
ExS-2



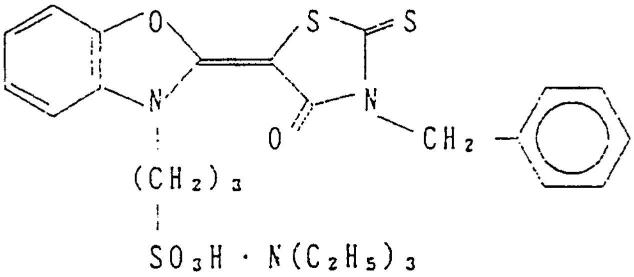
E x S - 3



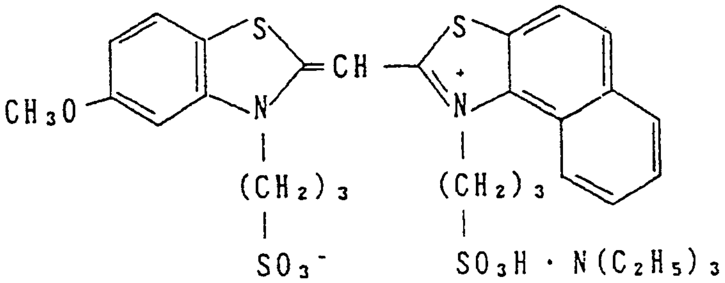
E x S - 4



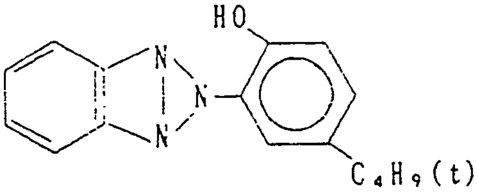
E x S - 5



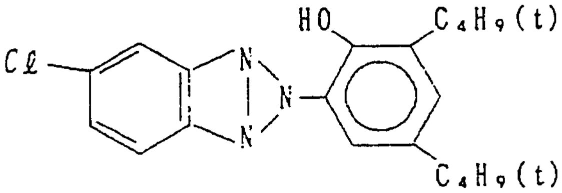
ExS-6



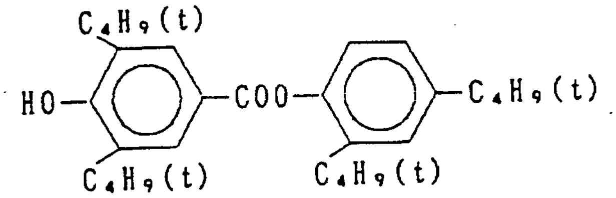
Cpd-1



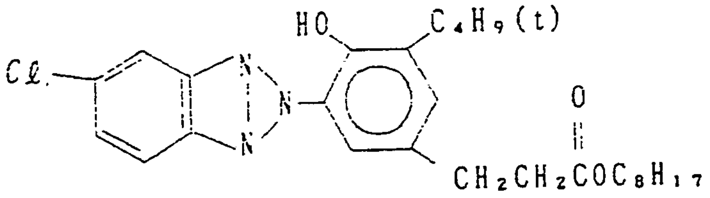
Cpd-2



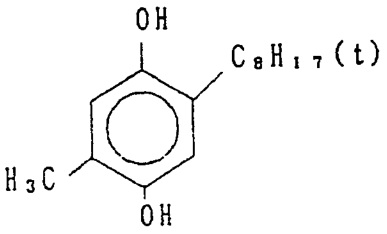
Cpd-3



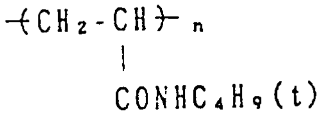
Cpd-4



Cpd-5



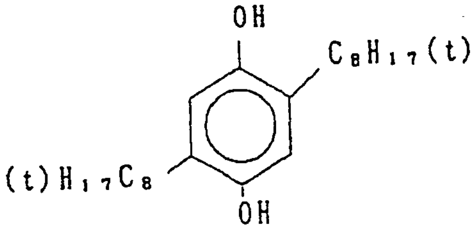
Cpd-6



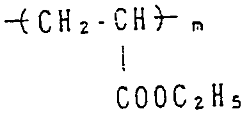
$$-\!\left(\mathrm{CH_2-\underset{\mathrm{CONHC_4H_9(t)}}{\underset{|}{CH}}}\right)_n$$

$n = 100 \sim 1000$

Cpd-7

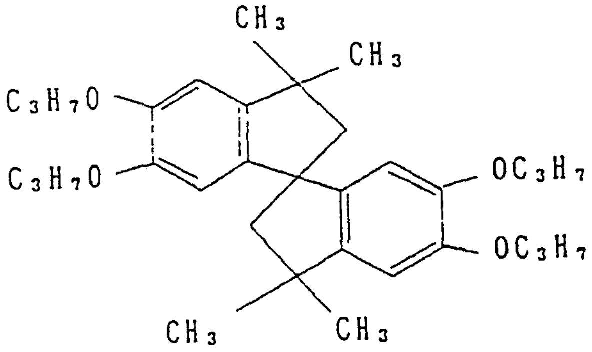


Cpd-8

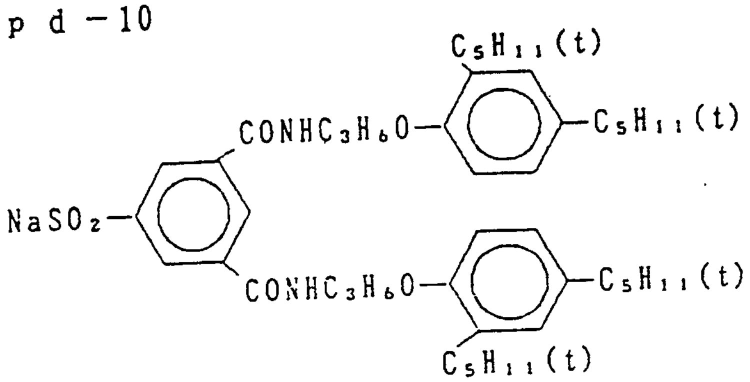


$$\left(\mathrm{CH_2-\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}}}\right)_m$$

