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(54) Light-sensitive silver halide photographic material.

(57) Disclosed is a light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support, which comprises at least one coupler represented by the following formula (I) and a fluorescent substance precursor which can form a fluorescent substance from an eliminated component released from the above coupler at the time of color development, or from an eliminated component released from the above coupler and a color developing solution component at the time of color development

$$Cp\text{-}SR_1 \qquad (I)$$

wherein Cp represents a coupler residue ; SR_1 represents a group eliminated at the time of coupling with an oxidized product of a color developing agent during development processing ; and R_1 represents an alkyl group, an aryl group, a heterocyclic group, a substituted alkyl group, a substituted aryl group and a substituted heterocyclic group,

and a method for processing a light-sensitive silver halide photographic material, which comprises color development of a light-sensitive silver halide photographic material under the presence of a coupler represented by the above formula (I) and a fluorescent substance precursor which can form a fluorescent substance from an eliminated component released from the above coupler at the time of color development, or from an eliminated component released from the above coupler and a color developing solution component at the time of color development.

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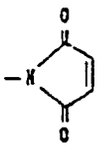
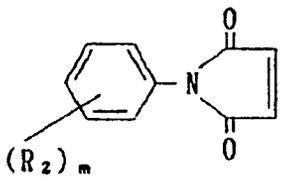


represents a compound with which a chromophore portion of the fluorescent compound is directly substituted; and n represents an integer of 1 or more.

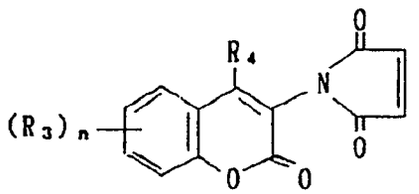
10. The method of Claim 9 wherein the compound represented by the above formula (II) is a compound represented by the following formula (II-1):



(II-1)

wherein R_2 represents a substituent group with which a benzene ring can be substituted; m represents an integer of 0 to 5; when m is 2 or more, plural R_2 may be the same or different; and R_2 which are adjacent to each other may be condensed mutually to form a ring.

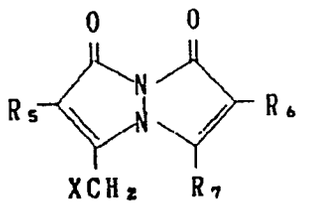
11. The method of Claim 9 wherein the compound rerpesented by the above formula (II) is a compound represented by the following formula (II-2):



(II-2)

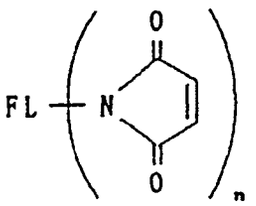
wherein R_3 represents a substituent group with which a benzene ring can be substituted; n represents an integer of 0 to 4; when n is 2 or more, plural R_3's may be the same or different; R_3 which are adjacent to each other may be condensed mutually to form a ring; and R_4 represents a hydrogen atom or a substituent group.

12. The method of Claim 8 wherein the above fluorescent substance precursor is at least one compound selected from the compounds represented by the following formulae (III) and (IV):



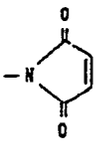
(III)

wherein R_5, R_6 and R_7 each represent a hydrogen atom or a substituent group; X represents a halogen atom; and R_5, R_6 and R_7 cannot represent a hydrogen atom at the same time.

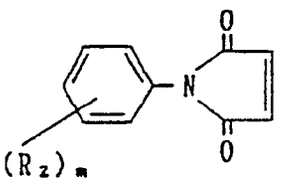


(II)

wherein FL represents a fluorescent compound;

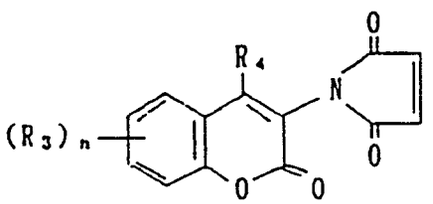


represents a compound with which a chromophore portion of the fluorescent compound is directly substituted; and n represents an integer of 1 or more,



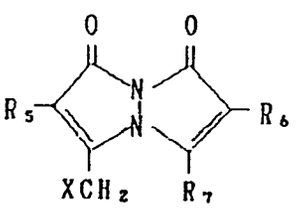
(II-1)

wherein R_2 represents a substitutent group with which a benzene ring can be substituted; m represents an integer of 0 to 5; when m is 2 or more, plural R_2 may be the same or different; and R_2 which are adjacent to each other may be condensed mutually to form a ring,



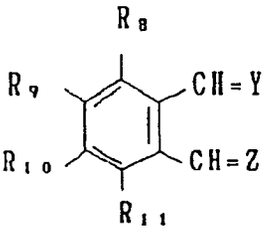
(II-2)

wherein R_3 represents a substituent group with which a benzene ring can be substituted; n represents an integer of 0 to 4; when n is 2 or more, plural R_3's may be the same or different; R_3's which are adjacent to each other may be condensed mutually to form a ring; and R_4 represents a hydrogen atom or a substituent group,



(III)

wherein R_5, R_6 and R_7 each represent a hydrogen atom or a substituent group; X represents a halogen atom; and R_5, R_6 and R_7 cannot represent a hydrogen atom at the same time, and

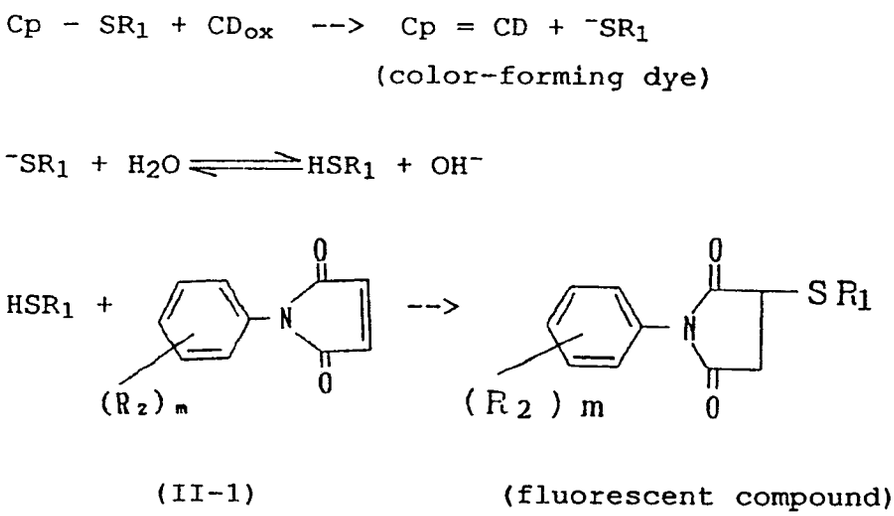


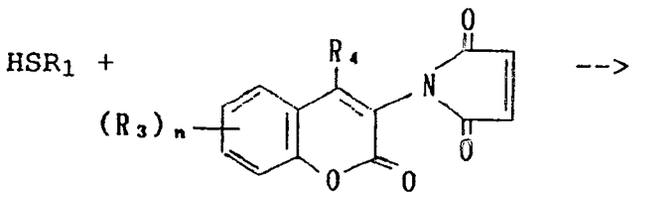
(IV)

wherein R_8, R_9, R_{10} and R_{11} each represent a hydrogen atom and a substituent group with which a benzene ring can be substituted; R_8 and R_9, R_9 and R_{10}, and R_{10} and R_{11} which are adjacent to each other, respectively, may be condensed mutually to form a hydrocarbon ring or a hetero ring; and Y and Z each represent O or N-R_{12} where R_{12} represents a substituent group.

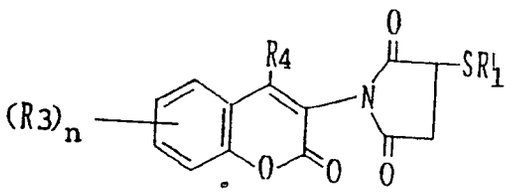
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The characteristic feature of the present invention resides in that a fluorescent substance precursor existing in an emulsion layer of a light-sensitive material causes substitution reaction with a mercapto compound released from a divalent coupler represented by the formula (I) during development processing under a basic condition to form a fluorescent substance having high quantum efficiency. In the following, a preferred reaction example of the above precursor is shown.

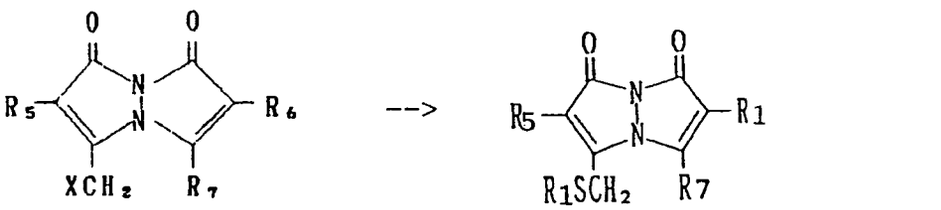




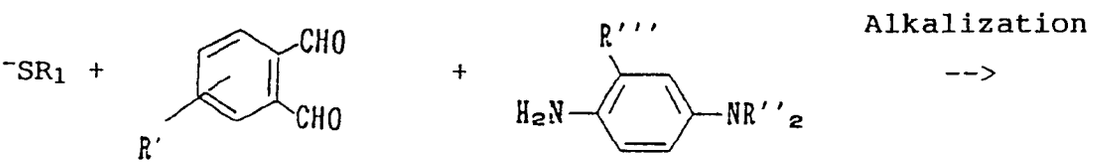
(II-2)



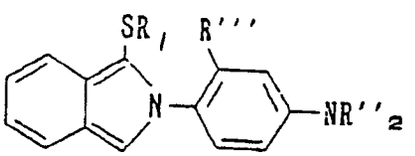
(fluorescent compound)



(III) (fluorescent compound)



(IV) (CD)



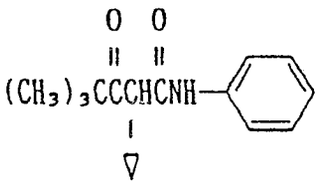
(fluorescent compound)

In the formulae, CD represents a color developing agent, and CD_{ox} represents an oxidized product of a color developing agent.

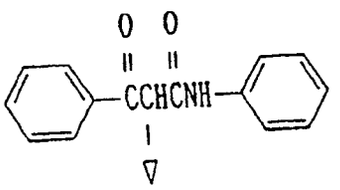
Next, the present invention is described in more detail.

In the formula (II), as a coupler residue represented by Cp, there can be used each mother nucleus of a yellow coupler, a magenta coupler and a cyan coupler, but preferred mother nuclei are those represented by the following formulae (V) to (XIII).

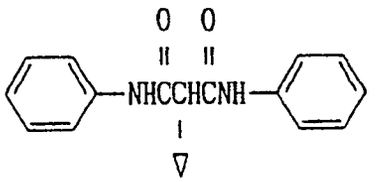
(V)



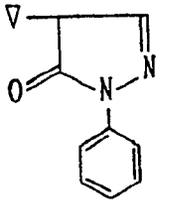
(VI)



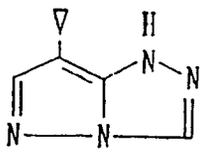
(VII)



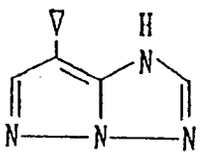
(VIII)



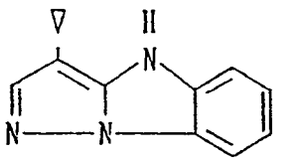
(IX)



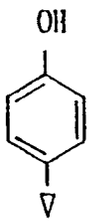
(X)



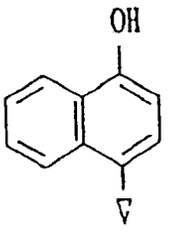
(XI)



(XII)



(XIII)



In the formulae, -Δ represents a position bonding to SR_1.

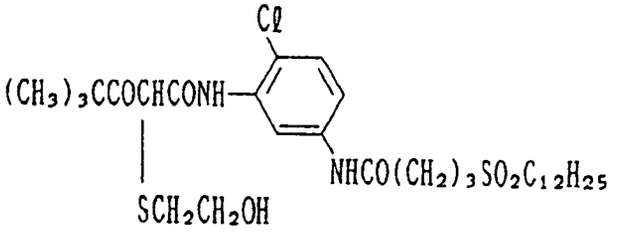
The coupler mother nuclei shown above may have a substituent group, and the substituent group may include those mentioned in the description of the above R_1. Preferred is the case where at least one substituent group is a diffusion-proof group.

In the formula (I), the substituent group represented by R_1 is not particularly limited, and may preferably include an alkyl group or an aryl group which are substituted with a hydroxyl group, a carboxyl group, an amino group, an ureido group, an acylamino group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an aryloxy group, an urethane group, an alkoxy group, a mercapto group, an alkylthio group, an arylthio group or a halogen atom.

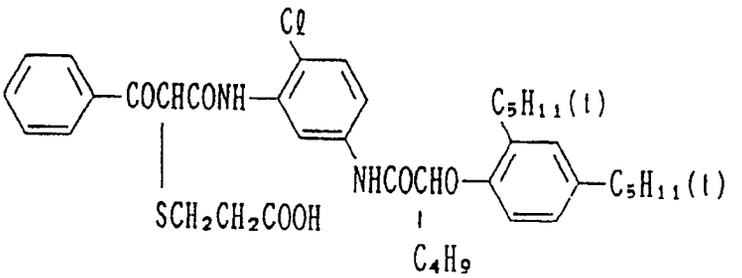
The fluorescent substance precursor may be added in a development processing solution or in an emulsion layer, but preferred is the case where it is added in an emulsion layer, and more preferred is the case where it is added in an emulsion layer containing a divalent coupler represented by the formula (I).

In the following, examples of the compound represented by the formula (I) to be used in the present invention are shown, but the present invention is not limited to these.

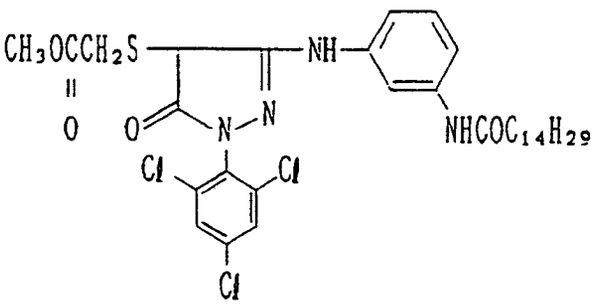
I-1



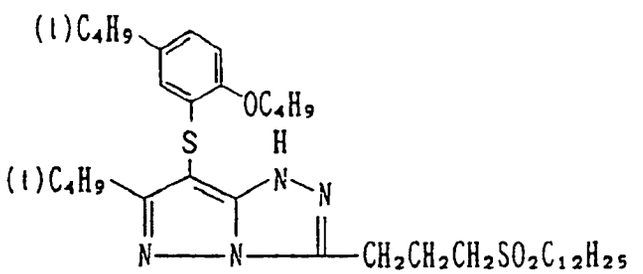
I-2



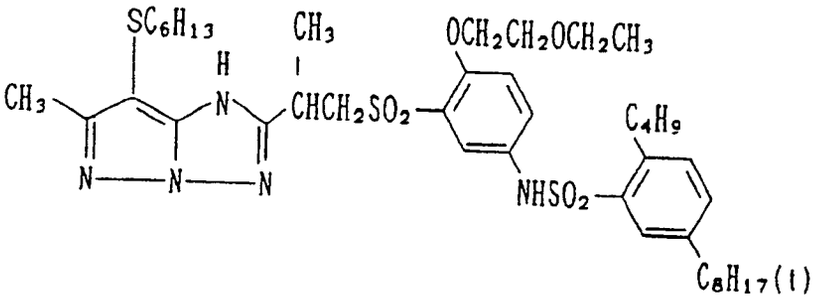
I-3



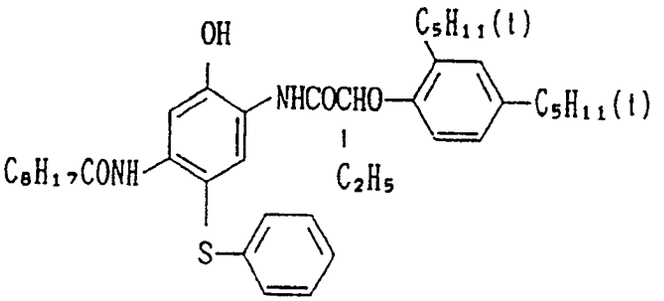
I-4



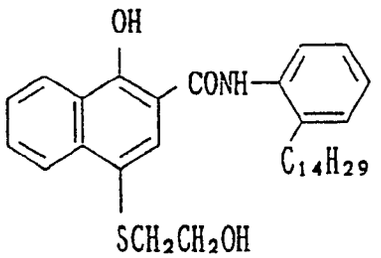
I-5



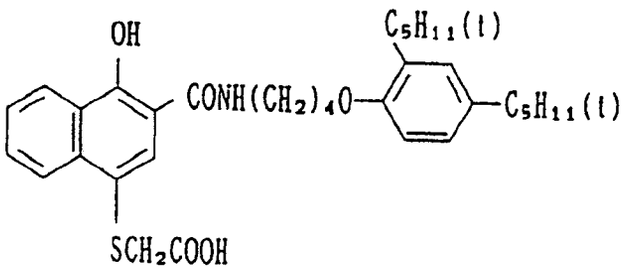
I-6



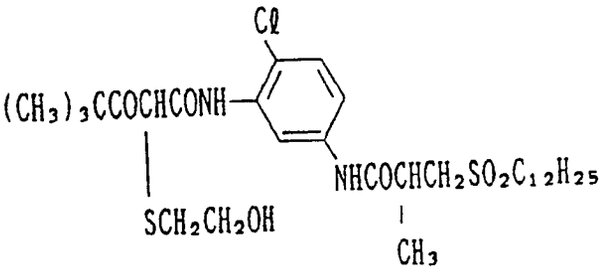
I-7



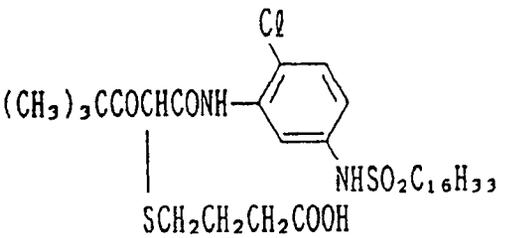
I-8



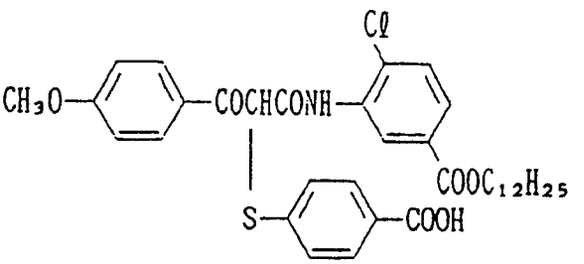
I-9



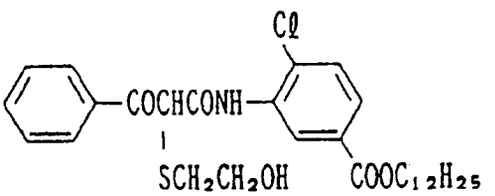
I-10



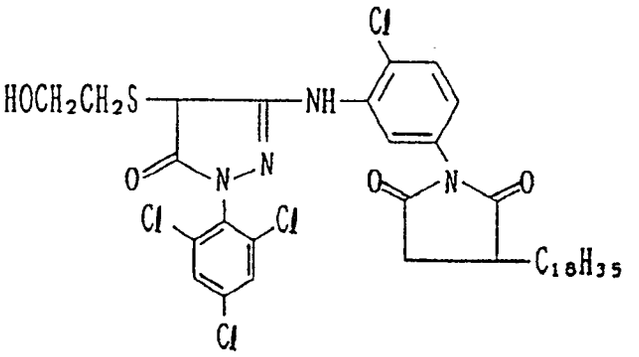
I-11



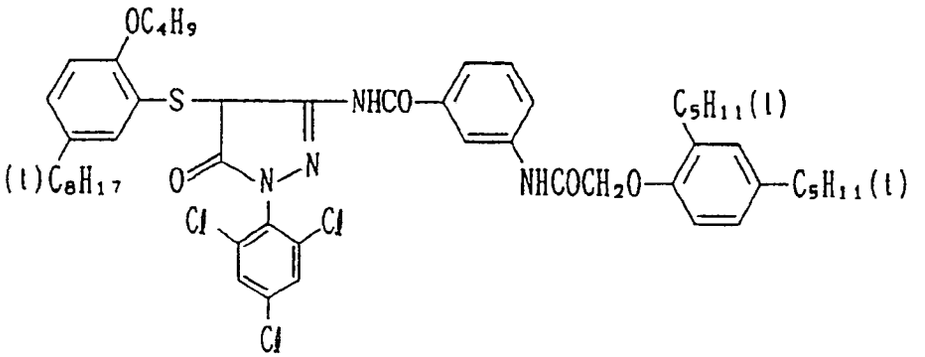
I-12



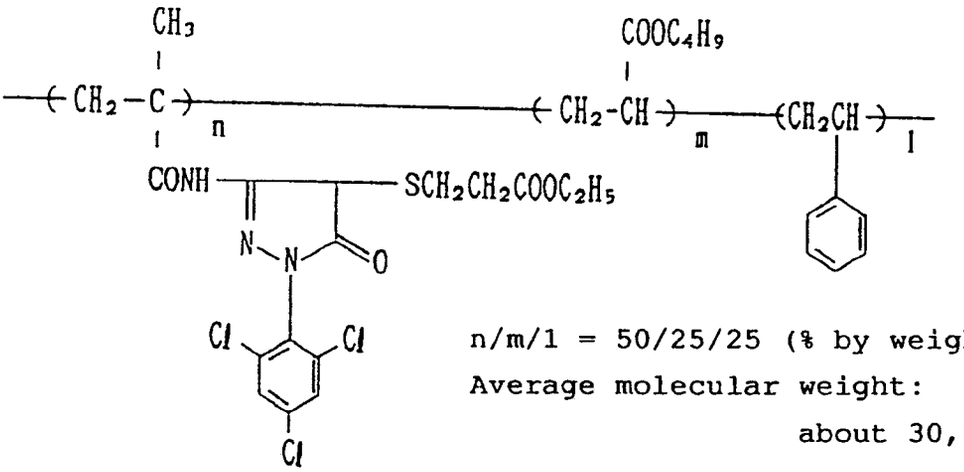
I-13



I-14



I-15

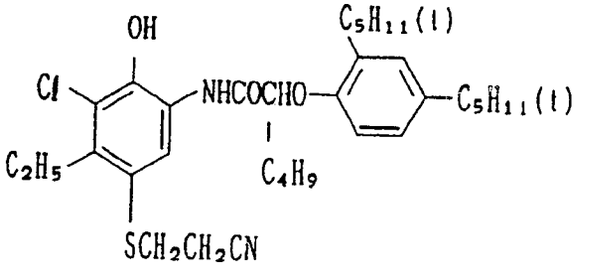


n/m/1 = 50/25/25 (% by weight)

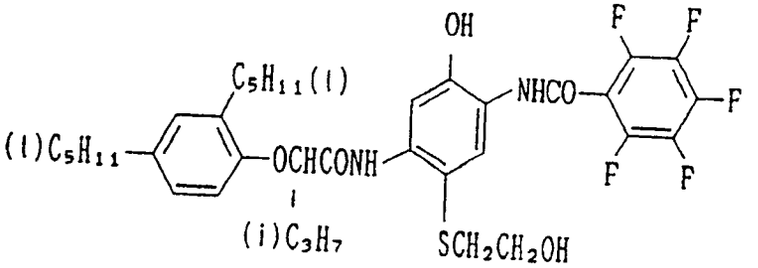
Average molecular weight:

about 30,000

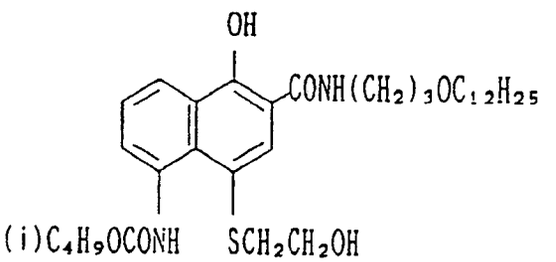
I-16



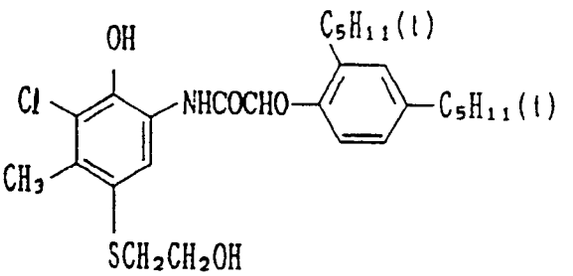
I-17



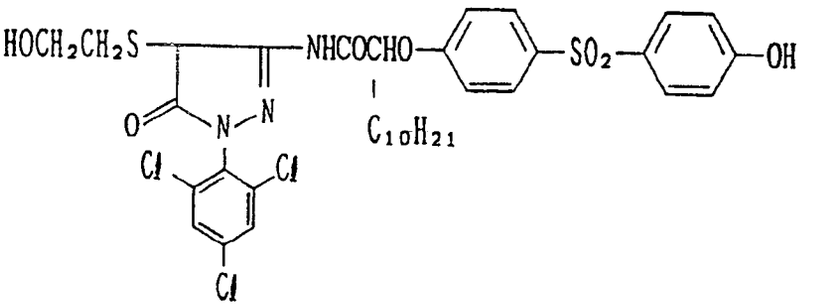
I-18



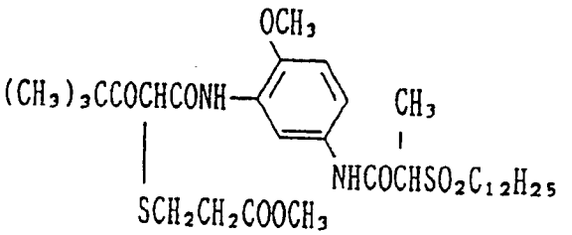
I-19



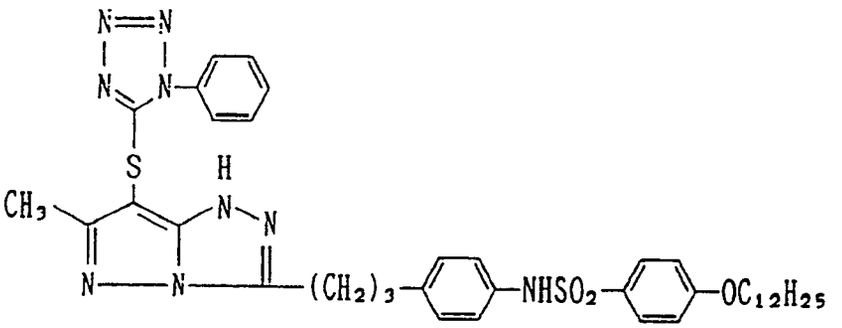
I-20



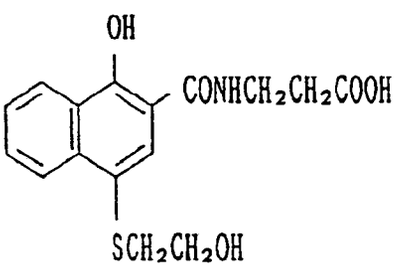
I-21



I-22

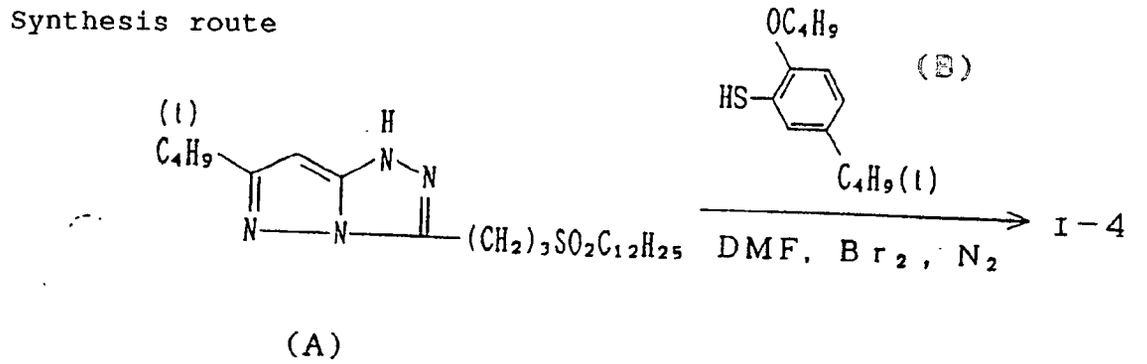


I-23



Next, a synthesis example of the compound represented by the formula (I) is shown.

Synthesis example 1 (synthesis method of I-4)

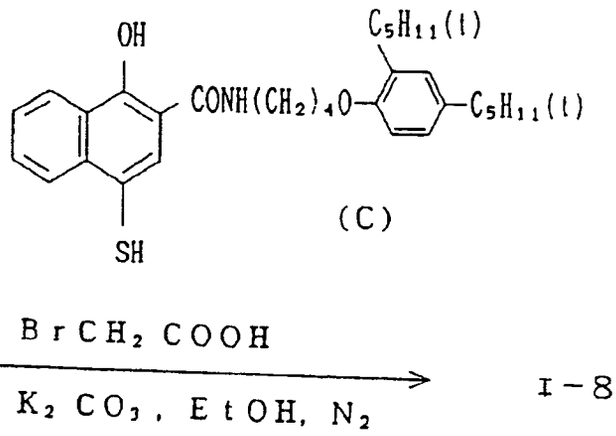


71.5 g of an intermediate product (B) was dissolved in 400 ml of dimethylformamide (DMF) at room temperature, and then 51.1 g of bromine was added dropwise to the solution under nitrogen atmosphere. After completion of the dropwise addition, the mixture was stirred for 5 minutes, and then 118.2 g of an intermediate product (A) was added thereto, followed by reaction at room temperature for 6 hours. To the reaction mixture, 600 ml of water and 800 ml of ethyl acetate were added to extract an organic substance, and then ethyl acetate was evaporated under reduced pressure to obtain 186 g of a yellow solid. This solid was recrystallized with 300 ml of acetonitrile to obtain 141 g of white crystals.

(The crystals were confirmed to be I-4 by ^{1}HNMR, IR and FD mass spectrum.)

Synthesis example 2 (synthesis method of I-8)

Synthesis route



To 25.4 g of an intermediate product (C), 300 ml of ethanol (EtOH) was added, and dissolved under nitrogen gas stream. To the solution, 7.6 g of anhydrous potassium carbonate and 7.0 g of bromoacetic acid were added, and the mixture was stirred under heating at a solution temperature of 65 to 70 °C for 4 hours.

Ethanol, a solvent was evaporated under reduced pressure, and then 200 ml of water and 400 ml of ethyl acetate were added, followed by neutralization with 5N hydrochloric acid, to extract a product formed. An organic phase was washed, and dried with anhydrous sodium sulfate. Thereafter, ethyl acetate, the solvent was evaporated under reduced pressure. The solid obtained was recrystallized with ethanol to obtain 20.8 g of I-8.

(The solid was confirmed to be I-8 by ^{1}HNMR, FD mass spectrum and IR spectrum.)

The coupler of the present invention represented by the formula (I) can be used as a material for forming color photographs according to any color-forming method. As a color-forming method, there may be specifically mentioned a coupler-in-developer type color-forming method and a coupler-in-emulsion type color-forming method. When a coupler-in-developer type color-forming method is used, the coupler of the present invention can be dissolved in an aqueous alkaline solution or an organic solvent (e.g. alcohol) and added in a developing

processing solution.

When the coupler of the present invention represented by the formula (I) is used as a material for forming color photographs according to a coupler-in-emulsion type color-forming method, the coupler of the present invention is used by incorporating in a light-sensitive photographic material. In this case, the coupler of the present invention represented by the formula (I) can be used generally in an amount of 1×10^{-3} mole to 1 mole, preferably in the range of 1×10^{-2} mole to 8×10^{-1} mole per mole of silver halide.

As the fluorescent substance precursor, the compounds represented by the formula (II) (particularly (II-1) or (II-2)), (III) or (IV) described above are preferred.

In the above formulae (II-1), (II-2), (III) and (IV), substituent groups represented by R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are not particularly limited, and may typically include each group of alkyl, aryl, anilino, acylamino, sulfonamide, alkylthio, arylthio, alkenyl and cycloalkyl, and otherwise a halogen atom and each group of cycloalkenyl, alkynyl, hetero ring, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, sulfonyloxy, carbamoyloxy, amino, alkylamino, imide, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl, heterocyclic thio, thioureido, carboxy, hydroxy, mercapto, nitro and sulfo, and also a spiro compound residue and a bridged hydrocarbon compound residue.

These substituent groups may further have a substituent group.

The above alkyl group as preferably 1 to 32 carbon atoms, and may be straight or branched.

The aryl group is preferably a phenyl group.

The acylamino group may include an alkylcarbonylamino group and an arylcarbonylamino group.

The sulfonamide group may include an alkylsulfonylamino group and an arylsulfonylamino group.

The alkyl component and aryl component in the alkylthio group and arylthio group may include the above alkyl group and aryl group.