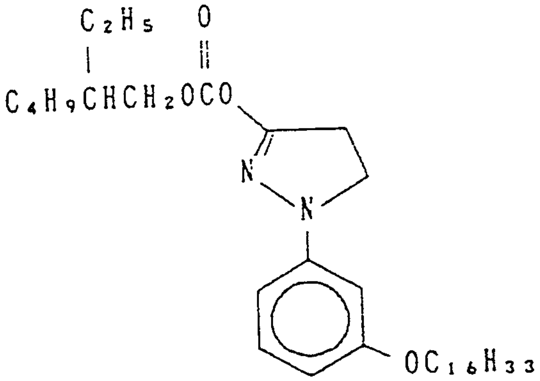
Cpd-9



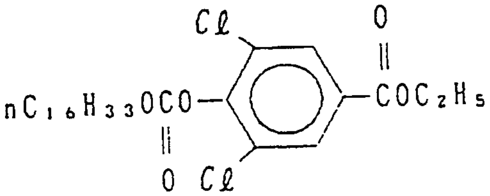
Cpd-10



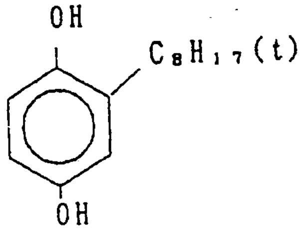
Cpd-11



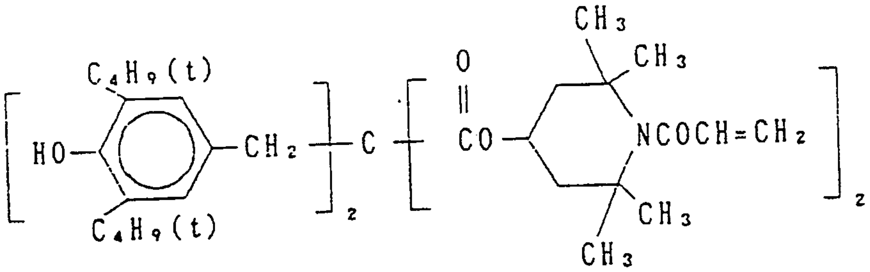
Cpd-12



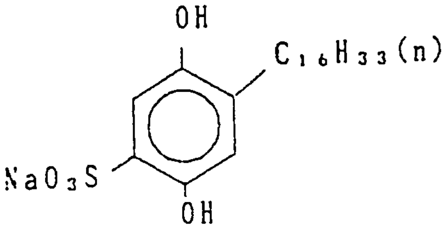
Cpd-13



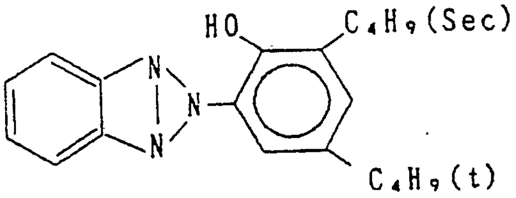
Cpd-14



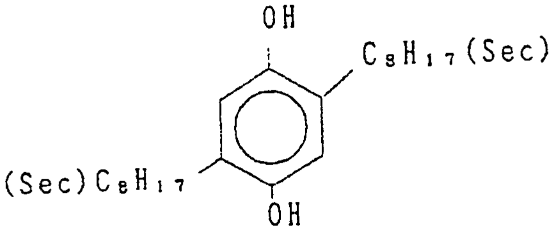
Cpd-15



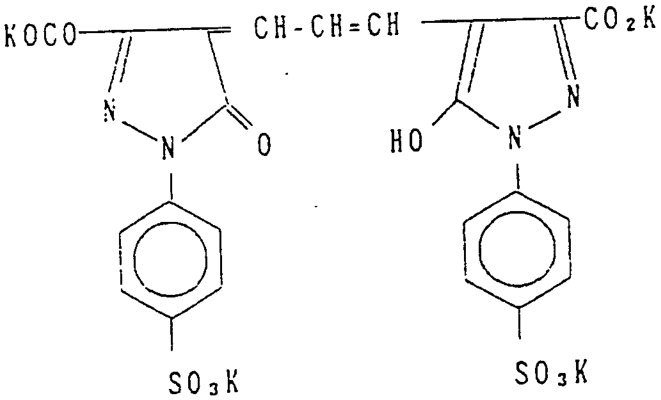
Cpd-16



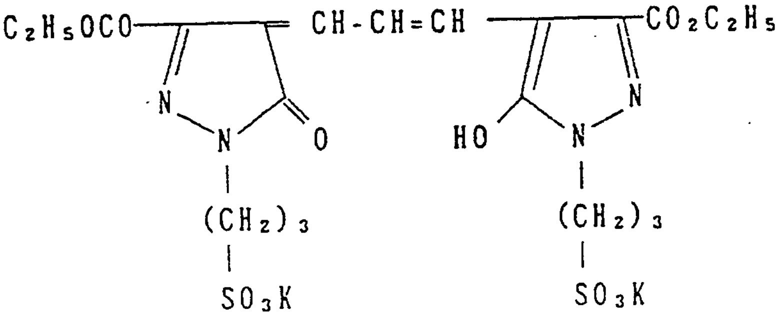
Cpd-17



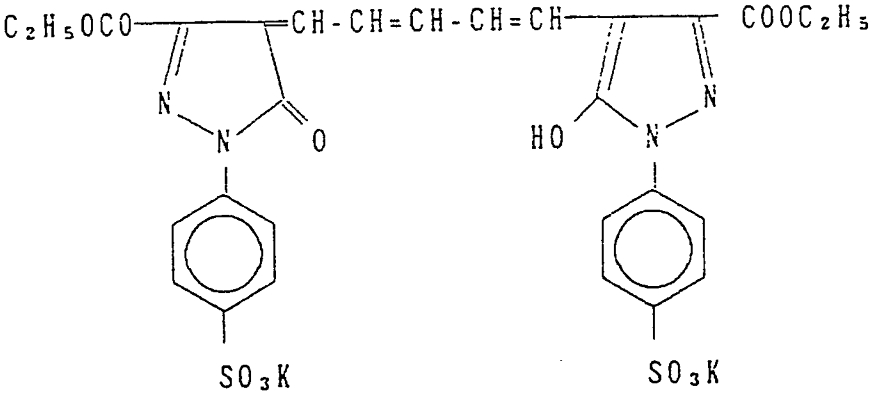
Cpd-18



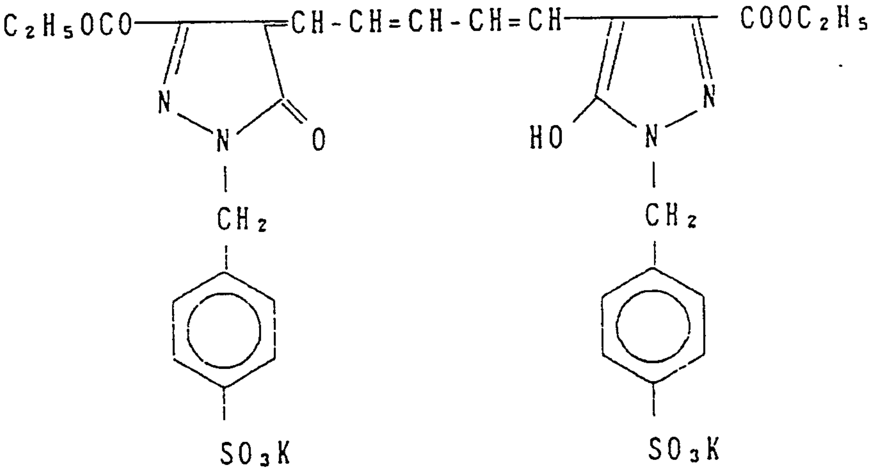
Cpd-19



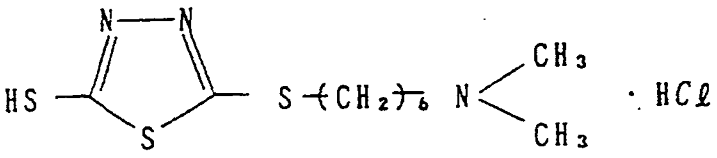
Cpd-20



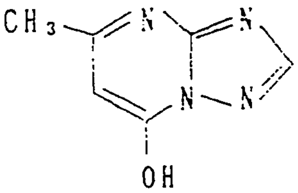
Cpd-21



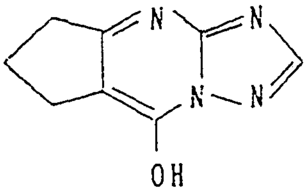
Cpd-22



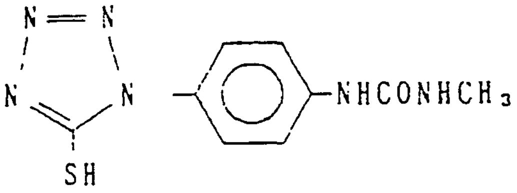
Cpd-23



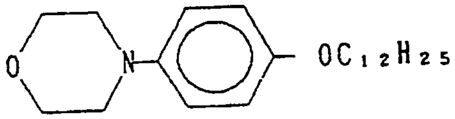
Cpd-24



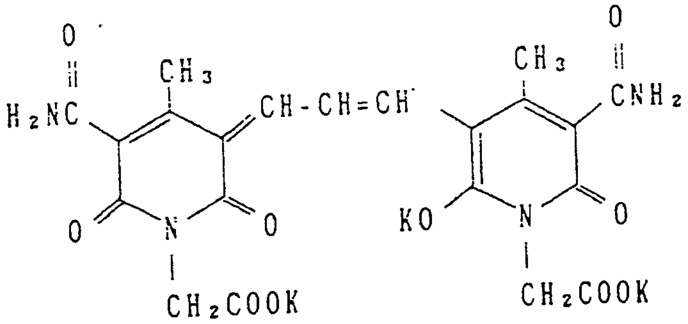
Cpd-25



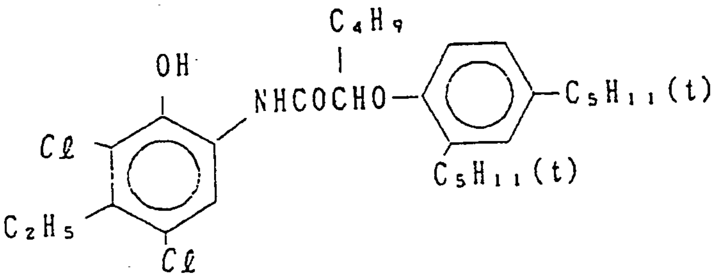
Cpd-26



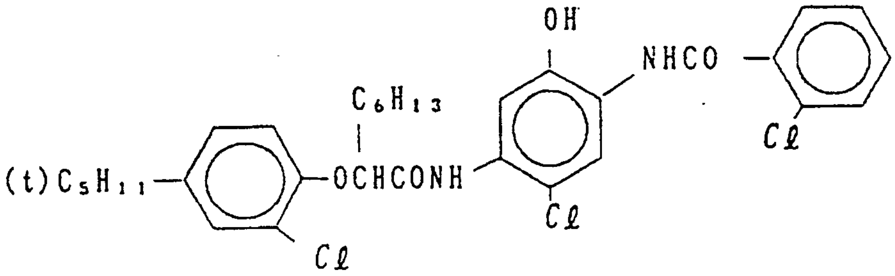
Cpd-27



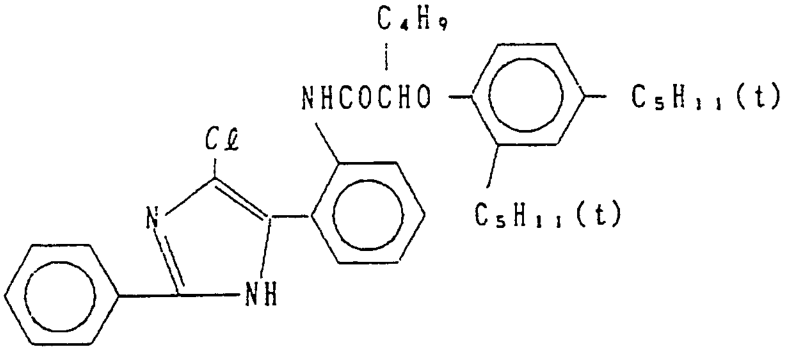
EXC-1



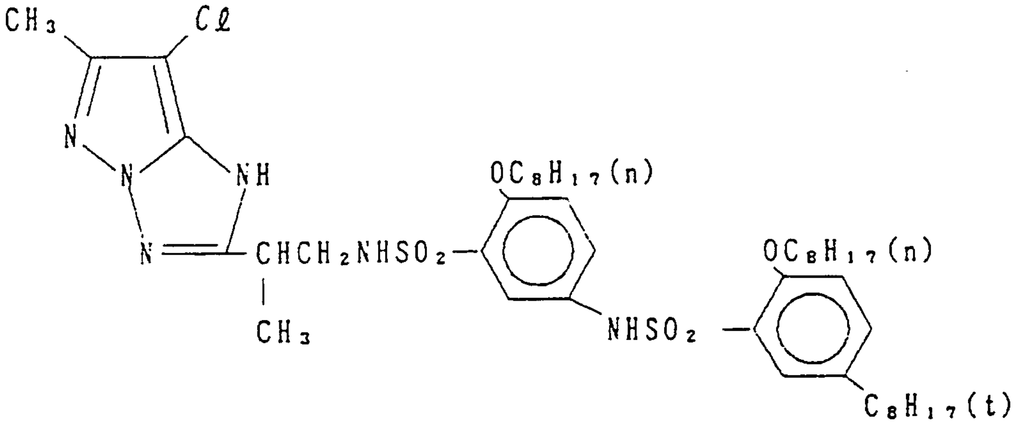
EXC-2



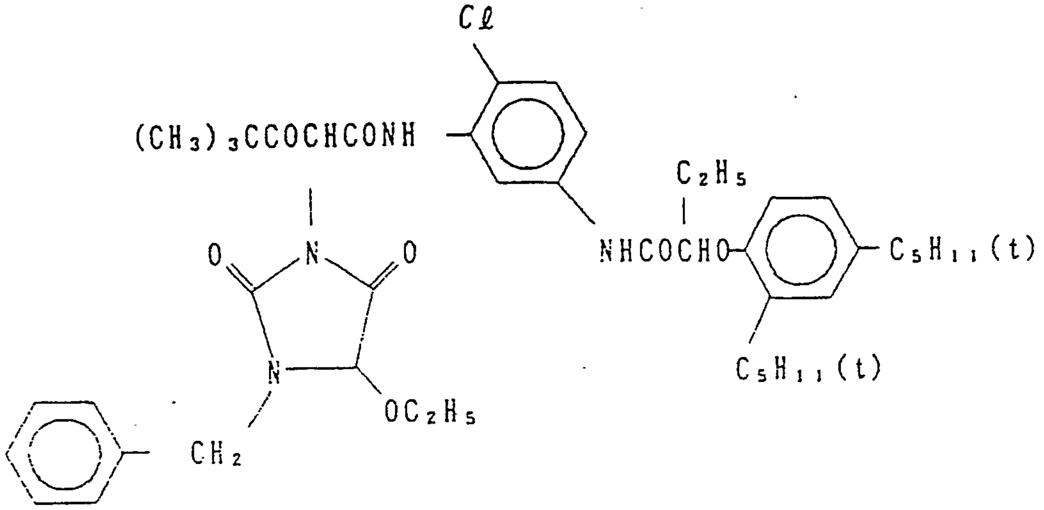
EXC-3



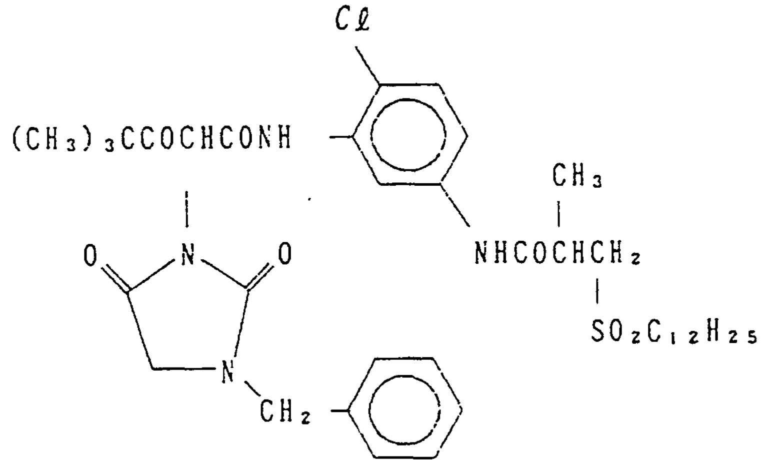
EXM-1



EXY-1



EXY-2



Solv-1 Di(2-ethylhexyl) sebacate
Solv-2 Trinonyl phosphate
Solv-3 Di(3-methylhexyl) phthalate
Solv-4 Tricresyl phosphate
Solv-5 Dibutyl phthalate
Solv-6 Trioctyl phosphate
Solv-7 Di(2-ethylhexyl) phthalate
H-1 1,2-Bis(vinylsulfonylacetamido)ethane
H-2 4,6-Dichloro-2-hydroxy-1,3,5-triazine sodium salt
ExZK-1 7-(3-Ethoxythiocarbonylaminobenzamido)-9-methyl-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
ExZK-2 2-[4-{3-[3-{3-[5-{3-[2-Chloro-5-(1-dodecyloxycarbonylethoxycarbonyl)phenylcarbamoyl]-4-hydroxy-1-naphthylthio}tetrazol-1-yl]phenyl}ureido]benzenesulfonamido}phenyl]-1-formylhydrazine

Samples 502 and 503 were prepared in the same manner as described for Sample 501, except that the amount of coupler solvent added to the sixth and seventh layers of Sample 501 was changed to 0.10 and 0.20 g/m², respectively.

Samples 504 and 506 were prepared in the same manner as described for Samples 501 to 503, except that an equimolar amount of Coupler M-16 according to the present invention was used in place of Magenta coupler (ExM-1) in Samples 501 to 503 respectively.

Samples 507 to 509 were prepared in the same manner as described for Samples 501 to 503, except that an equimolar amount of Coupler M-41 according to the present invention was used in place of Magenta coupler (ExM-1) in Samples 501 to 503 respectively.

Sample 501 thus prepared was imagewise exposed and then continuously processed in accordance with the processing method described below by an automatic developing machine until the total amount of replenisher added to the color developing solution was three times the volume of the tank for color development.

Processing Step	Time	Temperature	Tank Capacity	Amount of Replenishment
	(sec)	(°C)	(ℓ)	(ml/m²)
Color Development	80	38	8	300
Bleach-Fixing	40	33	3	300
Washing with Water (1)	40	33	3	-
Washing with Water (2)	40	33	3	-
Washing with Water (3)	15	33	0.5	320
Drying	30	80		

The replenishment system for the washing water was a countercurrent replenishment system in which a replenisher was added to water washing bath (3), and the overflow solution from water washing bath (3) was introduced into water washing bath (2) and the overflow solution from water washing bath (2) was introduced into water washing bath (1). In the processing method, the amount of the bleach-fixing solution carried over together with the photographic material being processed from the bleach-fixing bath to water washing bath (1) was 35 ml/m², and the volume of the replenisher of washing water to the amount of bleach-fixing solution carried over was 9.1 times.

The compositions of the processing solutions used were as follows.

Color Developing Solution	Mother Solution	Replenisher
Ethylenediaminetetramethylenephosphonic acid	0.5 g	0.5 g
Diethylene glyol	10 ml	10 ml
Benzyl alcohol	12.0 ml	14.4 ml
Potassium bromide	0.52 g	-
Sodium chloride	0.06 g	-
Sodium sulfite	2.4 g	2.9 g
N,N-Diethylhydroxylamine	4.0 g	4.8 g
Triethylenediamine (1,4-diazabicyclo[2,2,2]octane)	4.0 g	4.8 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate	5.6 g	6.6 g
Potassium carbonate	27.0 g	25.0 g
Fluorescent whitening agent (diaminostilbene type)	1.0 g	1.2 g
Water to make	1,000 ml	1,000 ml
pH (at 25°C)	10.50	10.80

Bleach-Fixing solution (both Mother Solution and Replenisher)	
Disodium ethylenediaminetetraacetate dihydrate	4.0 g
Ammonium iron(III) ethylenediaminetetraacetate dihydrate	46.0 g
Ammonium thiosulfate (700 g/liter)	155 ml
Sodium p-toluenesulfinate	20.0 g
Sodium bisulfite	12.0 g
Ammonium bromide	50.0 g
Ammonium nitrate	30.0 g
Water to make	1,000 ml
pH (at 25° C)	6.20

Washing Water (both Mother Solution and Replenisher)

City water was passed through a mixed bed type column filled with an H type strong acidic cation exchange resin (Amberlite IR-120B manufactured by Rohm & Haas Co.) and an OH type anion exchange resin (Amberlite IR-400 manufactured by Rohm & Haas Co.) to prepare water containing not more than 3 mg/liter of calcium ion and magnesium ion. To the water thus-treated were added sodium dichloroisocyanurate in an amount of 20 mg/liter and sodium sulfate in an amount of 1.5 g/liter. The pH of the solution was in a range from 6.5 to 7.5.

Thereafter, Samples 502 to 509 were imagewise exposed to green light and then processes according to the processing steps described above using the processing solution after the continuous processing.

A special absorption of the magenta color obtained in each sample was measured, and the magenta color staining after preservation of each sample under conditions of 80° C and 70% RH for 6 days was evaluated.

As a result, it was found that in Samples 505, 506, 508 and 509 according to the present invention, the formation of aggregation of dyes was very little a hue of the image appeared sharply and the occurrence of magenta staining was also slight.

EXAMPLE 6

On a paper support, both surfaces of which were laminated with polyethylene, were coated the First to Twelfth layers as shown below to prepare a multilayer color photographic light-sensitive material which was designated Sample 601. The polyethylene on the First layer side contained titanium white as a white pigment and a slight amount of ultramarine as bluish dye.

Construction of Layers

The components and the coated amounts thereof in terms of g/m^2 are shown below. The coated amounts of silver halide are indicated in terms of silver.

First Layer: Gelatin Layer	
Gelatin	1.30

Second Layer: Antihalation Layer	
Black colloidal silver	0.10
Gelatin	0.70

Third Layer: Low-Speed Red-Sensitive Layer

Silver chloroiodobromide emulsion EM1 (silver chloride: 1 mol%; silver iodide: 4 mol%; average grain size: 0.3 μm; size distribution: 10%; cubic, core iodide type core/shell grain) spectrally sensitized with Red Sensitizing Dyes (ExS-1, 2 and 3)	0.06
Silver iodobromide emulsion EM2 (silver iodide: 5 mol%; average grain size: 0.45 μm; size distribution: 20%; tabular (aspect ratio: 5) grain) spectrally sensitized with Red Sensitizing Dyes (ExS-1, 2 and 3)	0.10
Gelatin	1.00
Cyan coupler (ExC-1)	0.14
Cyan coupler (ExC-2)	0.07
Color fading preventing agent (Cpd-2, 3, 4 and 9 in equal amounts)	0.12
Coupler dispersing medium (Cpd-5)	0.03
Coupler solvent (Solv-1, 2 and 3)	0.06

Fourth Layer: High-Speed Red-Sensitive Layer

Silver iodobromide emulsion EM3 (silver iodide: 6 mol%; average grain size: 0.75 µm; size distribution: 25%; tabular (aspect ratio: 8), core iodide grain) spectrally sensitized with Red Sensitizing Dyes (ExS-1, 2 and 3)	0.15
Gelatin	1.00
Cyan coupler (ExC-1)	0.20
Cyan coupler (ExC-2)	0.10
Color fading preventing agent (Cpd-2, 3, 4 and 9 in equal amounts)	0.15
Coupler dispersing medium (Cpd-5)	0.03
Coupler solvent (Solv-1, 2 and 3)	0.10

Fifth Layer: Intermediate Layer	
Magenta colloidal silver	0.02
Gelatin	1.00
Color mixing preventing agent (Cpd-6 and 7)	0.08
Color mixing preventing agent solvent (Solv-4 and 5)	0.16
Polymer Latex (Cpd-8)	0.10