The alkenyl group has preferably 2 to 32 carbon atoms, and the cycloalkyl group has preferably 3 to 12, particularly preferably 5 to 7 carbon atoms. The alkenyl group may be straight or branched.

The cycloalkenyl group has preferably 3 to 12, particularly preferably 5 to 7 carbon atoms.

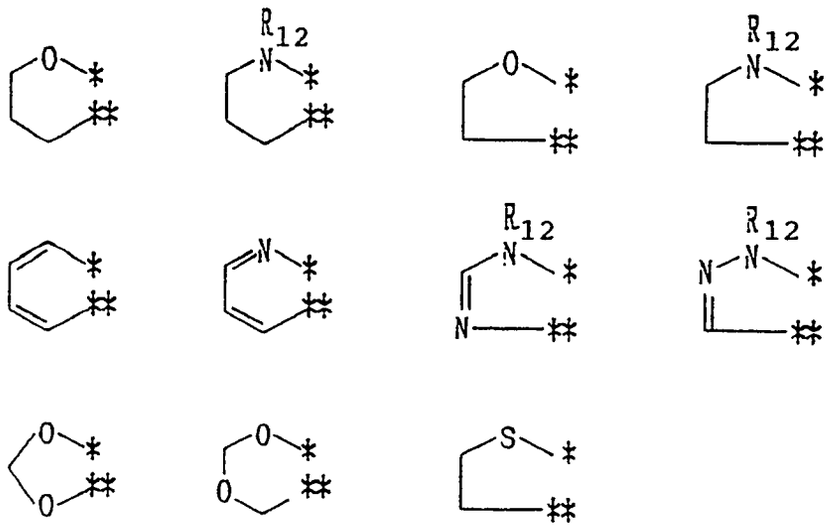
The sulfonyl group may include an alkylsulfonyl group and an arylsulfonyl group; the sulfinyl group, an alkylsulfinyl group and an arylsulfinyl group; the phosphonyl group, an alkylphosphonyl group, an alkoxyphosphonyl group, an aryloxyphosphonyl group and an arylphosphonyl group; the acyl group, an alkylcarbonyl group and an arylcarbonyl group; the carbamoyl group, an alkylcarbamoyl group and an arylcarbamoyl group; the sulfamoyl group, an alkylsulfamoyl group and an arylsulfamoyl group; the acyloxy group, an alkylcarbonyloxy group and an arylcarbonyloxy group; the sulfonyloxy group, an alkylsulfonyloxy group and an arylsulfonyloxy group; the carbamoyloxy group, an alkylcarbamoyloxy group and an arylcarbamoyloxy group; the ureido group, an alkylureido group and an arylureido group; the sulfamoylamino group, an alkylsulfamoylamino group and an arylsulfamoylamino group; the heterocyclic group, preferably 5- to 7-membered groups, specifically a 2-benzimidazole group, a 1-benzotriazole group, a 2-benzotriazole group, a 2-pyridyl group, a 3-pyridyl group, a 2-furyl group, a 2-thienyl group, a 2-pyrimidinyl group, a 2-benzothiazolyl group, a 1-pyrrolyl group and a 1-tetrazolyl group; the heterocyclic oxy group, preferably those having 5- to 7-membered hetero rings, for example, a 3,4,5,6-tetrahydropyranyl-2-oxy group and a 1-phenyltetrazole-5-oxy group; the heterocyclic thio group, preferably 5- to 7-membered heterocyclic thio groups, for example, a 2-pyridylthio group, a 2-benzothiazolylthio group and a 2,4-diphenoxy-1,3,5-triazole-6-thio group; the siloxy group, a trimethylsiloxy group, a triethylsiloxy group and a dimethylbutylsiloxy group; the imide group, a succinimide group, a 3-heptadecylsuccinimide group, a phthalimide group and a glutarimide group; the spiro compound residue, spiro[3.3]heptan-1-yl; the bridged hydrocarbon compound residue, bicyclo[2.2.1]heptan-1-yl, tricyclo[3.3.1.$1^{3,7}$]decan-1-yl and 7,7-dimethylbicyclo[2.2.1]heptan-1-yl, respectively.

Further, as the alkyl group having a substituent group, there may be mentioned a halogenated alkyl group, a hydroxyalkyl group, an aminoalkyl group (including a quaternary ammonium salt), a sulfonylalkyl group and an alkoxyalkyl group.

The above groups may further have a substituent group such as a diffusion-proof group including a long chain hydrocarbon group and a polymer residue.

Among the substituent groups represented by R_1 to R_{11}, preferred are each group of amino, hydroxy, acylamino, sulfonamide, alkylamino, anilino, alkoxy, aryloxy, alkylthio, arylthio, sulfonyl and sulfinyl, and more preferred are each group of alkylamino, acylamino and alkoxy.

In the formula (II-1) or (II-2), when m or n is 2 or more and plural R_1 or R_2 are adjacent to each other, the adjacent R_1 or R_2 may be condensed mutually to form a ring, and its preferred examples are shown below.



In the formulae, * and ** each represents a position consensing to a benzene ring, and R_{12} has the same meanings of the above R_1 to R_{11}. Further, a position which can be substituted in these condensed rings may be substituted with a substituent group represented by R_1 or R_2.

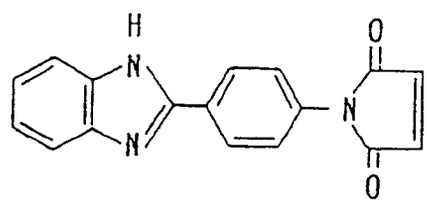
In the formula (II-2), among the substituent groups represented by R_4, preferred are each group of alkyl, aryl and halogenated alkyl, a halogen atom, and each group of carboxyl, cyano alkoxy and carbonyl, and more preferred are an alkyl group, a halogen atom and a halogenated alkyl group.

In the formula (III), among the substituent groups represented by R_5 and R_6, preferred are each group of alkyl and aryl, and among the substituent groups represented by R_7, preferred are each group of alkyl and substituted aryl.

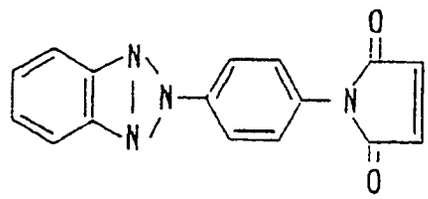
In the formula (III), the halogen atom represented by X may include fluorine, chlorine, bromine and iodine, preferably chlorine and bromine.

In the following, examples of the compound represented by the formula (II-1) to be used in the present invention are shown, but the present invention is not limited to these.

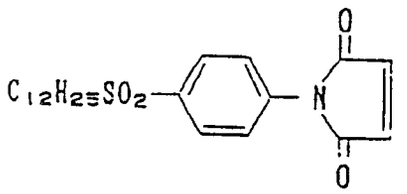
II-1-1



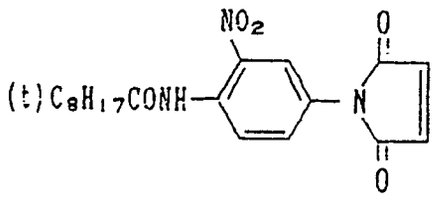
II-1-2



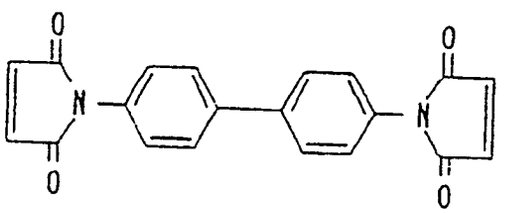
II-1-3



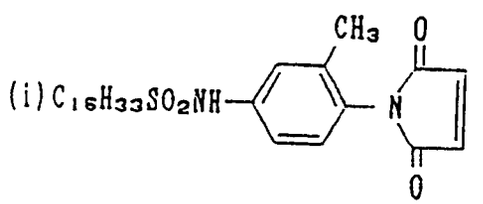
II-1-4



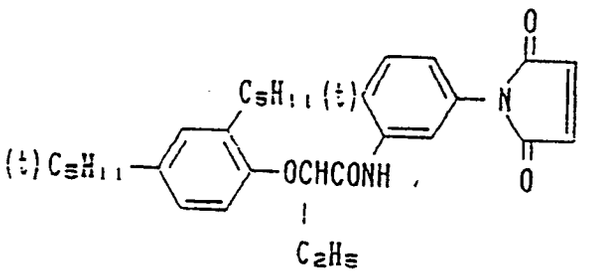
II-1-5



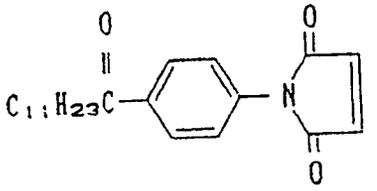
II-1-6



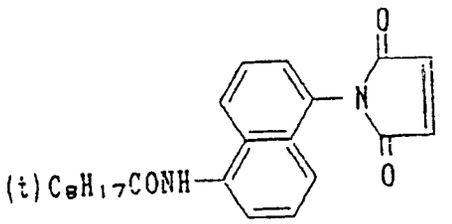
II-1-7



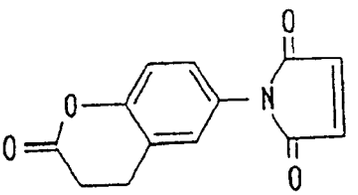
II-8-8



II-1-9



II-1-10



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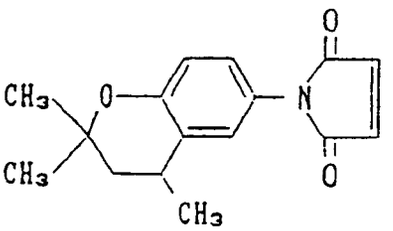
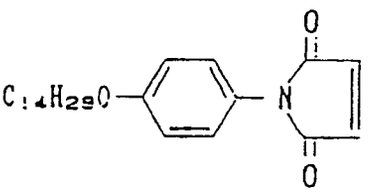
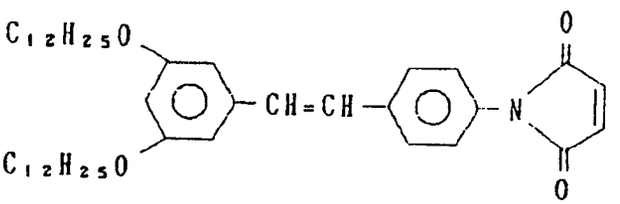