Sixth Layer: Low-Speed Green-Sensitive Layer

Silver chloroiodobromide emulsion EM4 (silver chloride: 1 mol%; silver iodide: 2.5 mol%; average grain size: 0.28 μm; size distribution: 12%; cubic core iodide type core/shell grain) spectrally sensitized with Green Sensitizing Dye (ExS-4)	0.04
Silver iodobromide emulsion EM5 (silver iodide: 2.8 mol%; average grain size: 0.45 μm; size distribution: 12%; tabular (aspect ratio: 5) grain) spectrally sensitized with Green Sensitizing Dye (ExS-4)	0.06
Gelatin	0.80
Magenta coupler (ExM-1)	0.10
Color fading preventing agent (Cpd-9)	0.10
Stain preventing agent (Cpd-10)	0.01
Stain preventing agent (Cpd-11)	0.001
Stain preventing agent (Cpd-12)	0.01
Coupler dispersing medium (Cpd-5)	0.05
Coupler solvent (Solv-4)	0.15

Seventh Layer: High-Speed Green-Sensitive Layer

Silver iodobromide emulsion EM6 (silver iodide: 3.5 mol%; average grain size: 0.9 µm; size distribution: 23%; tabular (aspect ratio: 9), uniform iodide type grain) spectrally sensitized with Green Sensitizing Dye (ExS-4)	0.10
Gelatin	0.80
Magenta coupler (ExM-1)	0.10
Color fading preventing agent (Cpd-9)	0.10
Stain preventing agent (Cpd-10)	0.01
Stain preventing agent (Cpd-11)	0.001
Stain preventing agent (Cpd-12)	0.01
Coupler dispersing medium (Cpd-5)	0.05
Coupler solvent (Solv-4 and 6)	0.15

Eighth Layer: Yellow Filter Layer	
Yellow colloidal silver	0.20
Gelatin	1.00
Color mixing preventing agent (Cpd-7)	0.06
Color mixing preventing agent solvent (Solv-4)	0.15
Polymer Latex (Cpd-8)	0.10

Ninth Layer: Low-Speed Blue-Sensitive Layer

Silver chloroiodobromide emulsion EM7 (silver chloride: 2 mol%; silver iodide: 2.5 mol%; average grain size: 0.35 μm; size distribution: 8%; cubic, core iodide type core/shell grain) spectrally sensitized with Blue Sensitizing Dye (ExS-5)	0.07
Silver iodobromide emulsion EM8 (silver iodide: 2.5 mol%; average grain size: 0.45 μm; size distribution: 16%; tabular (aspect ratio: 6) grain) spectrally sensitized with Blue Sensitizing Dye (ExS-5)	0.10
Gelatin	0.50
Yellow coupler (ExY-1)	0.20
Stain preventing agent (Cpd-11)	0.001
Color fading preventing agent (Cpd-6)	0.10
Coupler dispersing medium (Cpd-5)	0.05
Coupler solvent (Solv-2)	0.05

Tenth Layer: High-Speed Blue-Sensitive Layer

Silver iodobromide emulsion EM9 (silver iodide: 2.5 mol%; average grain size: 1.2 μm; size distribution: 21%; tabular (aspect ratio: 14) grain) spectrally sensitized with Blue Sensitizing Dye (ExS-5)	0.25
Gelatin	1.00
Yellow coupler (ExY-1)	0.40
Stain preventing agent (Cpd-11)	0.002
Color fading preventing agent (Cpd-6)	0.10
Coupler dispersing medium (Cpd-5)	0.15
Coupler solvent (Solv-2)	0.10

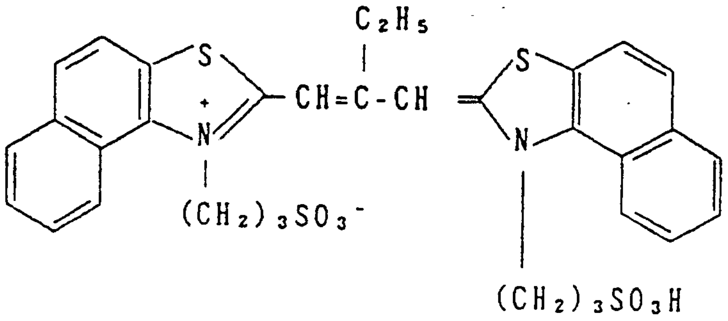
Eleventh Layer: Ultraviolet Light Absorbing Layer	
Gelatin	1.50
Ultraviolet light absorbing agent (Cpd-1, 3 and 13)	1.00
Color mixing preventing agent (Cpd-6 and 14)	0.06
Dispersing medium (Cpd-5)	
Ultraviolet light absorbing agent solvent (Solv-1 and 2)	0.15
Anti-irradiation dye (Cpd-15 and 16)	0.02
Anti-irradiation dye (Cpd-17 and 18)	0.02

Twelfth Layer: Protective Layer	
Fine silver chlorobromide grains (silver chloride: 97 mol%; average grain size, 0.2 μm)	0.07
Modified poval	0.02
Gelatin	1.50
Gelatin hardener (H-1)	0.17

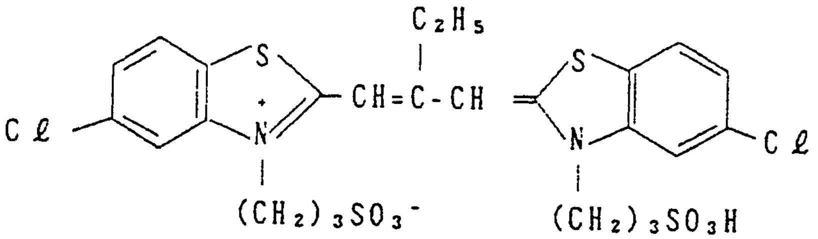
Each of the layers contained Alkanol XC (manufactured by Du Pont) and sodium alkylbenzenesulfonate as emulsifying and dispersing aids, and a succinic acid ester and Magefac F-120 (manufactured by Dai Nippon Ink and Chemical Co. Ltd.) as coating aids. In the layers containing silver halide or colloidal silver, stabilizers (Cpd-19, 20 and 21) were employed.

The compounds used in this example are illustrated below.

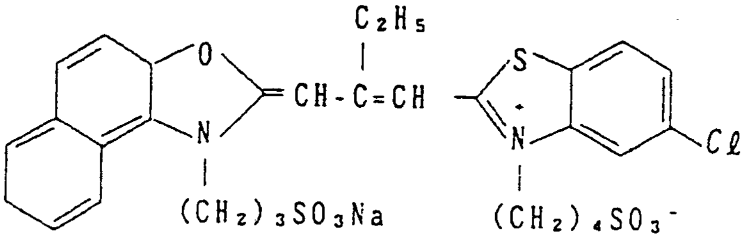
ExS-1



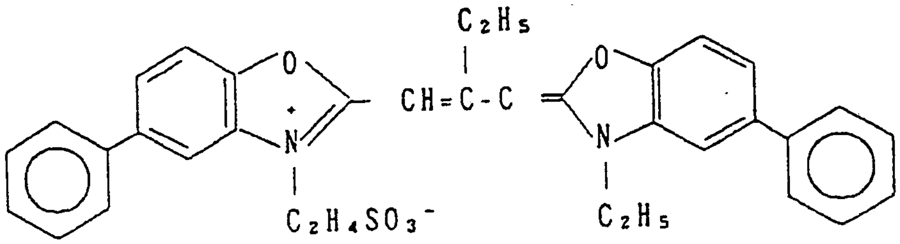
ExS-2



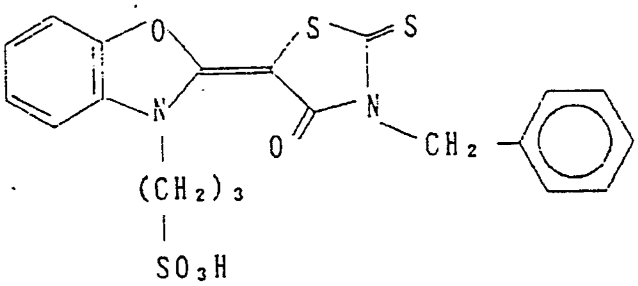
ExS-3



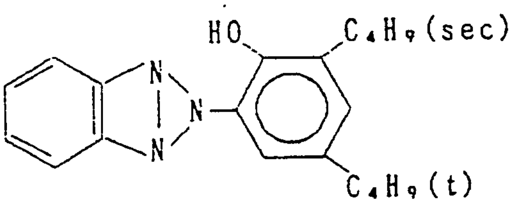
ExS－4



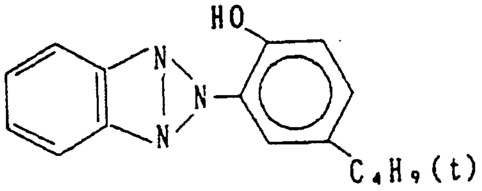
ExS－5



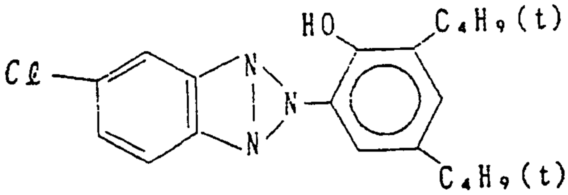
Cpd－1



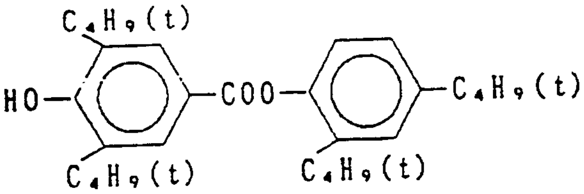
Cpd-2



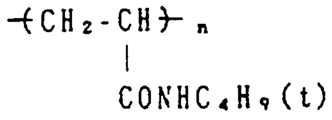
Cpd-3



Cpd-4



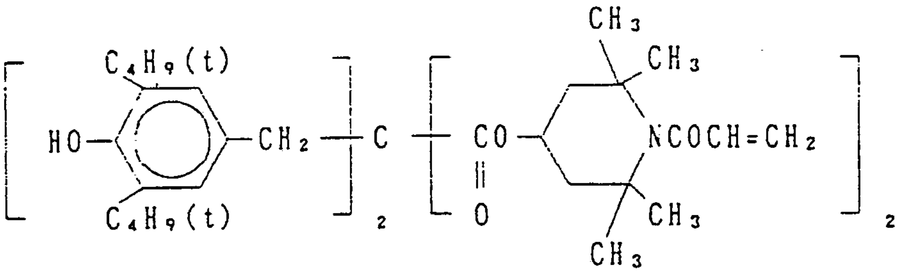
Cpd-5



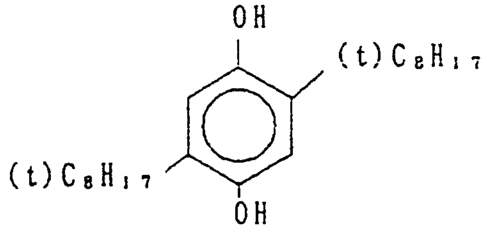
$$-\!\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{\underset{|}{CH}}\right)_{\!n}-$$