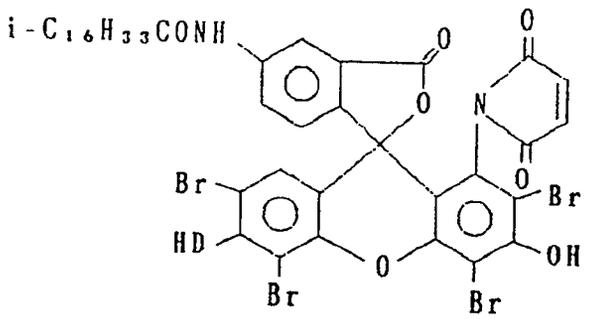
II-1-12



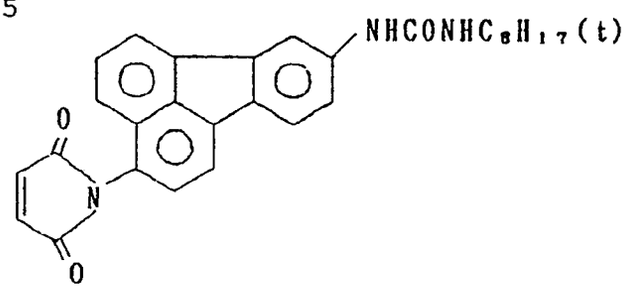
II-1-13



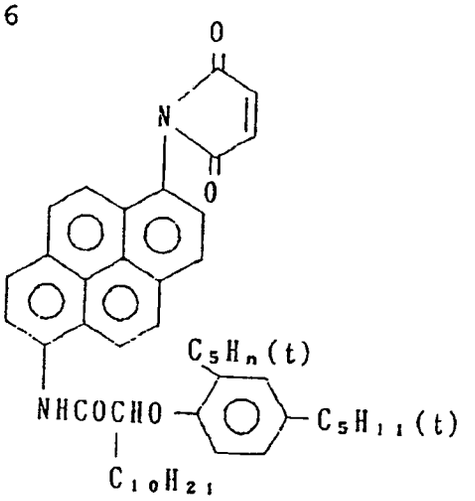
II-1-14



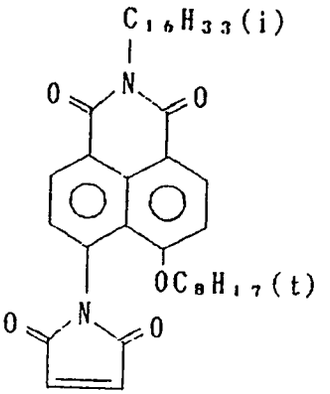
II-1-15



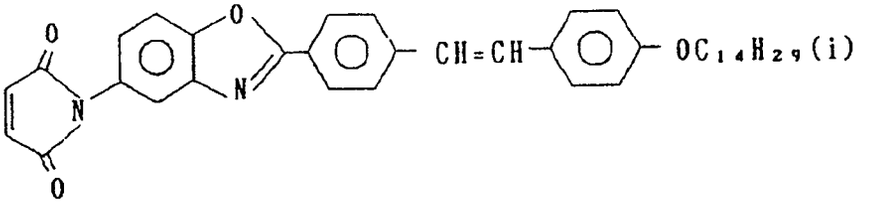
II-1-16



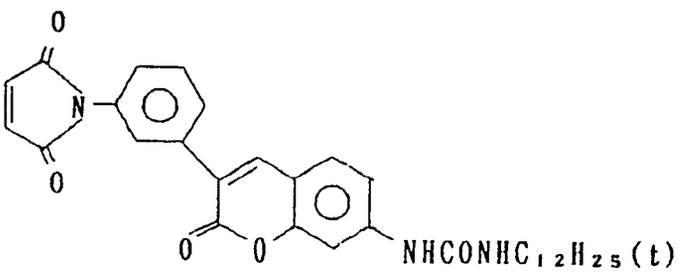
II-1-17



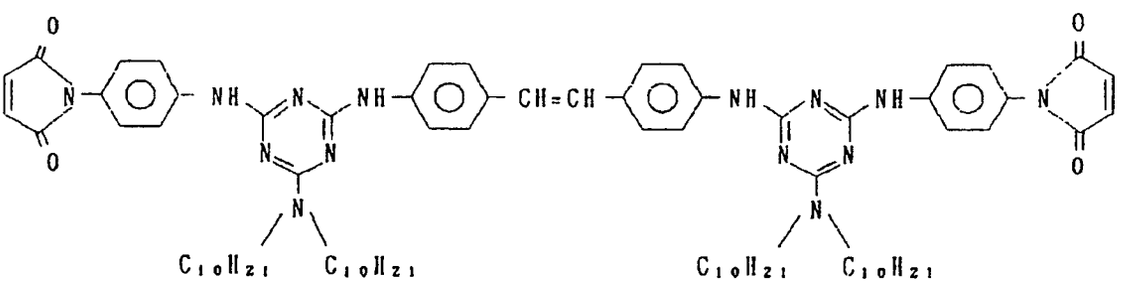
II-1-18



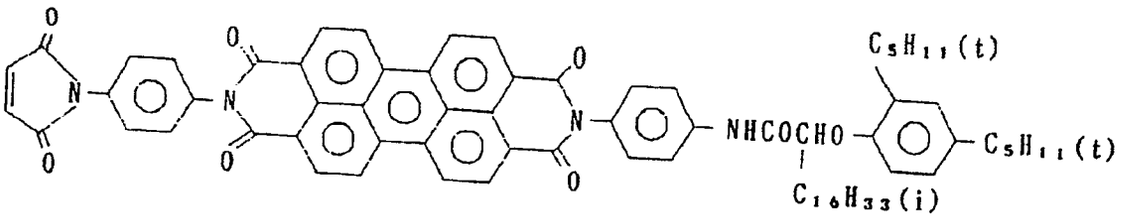
II-1-19



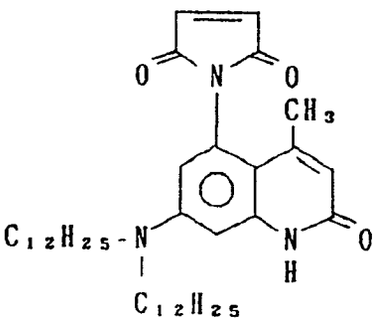
II-1-20



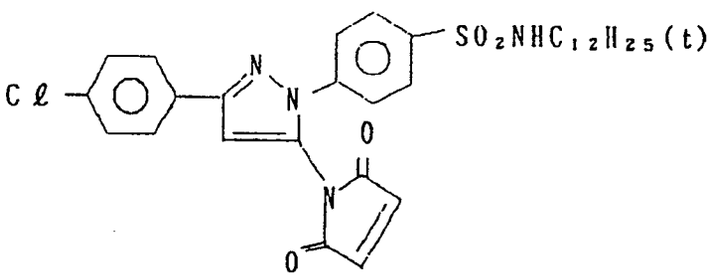
II-1-21



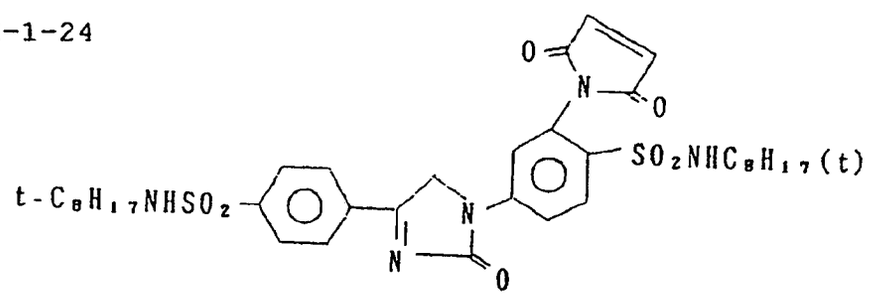
II-1-22



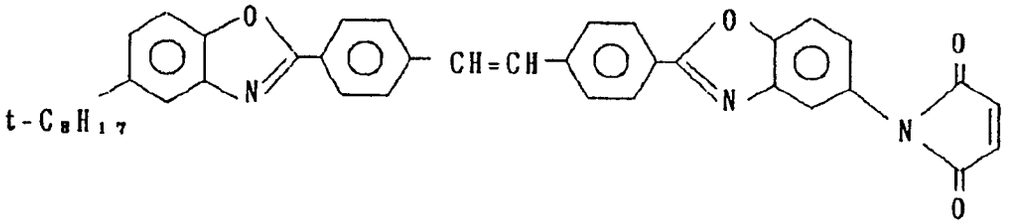
II-1-23



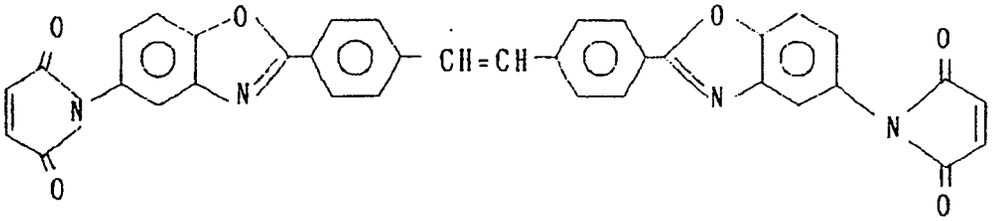
II-1-24



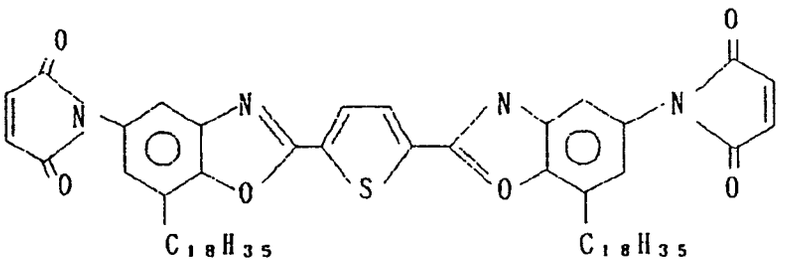
II-1-25



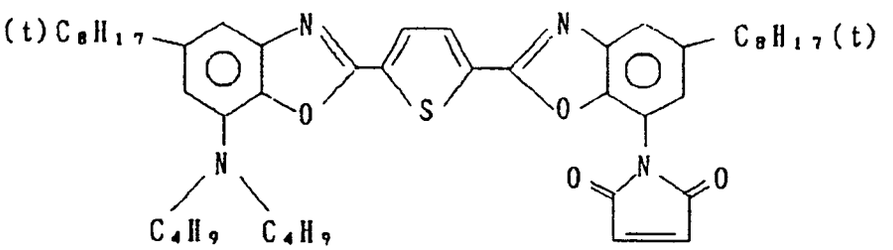
II-1-26



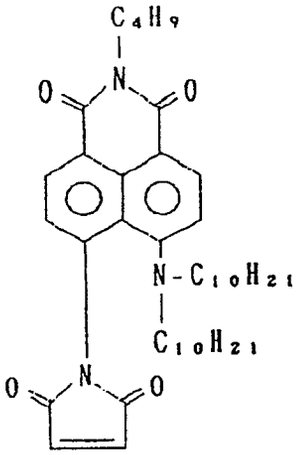
II-1-27



II-1-28

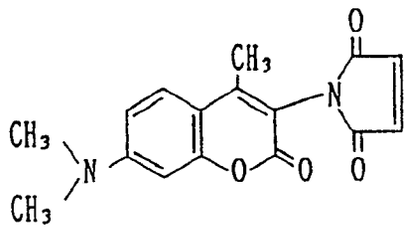


II-1-29

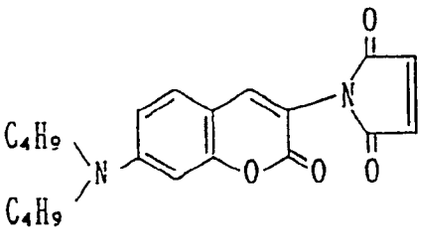


In the following, examples of the compound represented by the formula (II-2) are shown, but the present invention is not limited to these.

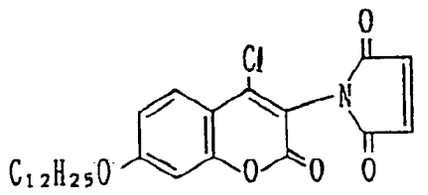
II-2-1



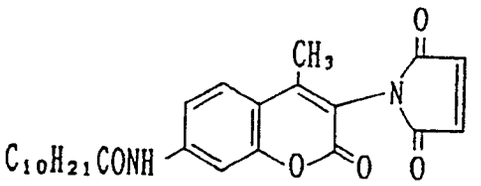
II-2-2



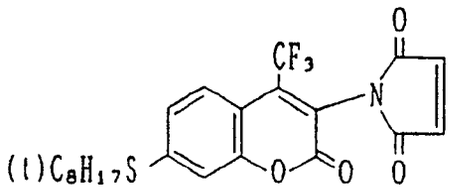
II-2-3



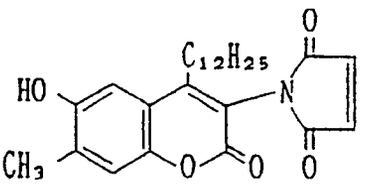
II-2-4



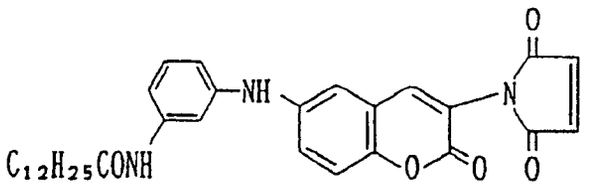
II-2-5



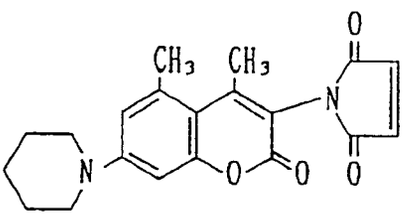
II-2-6



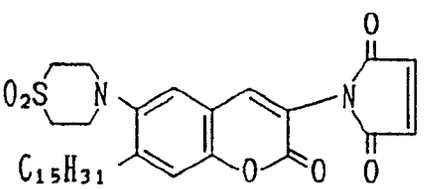
II-2-7



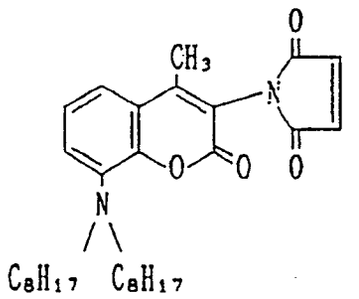
II-2-8



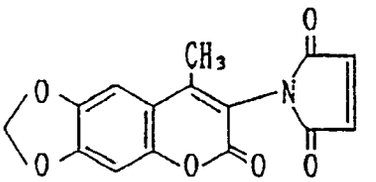
II-2-9



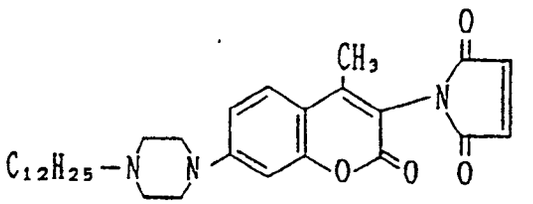
II-2-10



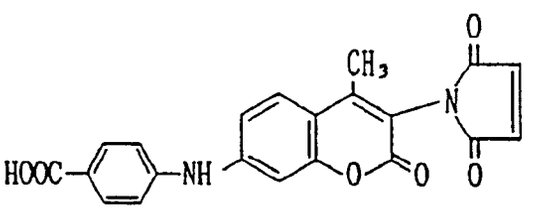
II-2-11



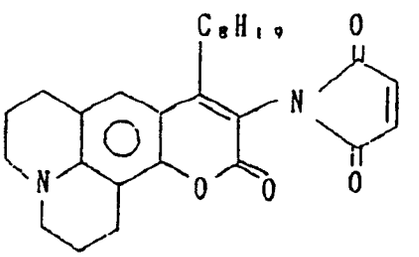
II-2-12



II-2-13



II-2-14

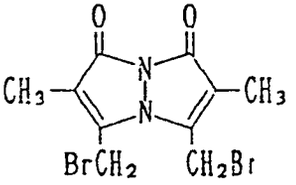


In the following, examples of the compound represented by the formula (III) are shown, but the present

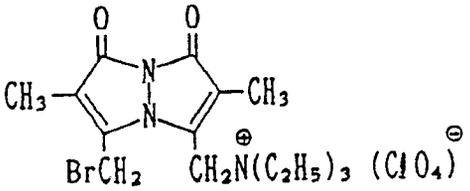
invention is not limited to these.

III-1

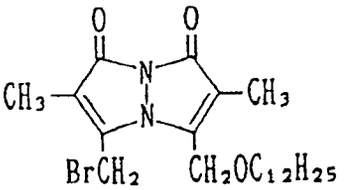
III-2



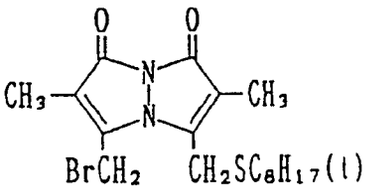
III-3



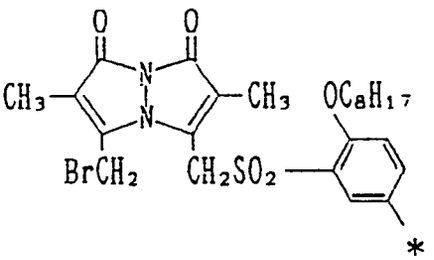
III-4



III-5

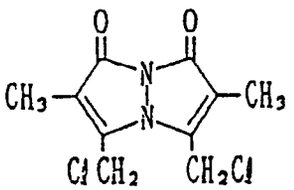


III-6

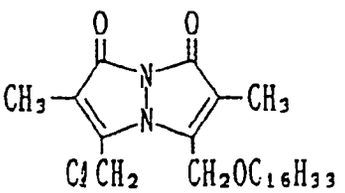


$*-C_8H_{17}(t)$

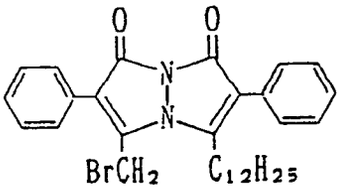
III-7



III-8



III-9



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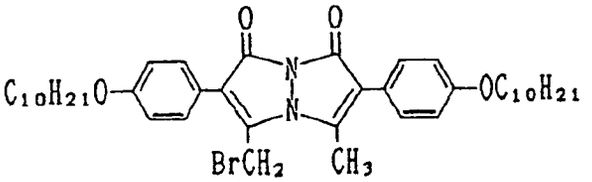

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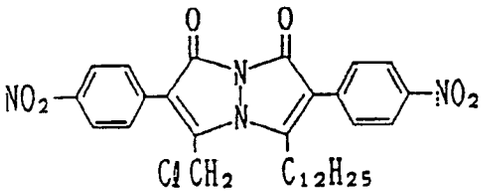
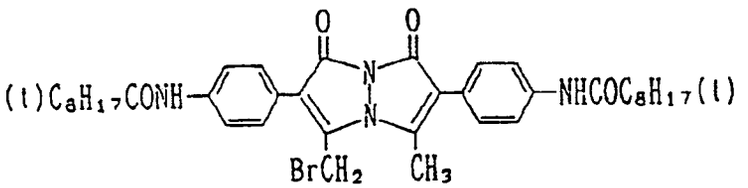
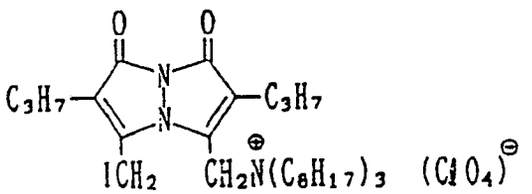


III-12

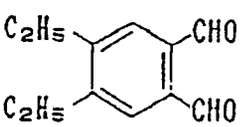


III-13



In the following, examples of the compound represented by the formula (IV) are shown below, but the present invention is not limited to these.

IV-1



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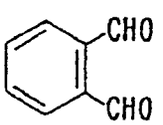
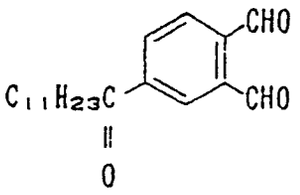
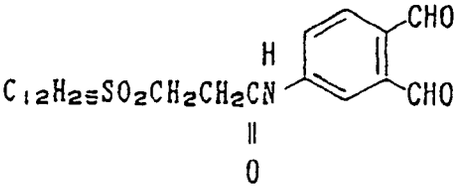


IV-3



IV-4



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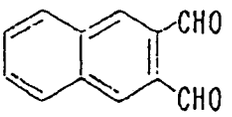

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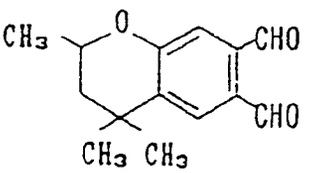

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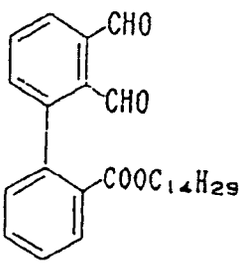
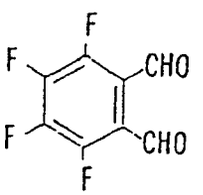
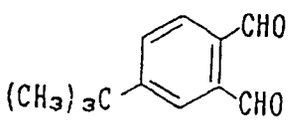


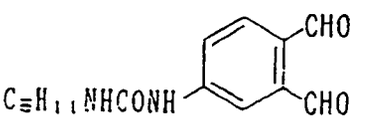
IV-8



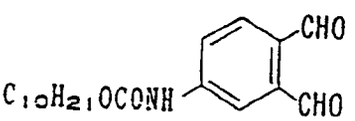
IV-9



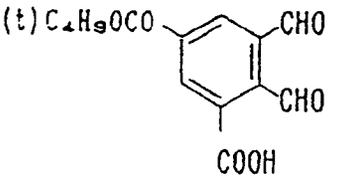
IV-10



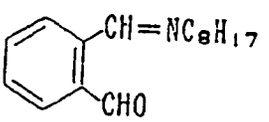
IV-11



IV-12



IV-13



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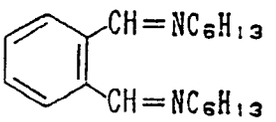
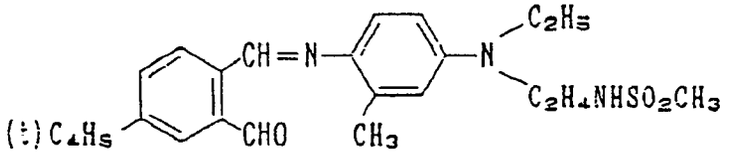
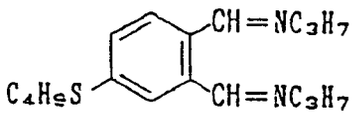