(n = 100∼1000)

Cpd-6

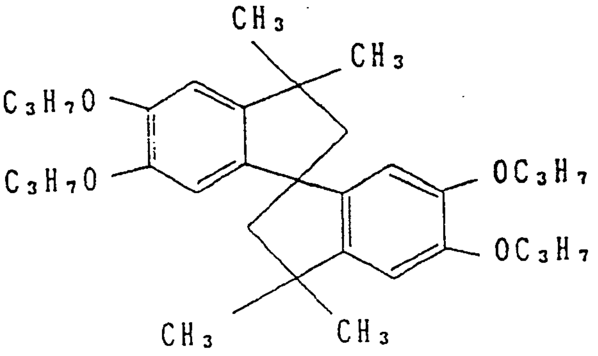


Cpd-7

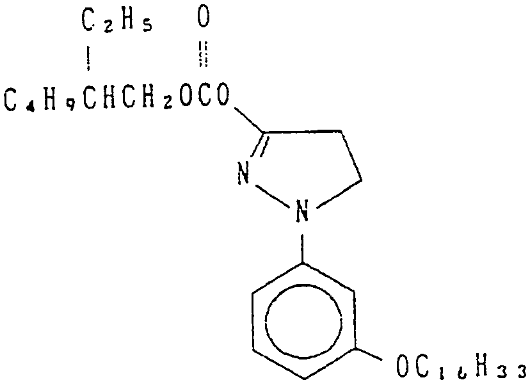


Cpd-8 Polyethylacrylate

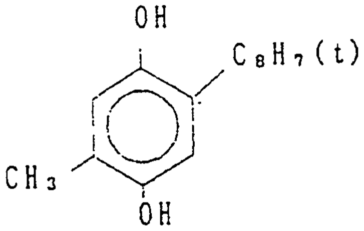
Cpd-9



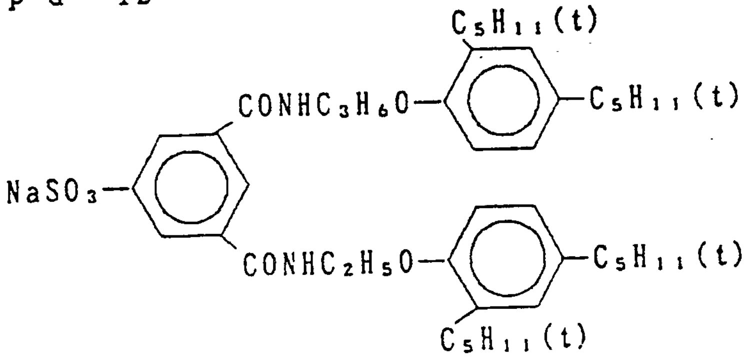
Cpd-10



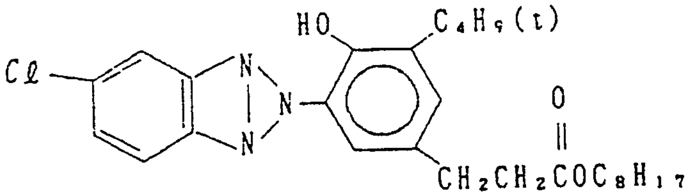
Cpd-11



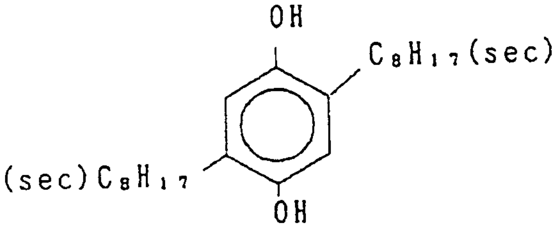
Cpd-12



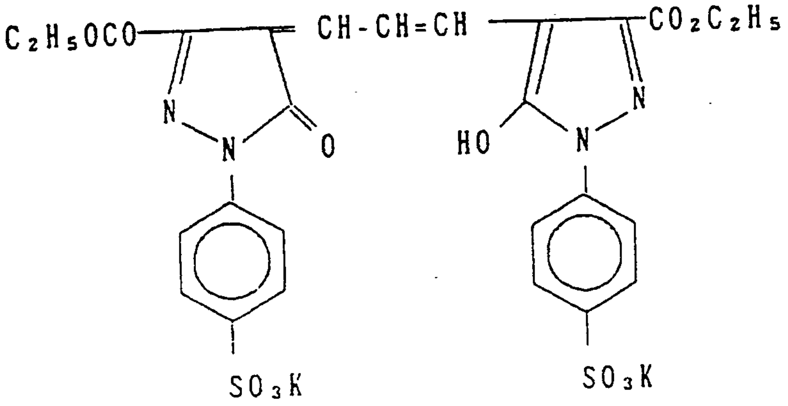
Cpd-13



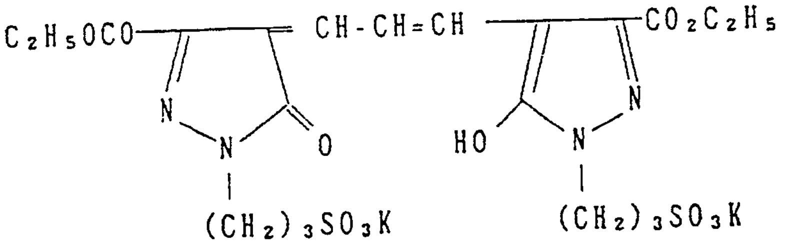
Cpd-14



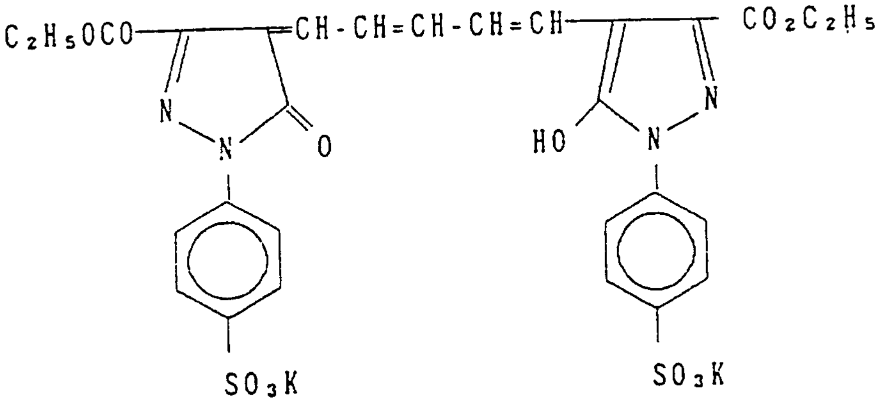
Cpd－15



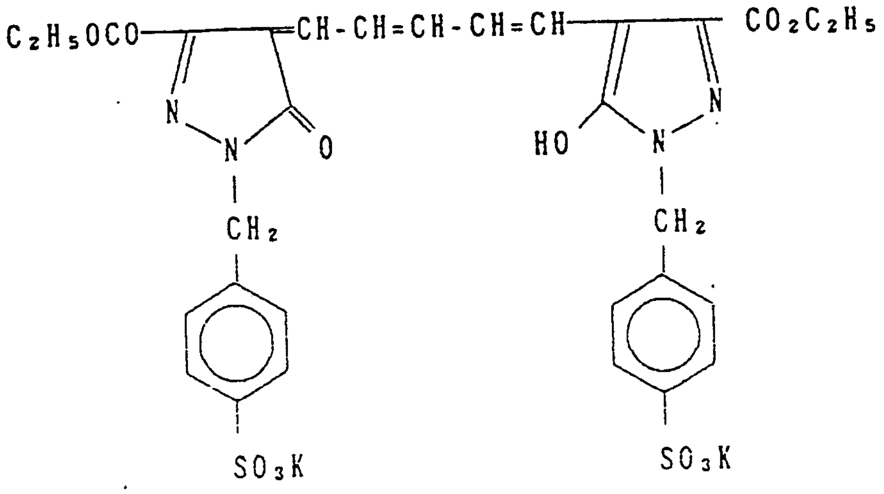
Cpd－16



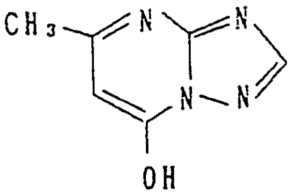
Cpd－17



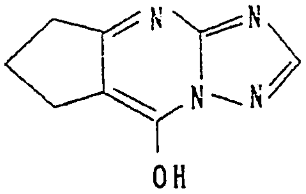
Cpd-18



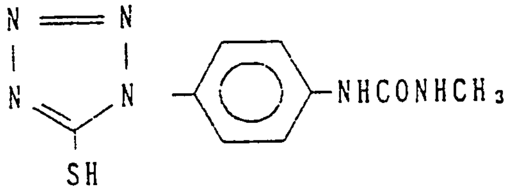
Cpd-19



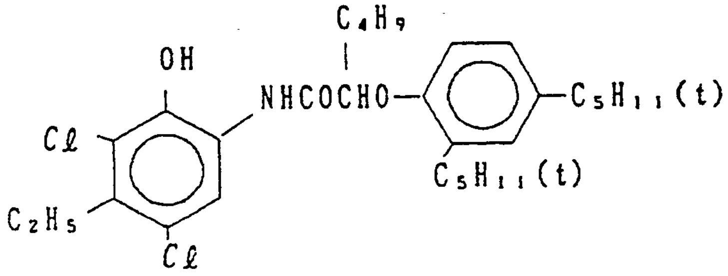
Cpd-20



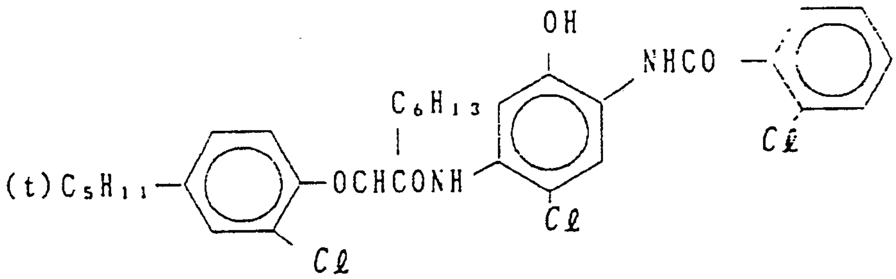
Cpd-21



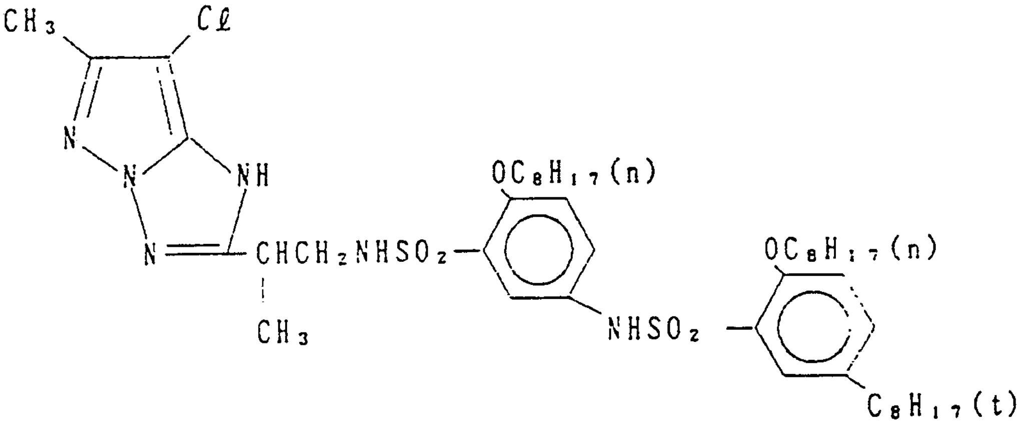
ExC-1



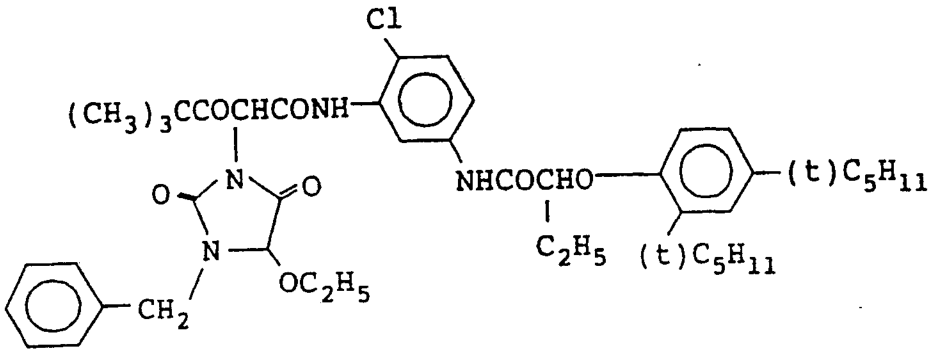
ExC-2



ExM-1



ExY-1



Solv-1 Di(2-ethylhexyl)phthalate
Solv-2 Trinonyl phosphate
Solv-3 Di(3-methylhexyl)phthalate
Solv-4 Tricresyl phosphate
Solv-5 Dibutyl phthalate
Solv-6 Trioctyl phosphate
H-1 1,2-Bis(vinylsulfonylacetamido)ethane

Samples 602 to 609 were prepared in the same manner as described for Sample 601, except that the amounts of Coupler solvent (Solv-4) and Magenta coupler (ExM-1) used in the sixth and seventh layers were changed to those as described in Samples 502 to 509 of Example 5, respectively.

Samples 601 to 609 thus obtained were exposed uniformly to blue light and red light, and further exposed wedgewise to green light, and then subjected to development processing according to the processing steps described below.

In the same manner as described in Example 3, hue and magenta staining were evaluated. Similar results to those in Example 5 were obtained.

Processing Steps	Temperature	Time
First Development (Black-and-white development)	38° C	75 sec
Washing with Water	38° C	90 sec
Reversal Exposure	100 lux or more	1 sec or more
Color Development	38° C	135 sec
Washing with Water	38° C	45 sec
Bleach-Fixing	38° C	120 sec
Washing with Water	38° C	135 sec

The processing solutions used had the following compositions.

First Developing Solution:	
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	0.6 g
Pentasodium diethylenetriaminepentaacetate	4.0 g
Potassium sulfite	30.0 g
Potassium thiocyanate	1.2 g
Potassium carbonate	35.0 g
Potassium hydroquinonemonosulfonate	25.0 g
Diethylene glycol	15.0 ml
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	2.0 g
Potassium bromide	0.5 g
Potassium iodide	5.0 mg
Water to make	1 ℓ (pH 9.70)

Color Developing Solution:	
Benzyl alcohol	15.0 ml
Diethylene glycol	12.0 ml
3,6-Dithia-1,8-octanediol	0.2 g
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	0.5 g
Pentasodium diethylenetriaminepentaacetate	2.0 g
Sodium sulfite	2.0 g
Potassium carbonate	25.0 g
Hydroxylamine sulfate	3.0 g
N-Ethyl-N-(β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5.0 g
Potassium bromide	0.5 g
Potassium iodide	1.0 mg
Water to make	1 ℓ (pH 10.40)

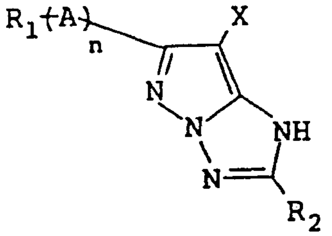
Bleach-Fixing Solution:	
2-Mercapto-1,3,4-triazole	1.0 g
Disodium ethylenediaminetetraacetate dihydrate	5.0 g
Ammonium Fe(III) ethylenediaminetetraacetate monohydrate	80.0 g
Sodium sulfite	15.0 g
Sodium thiosulfate (700 g/ℓ-solution)	160.0 ml
Glacial acetic acid	5.0 ml
Water to make	1 ℓ (pH 6.50)

As explained in detail hereinbefore, when couplers according to the present invention are used, magenta hues are maintained sharp even if the amount of organic solvent having a high boiling point is reduced. Such an effect has not been hitherto known, and the present invention can achieve improvements in color reproducibility where pyrazolotriazole couplers are used, decreases in staining when rapid processing is employed, and improvements in sharpness due to a reduction in the amount of the organic solvent having a high boiling point.

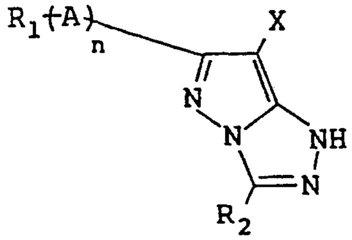
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide color photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one light-insensitive layer, wherein at least one layer of the light-sensitive silver halide emulsion layers contains at least one dye forming coupler represented by the general formulas (I) or (II) described below and the weight ratio of an organic solvent having a high boiling point to the dye forming coupler in the layer is not more than 1:



(I)



(II)

wherein R_1 represents a branched chain alkyl group or an aryl group; R_2 represents a hydrogen atom or a sub stituent; X represents a hydrogen atom or a substituent being released upon a coupling reaction with an oxidation product of an aromatic primary amine developing agent; A represents an oxygen atom, a nitrogen atom or a sulfur atom; and n represents 0 or 1..

2. A silver halide color photographic material as claimed in Claim 1, wherein a substituent for the branched chain alkyl group represented by R_1 is selected from a halogen atom, a hydroxy group, a cyano group, a carboxy group, a sulfo group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, an alkylamino group, an anilino group, a carbamoylamino group, an alkoxycarbonylamino group, an acyloxy group, and a sulfonyl group.

3. A silver halide color photographic material as claimed in Claim 1, wherein a substituent for the aryl group represented by R_1 is selected from a halogen atom, a hydroxy group, a cyano group, a carboxy group, a sulfo group, an alkyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbamoyl group, an alkyl amino group, an anilino group, a carbamoylamino group, an alkoxycarbonylamino group, and a sulfonyl group.

4. A silver halide color photographic material as claimed in Claim 1, wherein the substituent represented by R_2 is a straight chain or branched chain alkyl group having from 1 to 30 carbon atoms, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an amino group, an anilino group, a heterocyclic amino group, an amido group, a urethane group, a ureido group, a sulfonamido group, an alkylthio group, an arylthio group, a sulfinyl group, a sulfonyl group, a sulfo group, a cyano group, or a nitro group.

5. A silver halide color photographic material as claimed in Claim 4, wherein R_2 is a straight chain or branched chain alkyl group or an aryl group.

6. A silver halide color photographic material as claimed in Claim 1, wherein the substituent capable of being released upon coupling is selected from an aryloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, a halogen atom, and a nitrogen-containing heterocyclic group bonded at the nitrogen atom.

7. A silver halide color photographic material as claimed in Claim 1, wherein the dye forming coupler is a compound represented by general formula (I).

8. A silver halide color photographic material as claimed in Claim 7, wherein R_1 is a branched chain alkyl group and n is 0.

9. A silver halide color photographic material as claimed in Claim 7, wherein R_1 is a branched chain alkyl group, A is an oxygen atom and n is 1.

10. A silver halide color photographic material as claimed in Claim 7, wherein R_1 is an aryl group, A is an oxygen atom and n is 1.