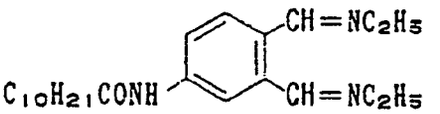
IV-15



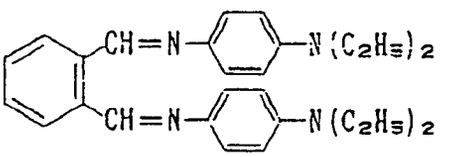
IV-16



IV-17



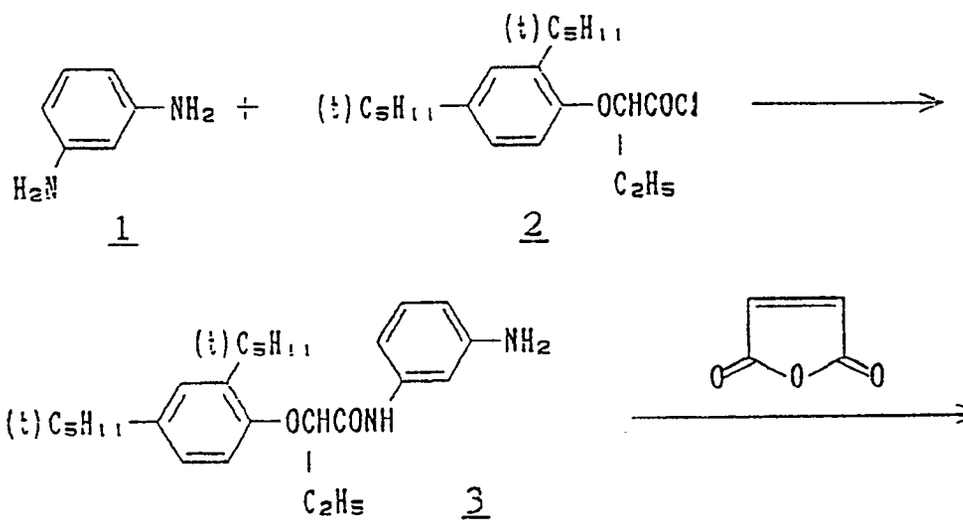
IV-18

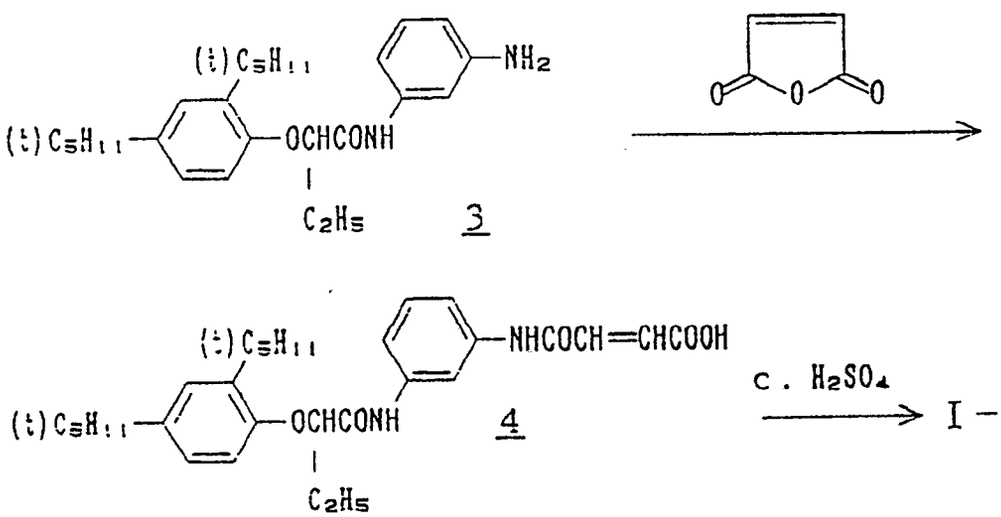


Next, a synthesis example of the fluorescent substance precursor is shown.

Synthesis example 3 (synthesis method of II-1-7)

Synthesis route





Synthesis of intermediate product 3

21.6 g of 1 and 67.8 g of 2 were dissolved in 400 ml of ethyl acetate, and the solution was refluxed under heating for 3 hours. The ethyl acetate solution was neutralized with an aqueous 5 % sodium hydrogen carbonate solution, and then washed. Thereafter, the solution was dried with anhydrous magnesium sulfate, and ethyl acetate, a solvent was evaporated under reduced pressure. The product obtained was recrystallized with acetonitrile to obtain 69.0 g of an intermediate product 3.

(The product was confirmed to be an intermediate product 3 by ^{1}HNMR, FD mass spectrum and IR spectrum.)

Synthesis of II-1-7

61.6 g of the intermediate product 3 was dissolved in 500 ml of pyridine, and further 14.7 g of maleic anhydride was added thereto. The mixture was stirred at room temperature for 3 hours. The reaction mixture was neutralized with addition of 4N hydrochloric acid, and extraction was carried out by using 300 ml of ethyl acetate. The organic phase obtained was washed and dried, and then 7.7 g of concentrated sulfuric acid was added thereto, followed by reflux under heating for 2 hours. This solution was washed and dried, and then ethyl acetate, a solvent was evaporated under reduced pressure, followed by purification by a silica gel column chromatography, to obtain 26.4 g of II-1-7.

(The product was confirmed to be II-1-7 by ^{1}HNMR, FD mass spectrum and IR spectrum.)

Synthesis example 4 (synthesis method of IV-3)

To 67.1 g of o-phthalaldehyde, 500 ml of chloroform and 120.3 g of dodecanoyl chloride were added, and then 73.3 g of aluminum chloride was added gradually over about 1 hour under ice cooling. The mixture was reacted at 5 °C for 4 hours, and then 500 ml of water was added to wash a chloroform phase. After evaporation of chloroform in a solvent under reduced pressure, purification was carried out by a column chromatography to obtain 62.0 g of white crystals IV-3.

(The crystals were confirmed to be IV-3 by ^{1}HNMR, FD mass spectrum and IR spectrum.)

The method for processing the light-sensitive silver halide photographic material of the present invention can be practiced in the following manner.

(1) A light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support, which comprises at least one coupler represented by the formula (I) and at least one fluorescent substance precursor is subjected to color development processing.

(2) A light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support, which comprises at least one coupler represented by the formula (I) is subjected to development processing by a color developing solution containing at least one fluorescent substance precursor.

(3) A light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support is subjected to development processing by a color developing solution containing at least one coupler represented by the formula (I) and at least one fluorescent substance precursor.

(4) A light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support, which comprises at least one fluorescent substance precursor is subjected to development processing by a color developing solution containing at least one coupler represented by the formula (I).

The coupler of the present invention represented by the formula (I) is used in light-sensitive color photographic materials such as color negative and positive films and color printing papers.

Typically, a method in which the coupler of the present invention is incorporated in a silver halide emulsion, and this emulsion is coated on a support to prepare a light-sensitive color material is preferably used.

The light-sensitive silver halide photographic material of the present invention including color printing papers may be monochromatic or polychromatic. Polychromatic light-sensitive materials have constituent units for forming dye images having sensitivities to respective 3 primary color regions of spectra. Each constituent unit can comprise single or multiple emulsion layers having sensitivity to a specific region of spectrum. Constituent layers of the light-sensitive material including constituent unit layers for forming images can be arranged in various orders as known in this field of the art.

A typical polychromatic light-sensitive material comprises a constituent unit for forming a cyan dye image comprising at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler, a constituent unit for forming a magenta dye image comprising at least one green-sensitive silver halide emulsion layer containing at least one magenta coupler, and a constituent unit for forming a yellow dye image comprising at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, which are carried

on a support.

The light-sensitive material can possess additional layers, for example, a filter layer, an intermediate layer, a protective layer and a subbing layer.

The coupler of the present invention represented by the formula (I) may be incorporated in an emulsion according to a known method in the art. For example, the coupler of the present invention or a combination thereof is dissolved in a high boiling point organic solvent having a boiling point of 175 °C or higher such as tricresyl phosphate and dibutyl phthalate or a low boiling point solvent such as butyl acetate and butyl propionate, or a mixture thereof, if necessary, and the solution was mixed with an aqueous gelatin solution containing a surfactant. Subsequently, the mixture was emulsified by a high speed rotary mixer or a colloid mill, and then added in silver halide. Thus, the silver halide emulsion to be used in the present invention can be prepared.

The silver halide composition preferably used in the light-sensitive material of the present invention is silver chloride, silver chlorobromide or silver chloroiodobromide. Further, it may be a mixture of a combination such as a mixture of silver chloride and silver bromide.

When the silver halide emulsion is used in a color printing paper, since rapid developability is particularly demanded, a chlorine atom is preferably contained as a halogen composition of silver halide, and silver chloride, silver chlorobromide or silver chloroiodobromide containing at least 1 % of silver chloride is particularly preferred.

The silver halide emulsion can be chemically sensitized according to a conventional method. Further, it can be optically sensitized to a desired wavelength region.

In the silver halide emulsion, compounds known as an antifoggant or a stabilizer in the photographic field can be added for the purpose of preventing fog during preparation of the light-sensitive material, storage or photographic processing and/or maintaining photographic performances stably.

In the light-sensitive color material of the present invention, a color antifoggant, a dye image stabilizer, an UV prevention agent, an antistatic agent, a matte agent and a surfactant which are generally used in a light-sensitive material can be used.

As to these additives, reference can be made to Research Disclosure, Vol. 176, pp. 22 to 31 (December, 1978).

Color development can be effected by using a color developing solution in which a color developing agent and other additives known in this field of the art are added.

Further, color development can be also effected by incorporating a color developing agent in a hydrophilic colloid layer of the light-sensitive silver halide photographic material as such or as its precursor, and processing by using an alkaline activated bath.

The light-sensitive silver halide photographic material of the present invention is subjected to bleaching processing and fixing processing after color development. Bleaching processing may be carried out simultaneously with fixing processing.

After fixing processing, washing processing is generally carried out. Also, stabilizing processing may be carried out in place of washing processing, or both processings may be used in combination.

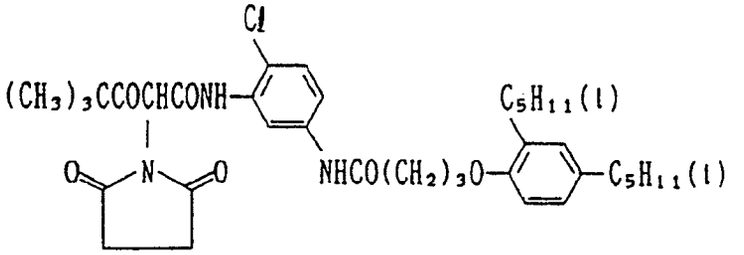
In the present invention, the coupler of the present invention represented by the formula (I) and a coupler known in this field of the art can be used in combination. Said coupler may be tetravalent or divalent. Further, there can be also used a coupler having effect of color correction, a competitive coupler and a compound which releases a photographically useful fragment such as a development accelerator, a bleaching accelerator, a developer, a silver halide solvent, a toning agent, a hardener, a fogging agent, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desenditizer by coupling with an oxidized product of a developing agent.

Further, a colorless coupler which undergoes a couling reaction with an oxidized product of an aromatic primary amine developer, but does not form a dye can be also used in combination.

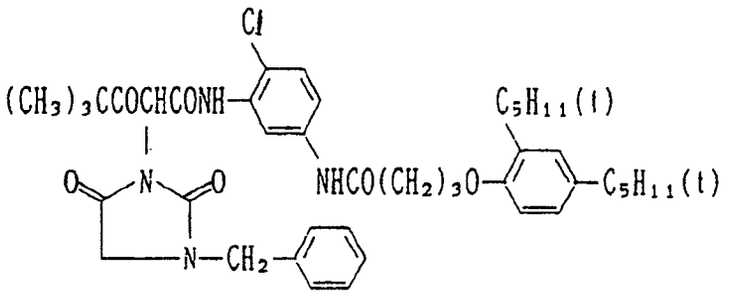
In the present invention, as a yellow coupler which can be used preferably in combination of the coupler of the present invention represented by the formula (I), there may be included benzoylacetanilide type and pivaloylacetanilide type couplers. As a magenta coupler, there may be mentioned 5-pyrazolone type, pyrazolotriazole type and indazolone type couplers. As a cyan dye-forming coupler, there may be mentioned phenol type, naphthol type, pyrazoloquinazolone type, pyrazolopyrimidine type, pyrazolotriazole type and imidazole type couplers.

In the following, representative specific examples of these yellow couplers which can be used in combination are shown.