11. A silver halide color photographic material as claimed in Claim 1, wherein R_1 is a substituted or unsubstituted isopropyl group or a substituted or unsubstituted tert-butyl group.

12. A silver halide color photographic material as claimed in Claim 1, wherein R_1 is an aryl group having substituents at its 2- and 6-positions.

13. A silver halide color photographic material as claimed in Claim 1, wherein the dielectric constant of the organic solvent having a high boiling point is 5 or more.

14. A silver halide color photographic material as claimed in Claim 1, wherein the light-sensitive silver halide emulsion layer containing the dye forming coupler is a green-sensitive silver halide emulsion layer and the silver halide color photographic light-sensitive material further comprises at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler and at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler.

15. A silver halide color photographic material as claimed in Claim 1, wherein the support is a reflective support.

16. A method for processing a silver halide color photographic material as claimed in Claim 1 comprising a black-and-white development step, a reversal treatment step and a color photographic step.

17. A method for processing a silver halide color photographic material as claimed in Claim 15 comprising a black-and-white development step, a reversal treatment step and a color photographic step.

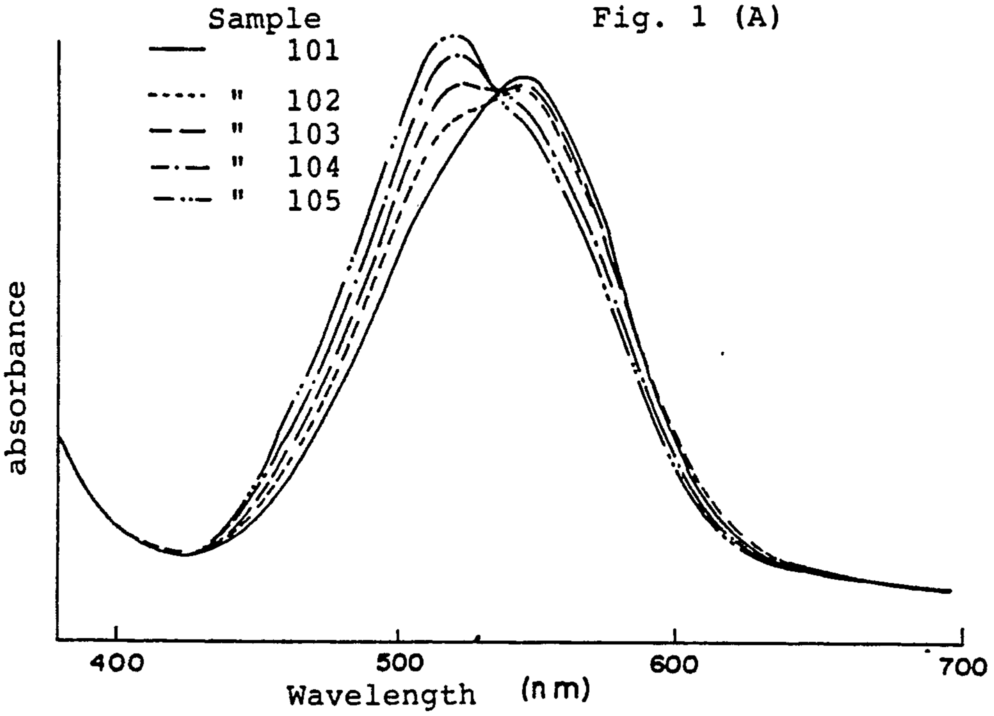


Fig. 1 (A)
Sample
101
" 102
" 103
" 104
" 105
absorbance
400
500
600
700
Wavelength (nm)

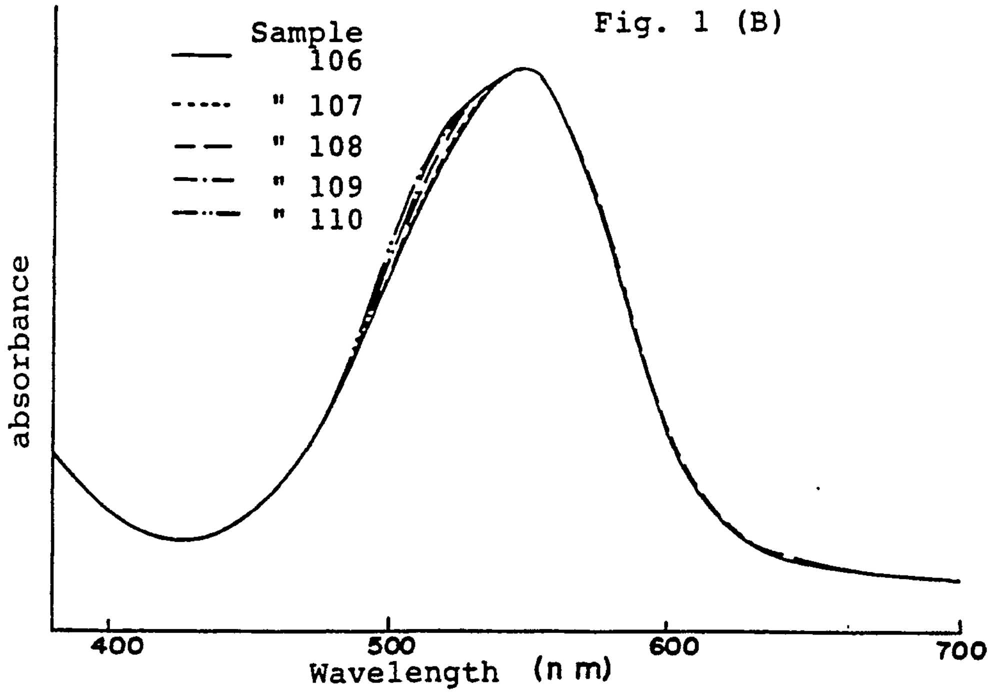


Fig. 1 (B)
Sample
106
" 107
" 108
" 109
" 110
absorbance
400
500
600
700
Wavelength (n m)

Fig. 1 (C)

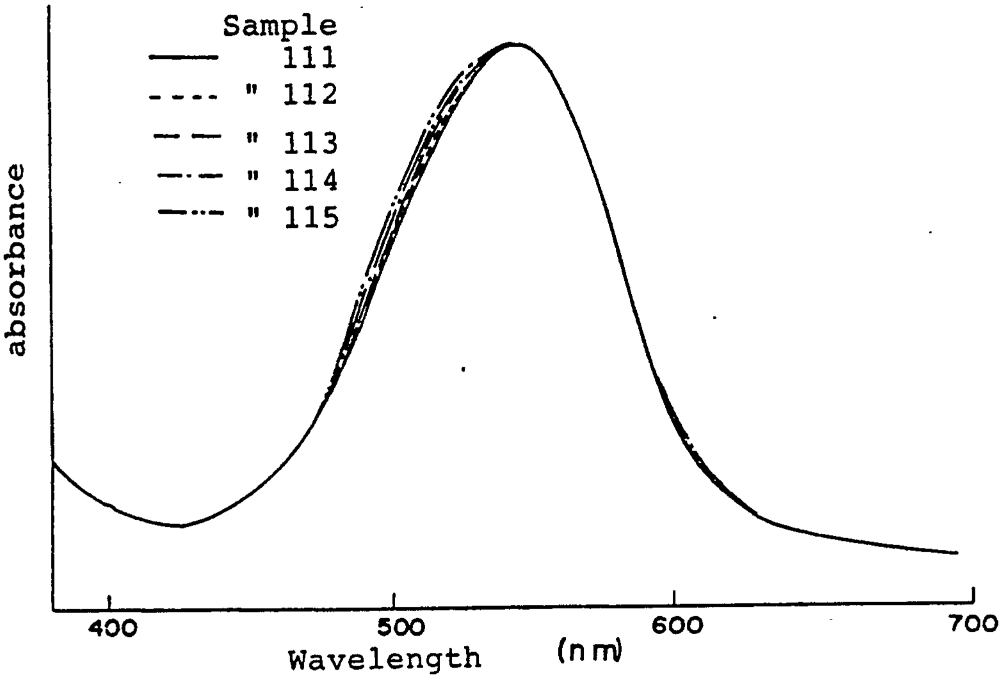

Sample
111
" 112
" 113
" 114
" 115
absorbance
400
500
600
700
Wavelength
(nm)

Fig. 1 (D)

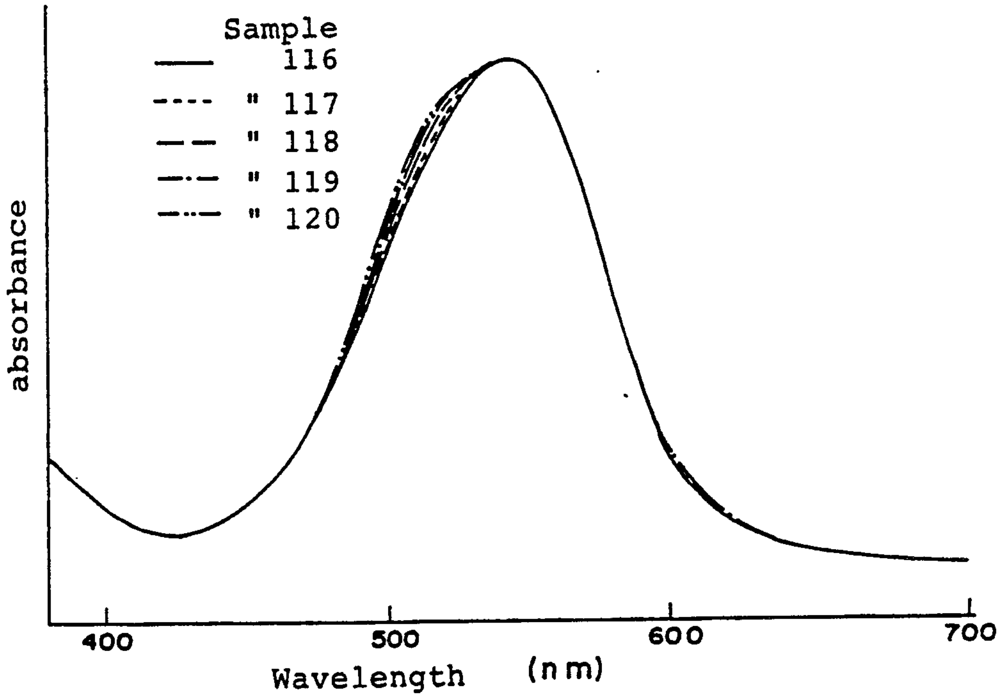

Sample
116
" 117
" 118
" 119
" 120
absorbance
400
500
600
700
Wavelength
(nm)