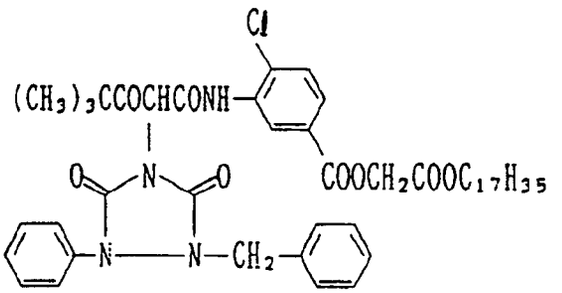
Y－1



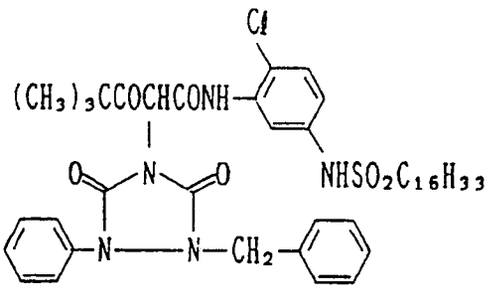
Y－2



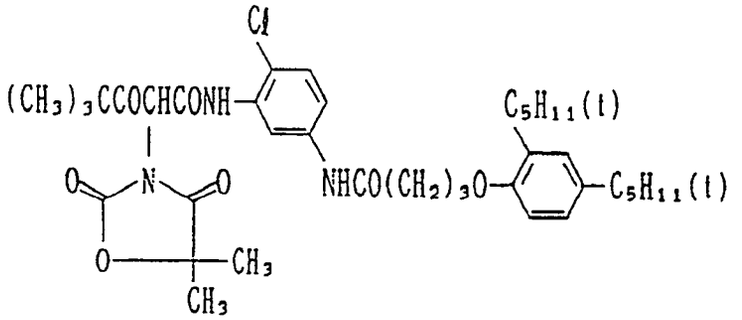
Y－3



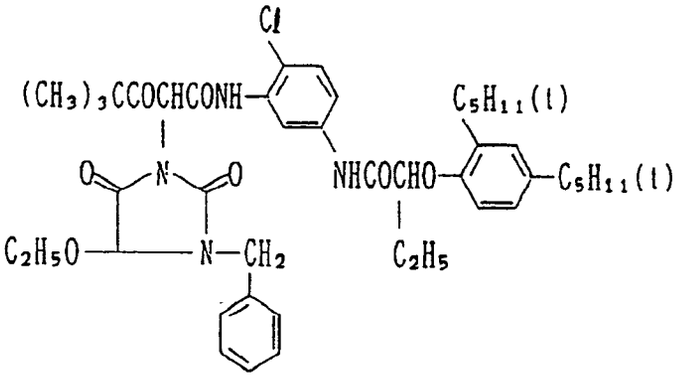
Y－4



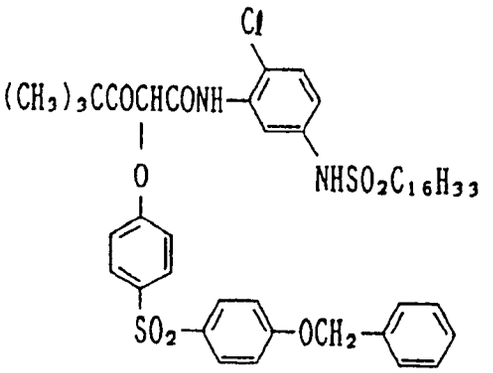
Y-5



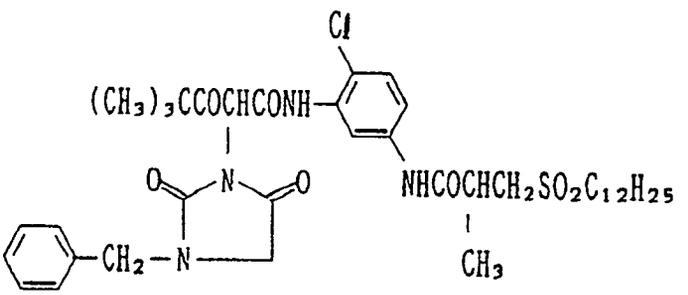
Y-6



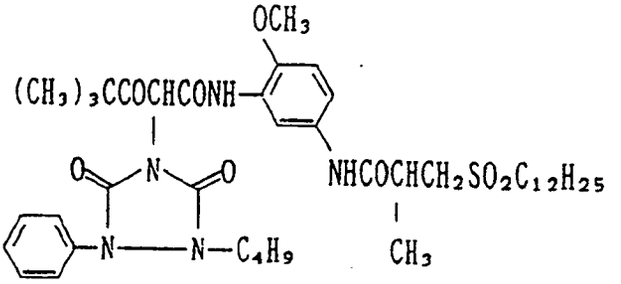
Y-7



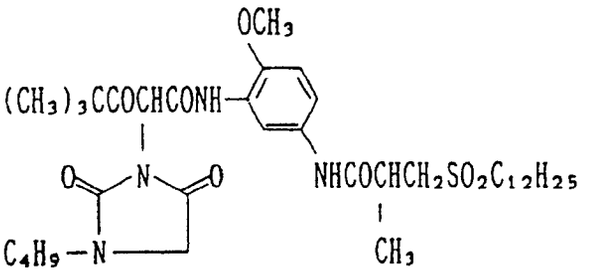
Y-8



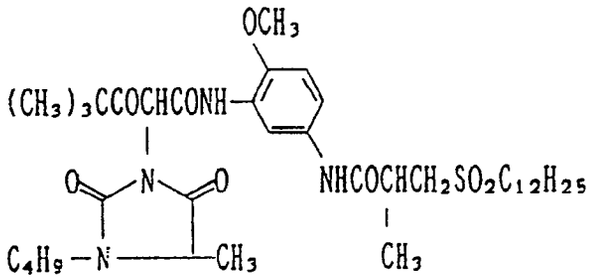
Y-9



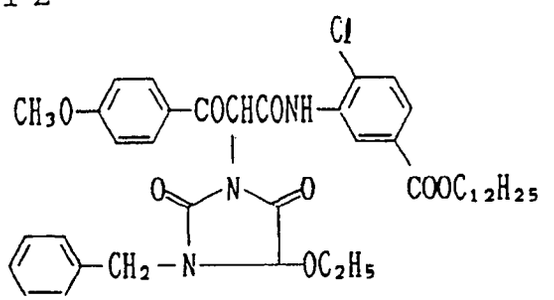
Y-10



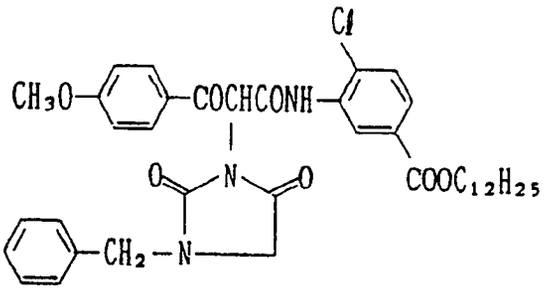
Y-11



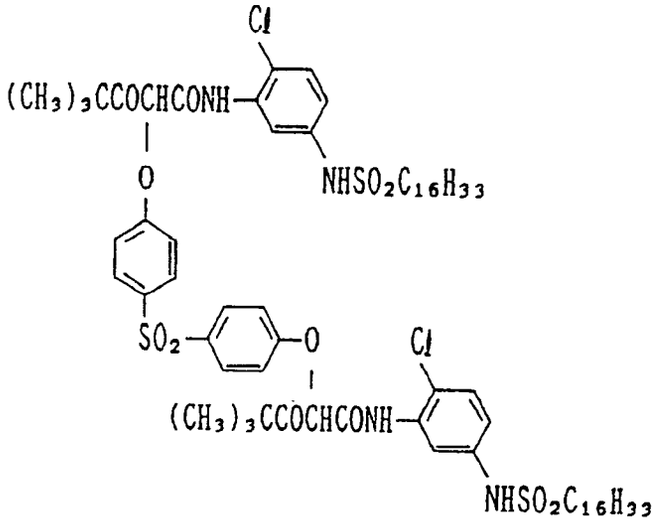
Y-12



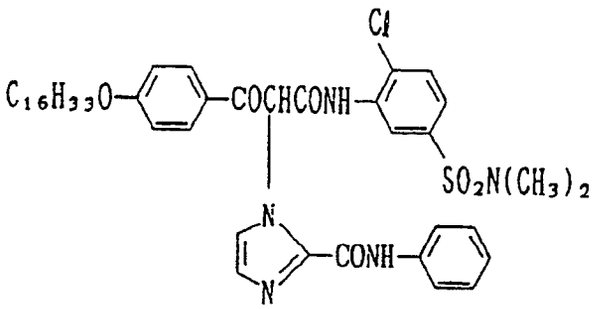
Y-13



Y－14



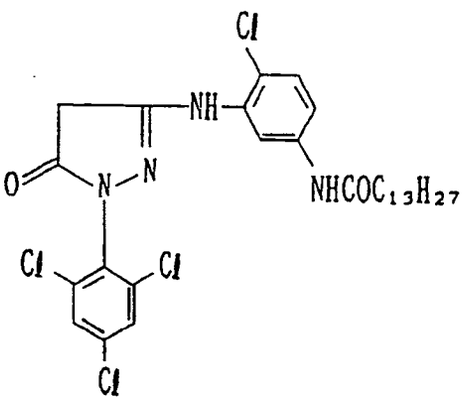
Y－15



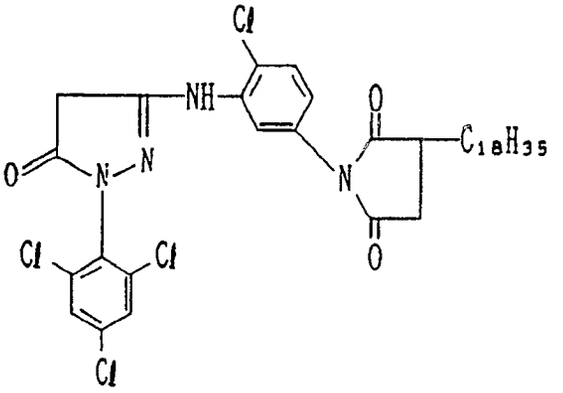
In addition to these couplers, as a yellow coupler which can be used in combination, there may be mentioned, for example, compounds disclosed in OLS 2,163.812, Japanese Unexamined Patent Publications No. 26133/1972, No. 29432/1973, No. 65321/1975, No. 3631/1976, No. 50734/1976, No. 102636/1976, No. 66835/1973, No. 94432/1973, No. 1229/1974 and No. 10736/1974, and Japanese Patent Publications No. 33410/1976 and No. 25733/1977, and these compounds can be synthesized according to methods disclosed in these publications.

Next, representative specific examples of the magenta couplers which can be used in combination are shown below.