Fig. 2 (A)

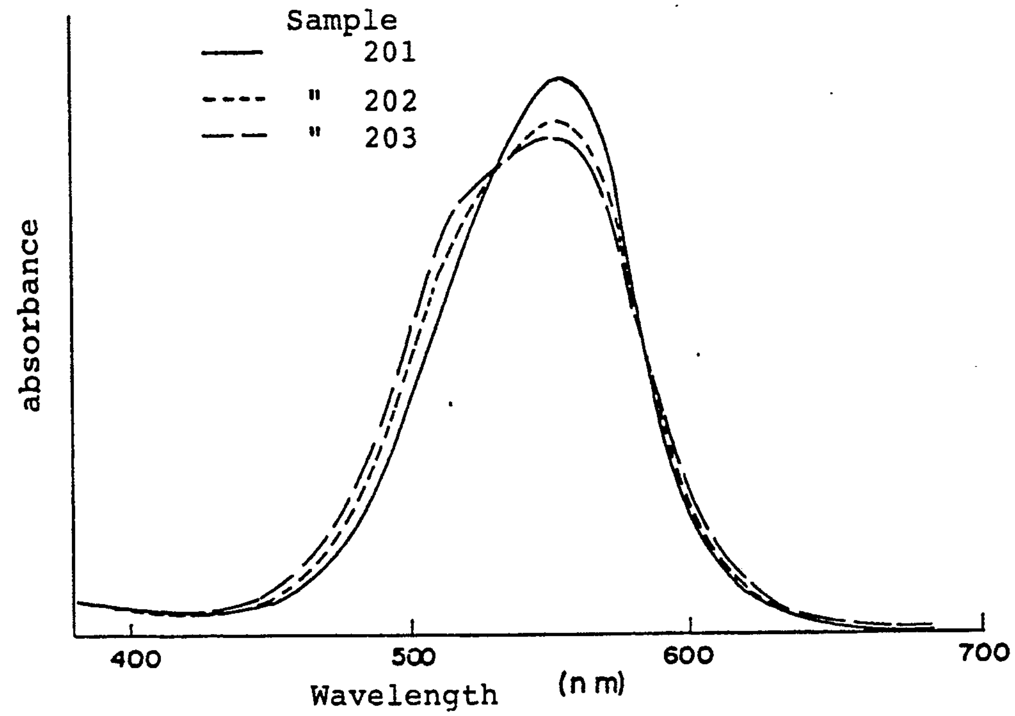

Sample
201
" 202
" 203
absorbance
400
500
600
700
Wavelength
(n m)

Fig. 2 (B)

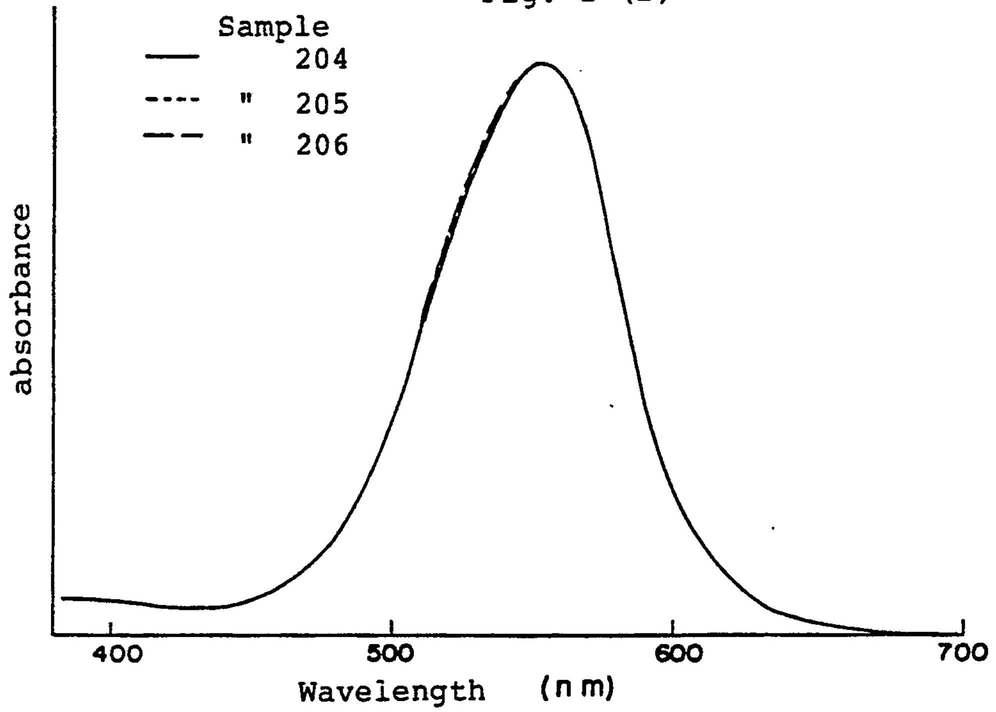

Sample
204
" 205
" 206
absorbance
400
500
600
700
Wavelength
(n m)

Fig. 2 (C)

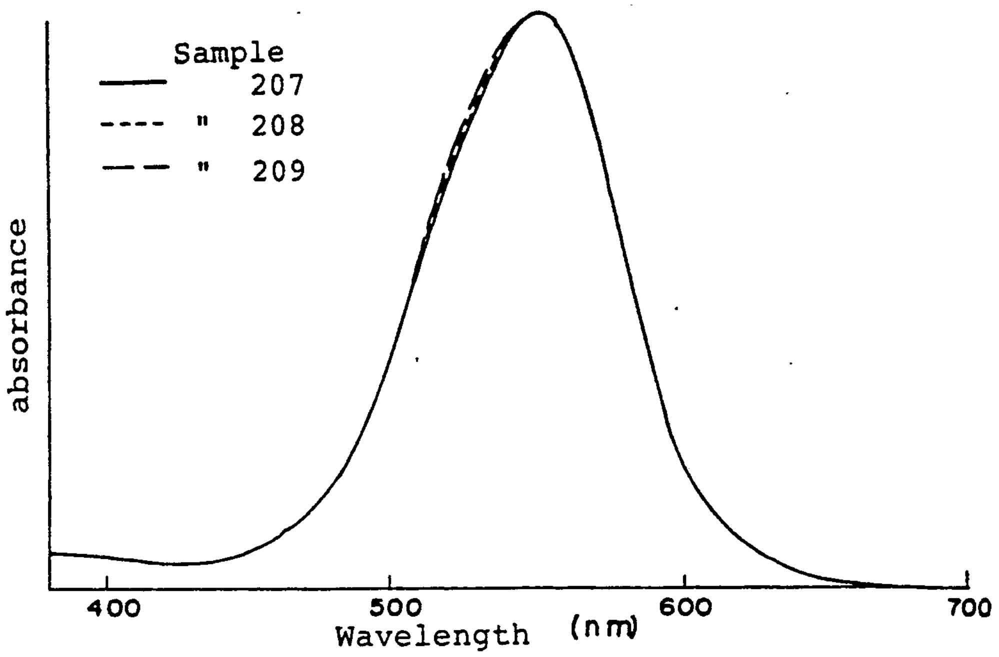
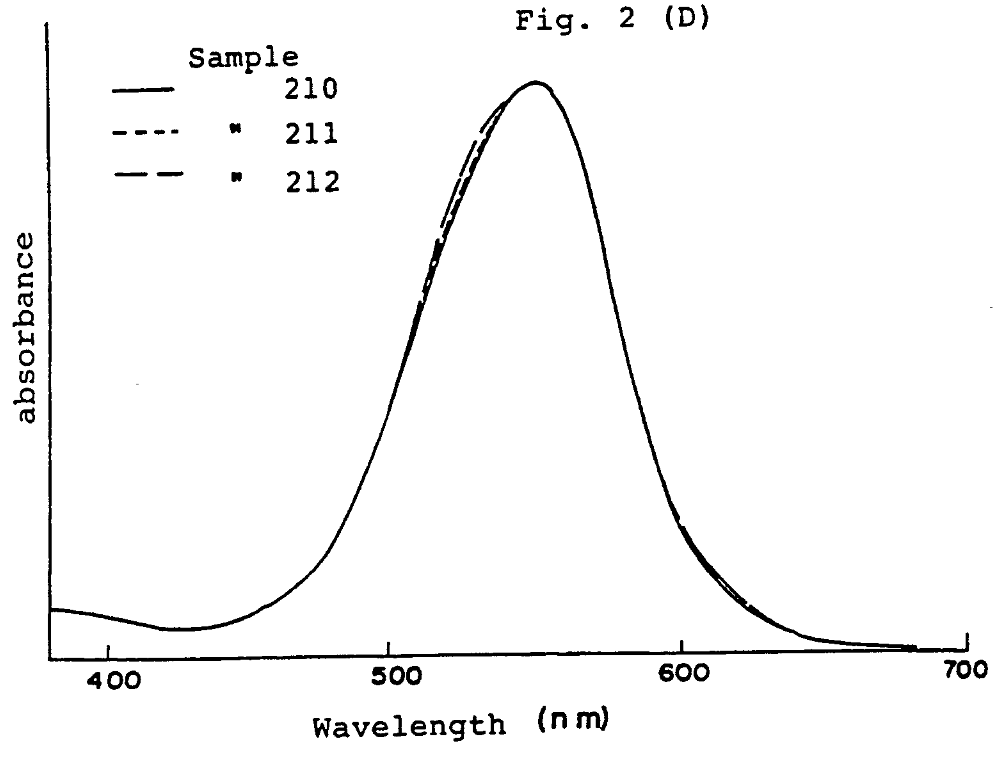

Sample
207
" 208
" 209
absorbance
400
500
600
700
Wavelength (nm)

Fig. 2 (D)


Sample
210
" 211
" 212
absorbance
400
500
600
700
Wavelength (nm)