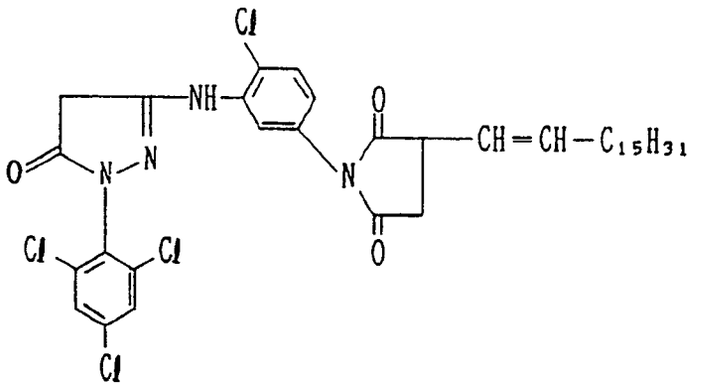
M－1



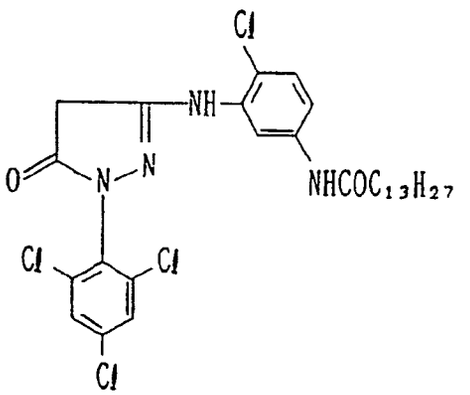
M-2



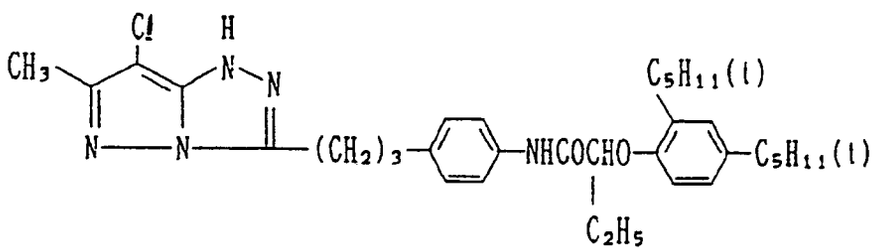
M-3



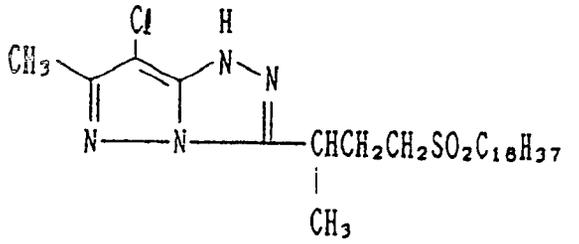
M-4



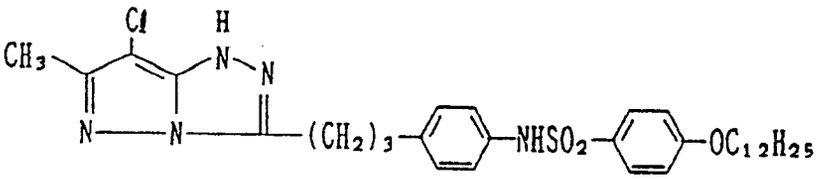
M-5



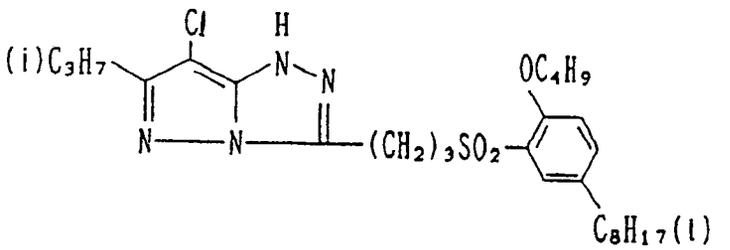
M-6



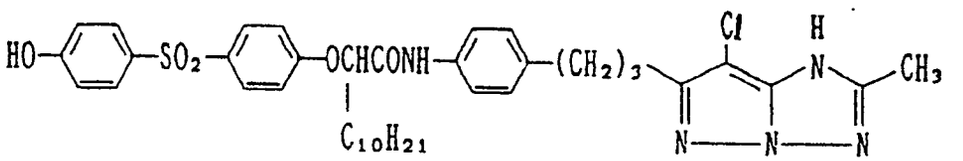
M-7



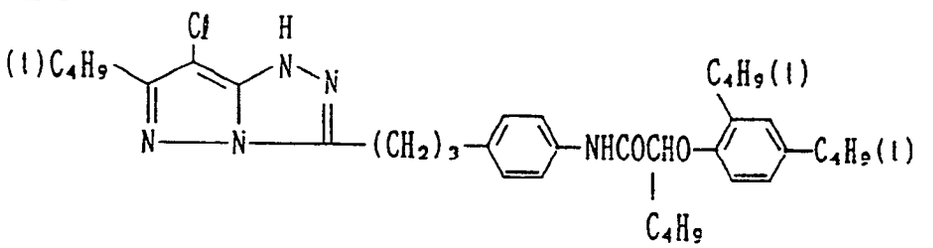
M-8



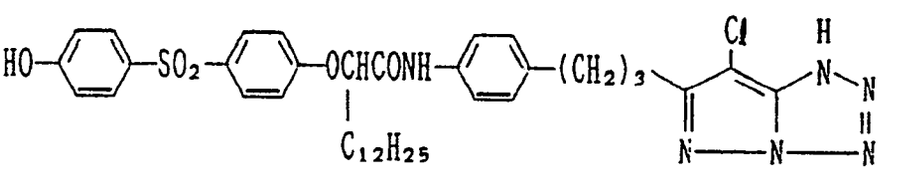
M-9



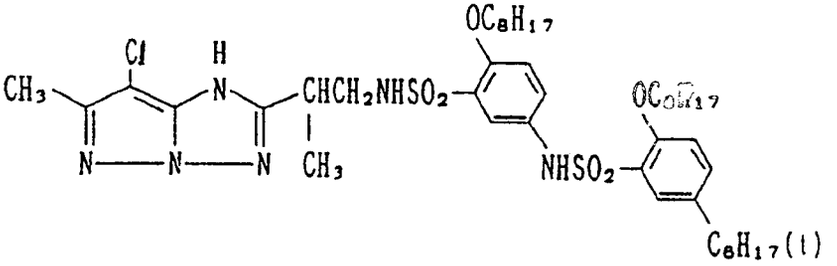
M-10



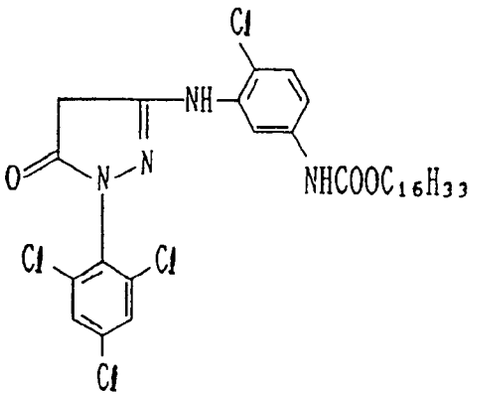
M-11



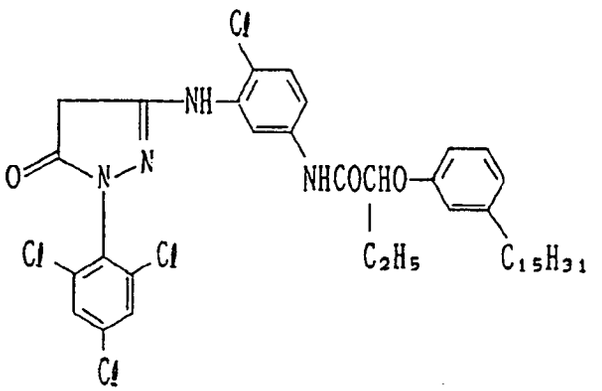
M-12



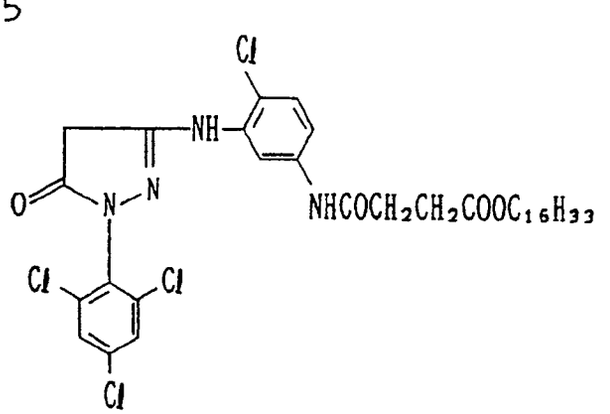
M-13



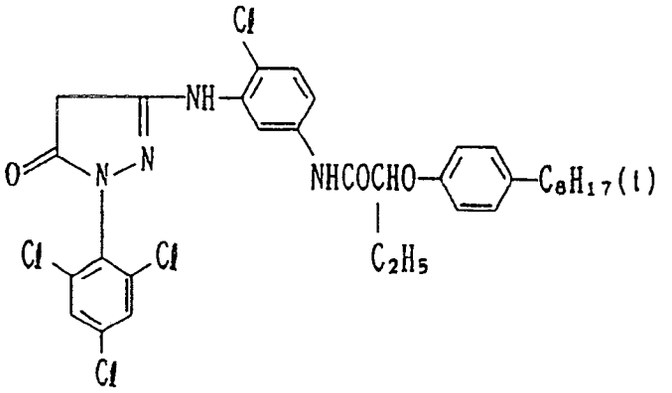
M-14



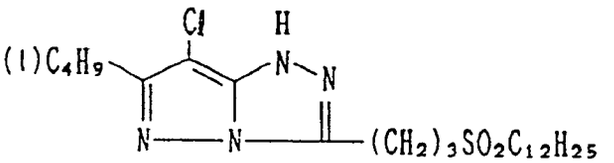
M-15



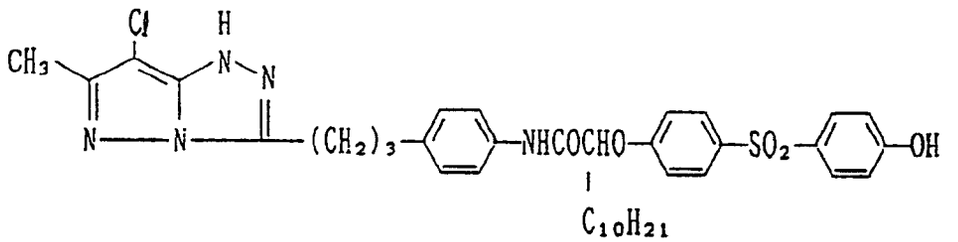
M-16



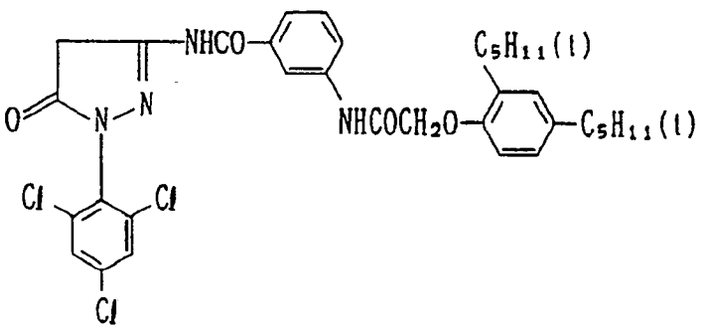
M-17



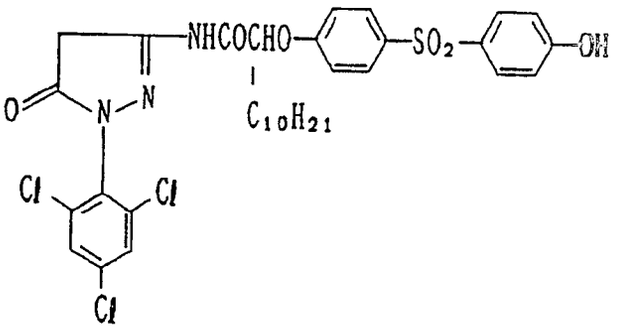
M-18



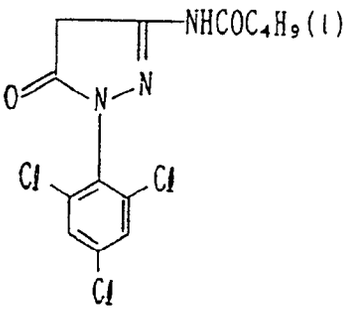
M-19



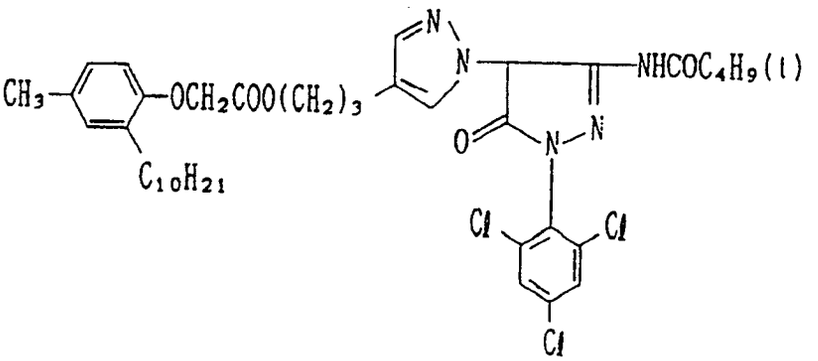
M-20



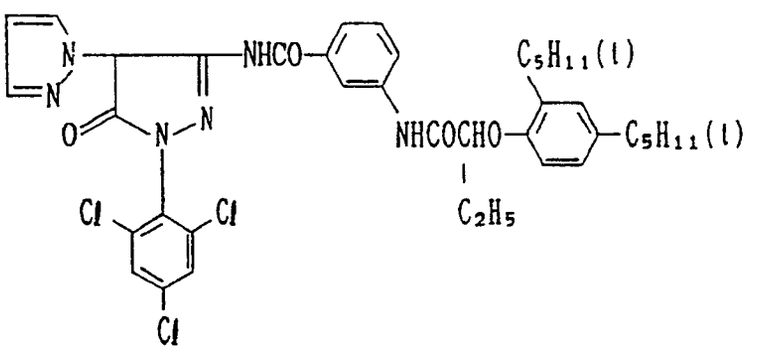
M-21



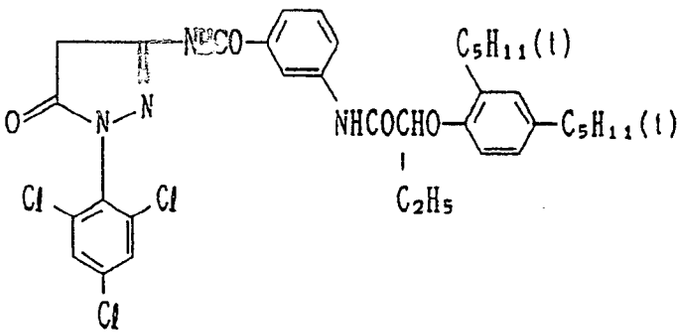
M-22



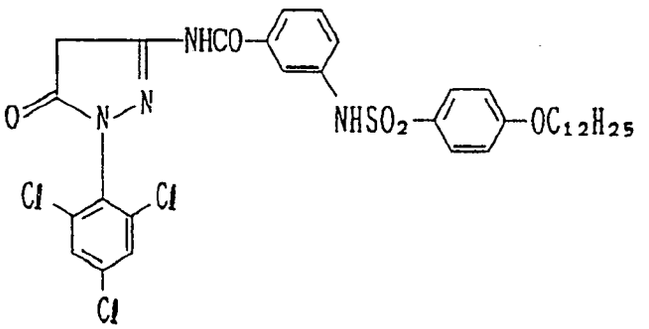
M-23



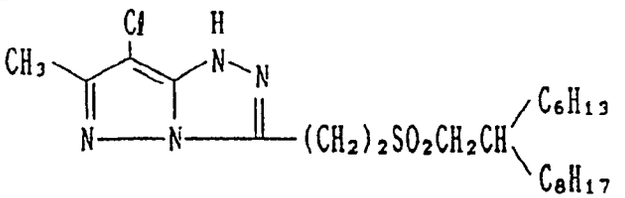
M-24



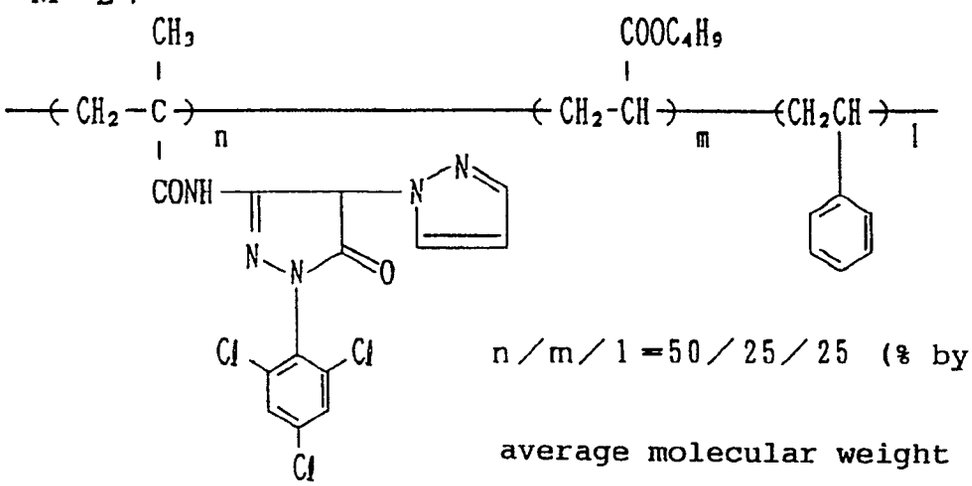
M-25



M-26



M-27

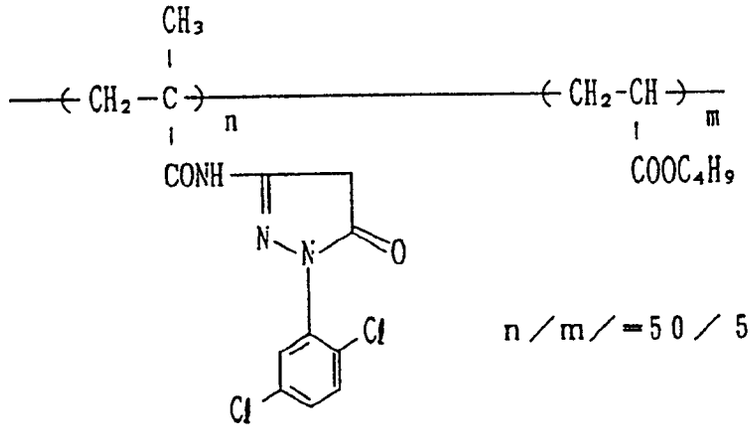


n/m/l = 50/25/25 (% by weight)

average molecular weight

about 30,000

M-28

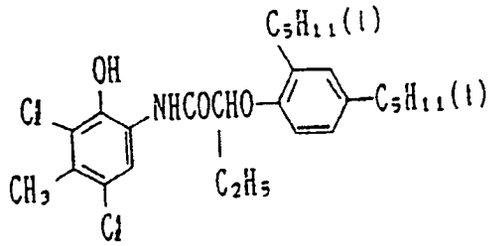


n/m/=50/50 (% by weight)

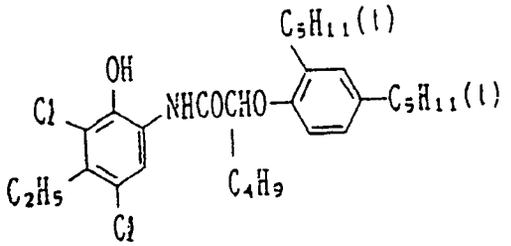
In addition to these couplers, as a magenta coupler which can be used in combination, there may be mentioned, for example, compounds disclosed in U.S. Patent No. 3,684,514, U.K. Patent No. 1,183,515, Japanese Patent Publications No. 6031/1965, No. 6035/1965, No. 15754/1969, No. 40757/1970 and No. 19032/1971, Japanese Unexamined Patent Publications No. 13041/1975, No. 129035/1978, No. 37646/1976 and No. 62454/1980, U.S. Patent No. 3,725,067, U.K. Patents No. 1,252,418 and No. 1,334,515, Japanese Unexamined Patent Publications No. 171956/1984, No. 162548/1984, No. 43659/1985 and No. 33552/1985, Research Disclosure No. 24626 (1984), and Japanese Unexamined Patent Publication No. 120147/1986, No. 120148/1986, No. 120149/1986, No. 120152/1986, No. 230146/1986, No. 230147/1986, and these compounds can be synthesized according to methods disclosed in these publications.

Next, representative specific examples of the cyan couplers which can be used in combination are shown below.

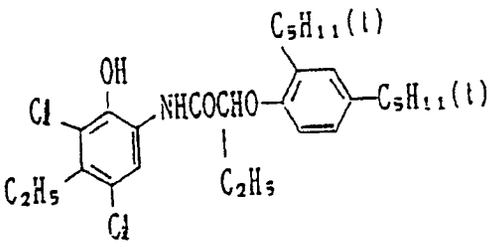
C-1



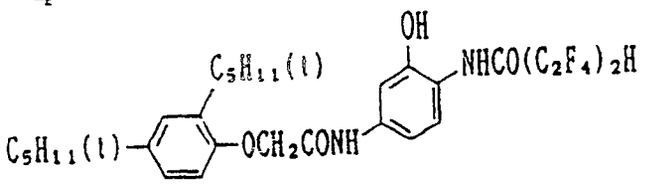
C-2



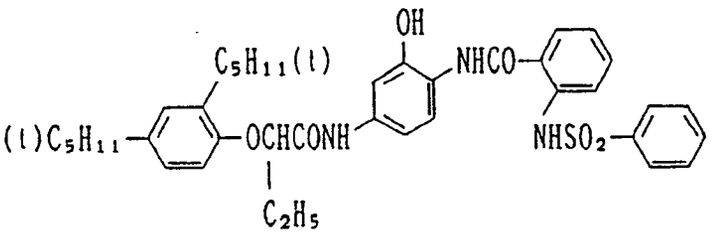
C-3



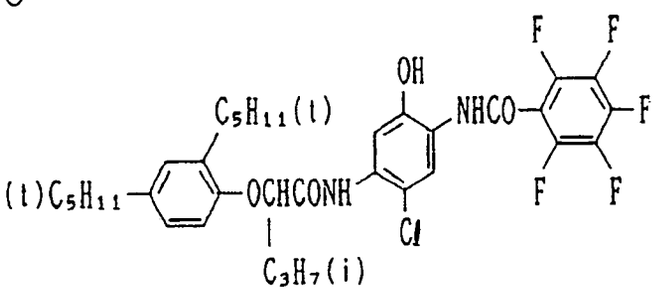
C－4



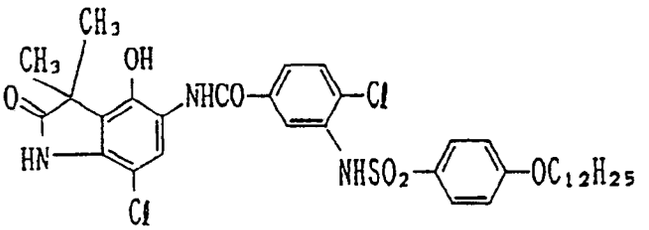
C－5



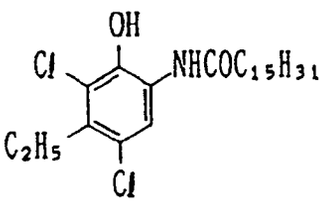
C－6



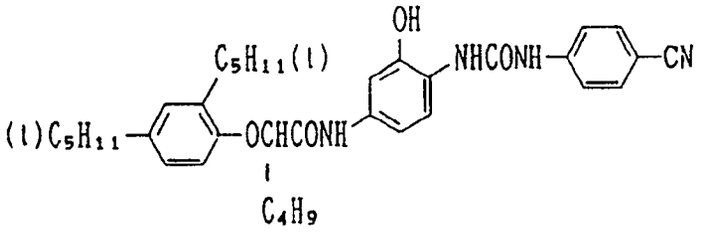
C－7



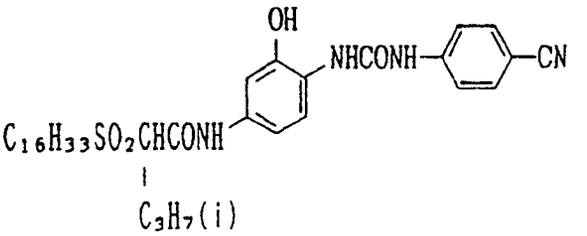
C－8



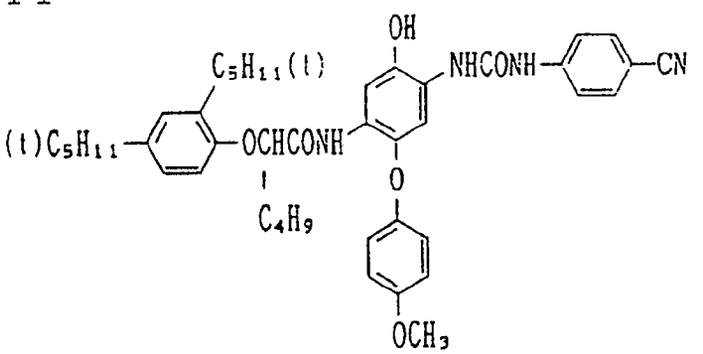
C-9



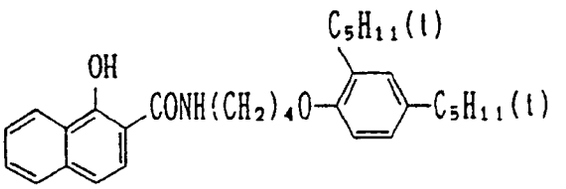
C-10



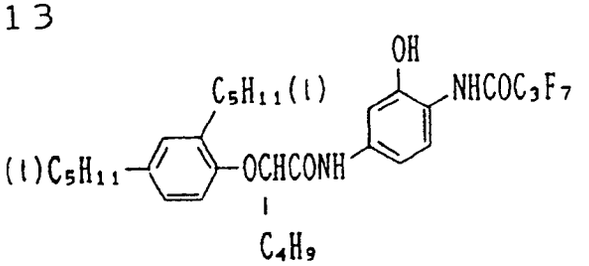
C-11



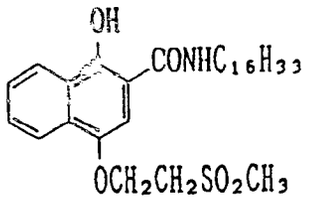
C-12



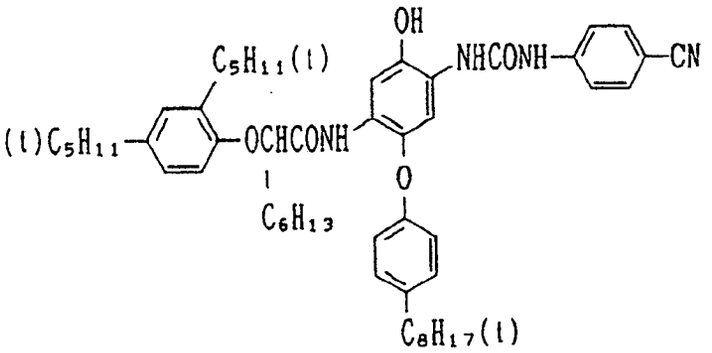
C-13



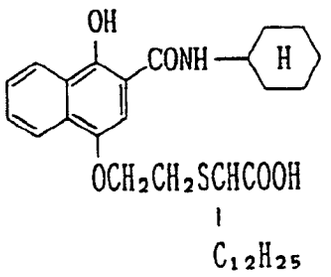
C－14



C－15



C－16



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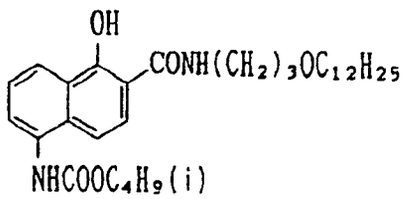
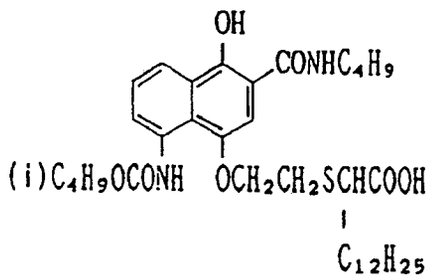
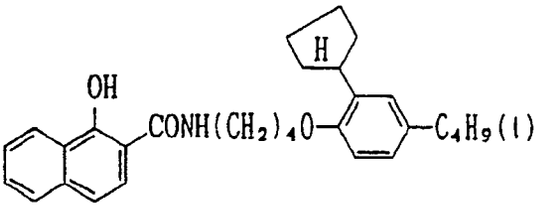


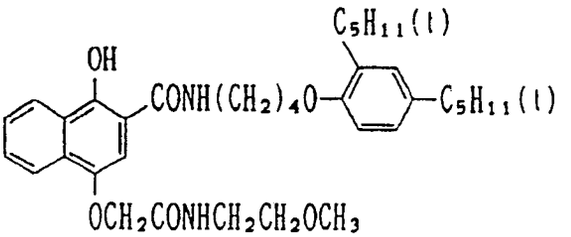
C－18



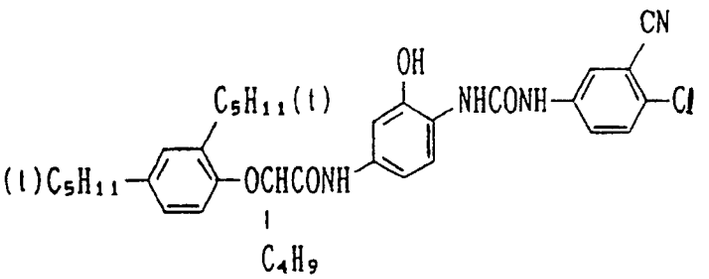
C-19



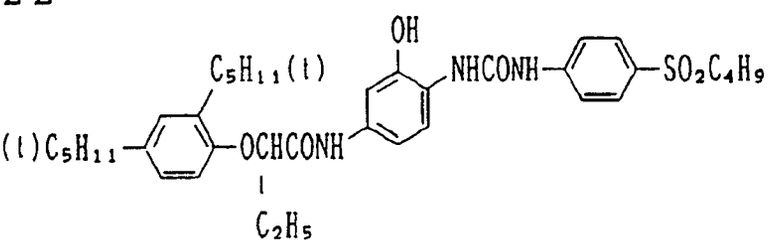
C-20



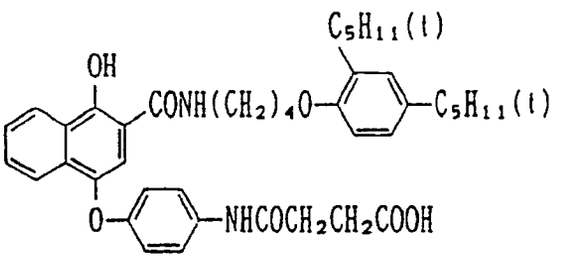
C-21



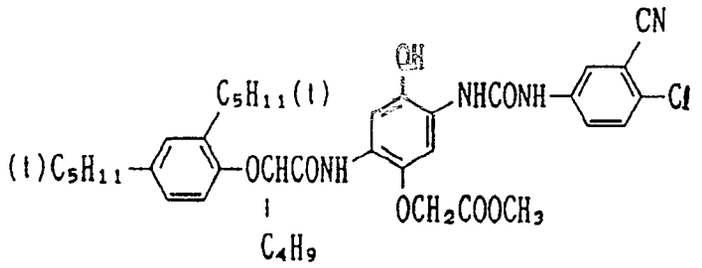
C-22



C-23



C-24



In addition to these couplers, as a cyan coupler which can be used in combination, there may be mentioned, for example, compounds disclosed in U.S. Patents No. 2,423,730 and No. 2,801,171, and Japanese Unexamined Patent Publications No. 112038/1975, No. 134644/1975, No. 109630/1978, No. 55380/1979, No. 65134/1981, No. 80045/1981, No. 155538/1982, No. 204545/1982, No. 98731/1983 and No. 31953/1984, and these compounds can be synthesized according to methods disclosed in these publications.

EXAMPLES

The present invention is described below in detail by referring to Examples, but the present invention is not limited by these Examples.

Example 1

On a paper support of which both surfaces were laminated with polyethylene, the following respective layers were provided by coating successively from a support side to prepare a red-sensitive light-sensitive color material Sample 101. Amounts of compounds added are amounts per 1 m^2 unless otherwise indicated (an amount of silver halide is an amount calculated on silver.).

First layer: Emulsion layer

A red-sensitive emulsion layer comprising 1.2 g of gelatin, 0.30 g of a red-sensitive silver chlorobromide emulsion (containing 96 mole % of silver chloride) and 19.1 x 10^{-4} mole of Cyan coupler C-1 dissolved in 1.35 g of dioctyl phosphate.

Second layer: Protective layer

A protective layer containing 0.50 g of gelatin. As a hardener, 2,4-dichloro-6-hydroxy-s-triazine sodium salt was added in an amount of 0.017 per gram of gelatin.

Next, the procedures were carried out in the same manner as in Sample 101 except for changing Cyan coupler C-1 to I-16 (the same equimolar amount as that of Cyan coupler C-1 was added) and further adding 9.1 x 10^{-4} mole of II-1-1 to prepare Sample 102 of the present invention.

Samples 101 and 102 obtained as described above were subjected to wedge exposure according to a conventional method, respectively, and development processing was carried out according to the following steps.

(Development processing steps)

Color development	38 °C	3 min 30 sec
Bleach-fixing	38 °C	1 min 30 sec
Stabilizing processing	25 °C to 30 °C	3 min
Drying	75 °C to 80 °C	2 min

The processing solutions used in the respective processing steps had compositions shown below.

(Color developing solution)

Benzyl alcohol	15 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g
Potassium bromide	0.7 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate	5.5 g
Fluorescent brightener (4,4'-diaminostylbene disulfonic acid derivative)	1.0 g
Potassium hydroxide	2.0 g

made up to 1 liter in total with addition of water, and adjusted pH to 10.20.

(Bleach-fixing solution)

Ferric ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70 % solution)	100 ml
Ammonium sulfite (40 % solution)	27.5 ml

adjusted pH to 7.1 with potassium carbonate or glacial acetic acid, and made up to 1 liter in total with addition of water.

(Stabilizing solution)

5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	10 g

made up to 1 liter with addition of water.

For Samples 101 and 102 processed as described above, visible absorption spectrum at a reflection density of 1.0 was measured, and reflection densities at 420 nm and 650 nm were determined. Also, maximum color density (Dm) was measured.

The results are shown in Table 1.

Table 1

	Cyan coupler	Compound II-1	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	-	2.82	0.37	1.00
Sample 102 (Present invention)	I-16	II-1-1	2.74	0.27	1.00

From the results in Table 1, it can be understood that in Sample 102 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 101, and also sufficient maximum color density can be obtained.

Example 2-1

The procedures were carried out in the same manner as in Sample 102 of Example 1 except for excluding Compound II-1-1 of the present invention used in Sample 102 to prepare Sample 103. This sample and Comparative sample 101 were subjected to wedge exposure according to a conventional manner, and then development processing was carried out according to the same steps as in Example 1. However, a color developing solution used in Example to which 2.4 g of Compound II-1-2 of the present invention was added was used as a color developing solution.

For the samples processed, entirely the same measurement as in Example 1 was conducted

The results are shown in Table 2.

Table 2

	Cyan coupler	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	2.82	0.39	1.0
Sample 103 (Present invention)	I-16	2.73	0.29	1.0

As shown in the results in Table 2, it can be understood that even when the compound represented by the formula (II-1) of the present invention is added in a color developing solution, the same effect as in Example 1 can be exhibited.

Example 2-2

The procedures were carried out in the same manner as in Sample 102 of Example 1 except for excluding Compound I-16 of the present invention used in Sample 102 to prepare Sample 104. When this sample was subjected to exposure in the same manner as in Example 1 and development processing was carried out by a color developing solution in which Compound I-23 of the present invention was added, the same effect as in Example 1 was obtained.

Example 2-3

The procedures were carried out in the same manner as in Sample 102 of Example 1 except for excluding Compounds I-16 and II-1-1 of the present invention used in Sample 102 to prepare Sample 105. When this sample was subjected to exposure in the same manner as in Example 1 and development processing was car-

ried out by a color developing solution in which Compounds I-23 and II-1-2 of the present invention were added, the same effect as in Example 1 was obtained.

Example 3

On a support having an antihalation layer provided by coating, layers were coated so as to have a layer constitution shown below to prepare a multilayer color film Sample 201.

Layer constitution: Pro layer, BH layer, BL layer, YF layer, GH layer, GL layer, IL layer, RH layer, RL layer and support.

Next, RL layer, RH layer, GL layer, GH layer, BL layer, BH layer, IL layer, YF layer and Pro layer are explained. Their amounts added are amouts per 1 m^2. Amounts of silver halide and colloidal silver are those calculated on silver.

RL layer (low sensitivity red-sensitive silver halide emulsion layer)

A layer containing 1.0 g of an emulsion having an average grain size ($\bar{r}$) of 0.47 μm and a variation coefficient ($S/\bar{r}$) of 0.12 and comprising AgBrI containing 8 mole % of AgI on average (Emulsion I) which was color sensitized to become red-sensitive, 1.0 g of an emulsion having an average grain size of 0.31 μm and a variation coefficient of 0.10 and comprising AgBrI containing 8 mole % of AgI on average (Emulsion II), and a dispersion obtained by emulsifying and dispersing 0.44 g of a cyan coupler (C-17) and 0.06 g of a DIR compound (D-1) dissolved in tricresyl phosphate (called TCP) in an aqueous solution containing 2.4 g of gelatin.

RH layer (high sensitivity red-sensitive silver halide emulsion layer)

A layer containing 2.0 g of an emulsion having an average grain size of 0.7 μm and a variation coefficient of 0.12 and comprising AgBrI containing 6 mole % of AgI on average (Emulsion III) which was color sensitized to become red-sensitive, and a dispersion obtained by emulsifying and dispersing 0.22 g of a cyan coupler (C-17) dissolved in 0.23 g of TCP in an aqueous solution containing 1.2 g of gelatin.

GL layer (low sensitivity green-sensitive silver halide emulsion layer)

A layer containing 1.5 g of Emulsion I which was color sensitized to become green-sensitive, 1.5 g of Emulsion II which was color sensitized to become green-sensitive, and a dispersion obtained by emulsifying and dispersing 0.40 g of a magenta coupler (M-19) and 0.04 g of a DIR compound (D-1) dissolved in 0.68 g of TCP in an aqueous solution containing 2.4 g of gelatin.

GH layer (high sensitivity green-sensitive silver halide emulsion layer)

A layer containing 2.0 g of Emulsion III which was color sensitized to become green-sensitive, and a dispersion obtained by emulsifying and dispersing 0.40 g of a magenta coupler (M-19) dissolved in 0.27 g of TCP in an aqueous solution containing 2.4 g of gelatin.

BL layer (low sensitivity blue-sensitive silver halide emulsion layer)

A layer containing 0.5 g of Emulsion I which was color sensitized to become blue-sensitive, 0.5 g of Emulsion II which was color sensitized to become blue-sensitive, and a dispersion obtained by emulsifying and dispersing 0.7 g of a yellow coupler (Y-12) and 0.02 g of a DIR compound (D-1) dissolved in 0.68 g of TCP in an aqueous solution containing 1.8 g of gelatin.

BH layer (high sensitivity blue-sensitive silver halide emulsion layer)

A layer containing 0.9 g of an emulsion having an average grain size of 0.80 μm and a variation coefficient of 0.14 and comprising AgBrI containing 6 mole % of AgI on average which was color sensitized to become blue-sensitive, and a dispersion obtained by emulsifying and dispersing 0.25 g of a yellow coupler (Y-12) dissolved in 0.25 g of TCP in an aqueous solution containing 2.0 g of gelatin.

IL layer (intermediate layer)

A layer containing 0.07 g of 2,5-di-t-octylhydroquinone (HQ-1) dissolved in 0.07 g of dibutyl phthalate (called DBP), and 0.70 g of gelatin.

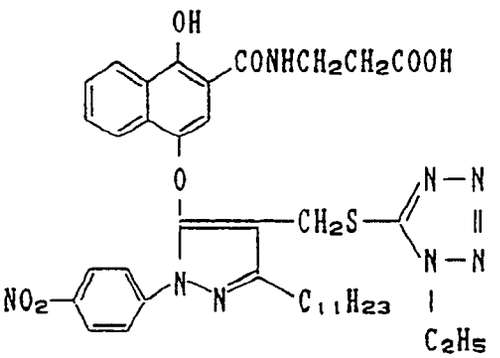
YF layer (yellow filter layer)

A layer containing 0.15 of yellow colloidal silver, 0.3 g of HQ-1 dissolved in 0.11 g of DBP, and 1.0 g of gelatin.

Pro layer (protective layer)

A layer comprising 2.3 g of gelatin.

D-1



The procedures were carried out in the same manner as in Sample 201 except for replacing Cyan coupler C-17 in RL layer and RH layer of Sample 201 thus prepared with an equimolar amount of Compound I-18 of the present invention, and further adding 0.24 g and 0.12 g of II-1-2 to RL layer and RH layer, respectively, to prepare Sample 202. The procedures were carried out in the same manner as in Sample 202 except for replacing II-1-2 in Sample 202 with an equimolar amount of II-1-9 to prepare Sample 203.

The respective samples were subjected to wedge exposure by using green lights, and color development processing was carried out according to the following processing steps.

(Processing steps)		Processing time
Color development	38 °C	3 min 15 sec
Bleaching	38 °C	6 min 30 sec
Washing	25 to 30 °C	3 min 15 sec
Fixing	38 °C	6 min 30 sec
Washing	25 to 30 °C	3 min 15 sec
Stabilizing	25 to 30 °C	1 min 30 sec
Drying	75 to 80 °C	

The processing solutions used in the respective processing steps had compositions shown below.

(Color developing solution)

4-Amino-3-methyl-N-ethyl-N-β-hydroxy-ethylaniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid·trisodium (monohydrate)	2.5 g
Potassium hydroxide	1.0 g

made up to 1 liter with addition of water, and adjusted pH to 10.6 with sodium hydroxide.

(Bleaching solution)

Ferrous ammonium ethylenediaminetetra-acetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g

made up to 1 liter with addition of water, and adjusted pH to 8.0 with aqueous ammonia.

(Fixing solution)

Ammonium thiosulfate	175.0 g
Anhydrous ammonium sulfite	8.6 g
Sodium metasulfite	2.3 g

made up to 1 liter with addition of water, and adjusted pH to 6.0 with acetic acid.

(Stabilizing solution)

Formalin (37 % by weight)	1.5 ml
Konidax (trade name, manufactured by Konica Corporation)	7.5 ml

made up to 1 liter with addition of water.

The respective samples processed as described above were placed on a white plate, and visible absorption spectrum at a reflection density of 1.0 was measured to determine reflection densities at 400 nm and 700 nm. Also, maximum color density (Dm) was measured.

The results are shown in Table 3.

Table 3

	Cyan coupler	Compound II	Reflection density at 400 nm	Reflection density at 700 nm	Maximum color density (Dm rate)*
Sample 201 (Comparative)	C-17	-	0.22	1.00	1.00
Sample 202 (Present invention)	I-18	II-1-2	0.13	1.00	1.05
Sample 203 (Present invention)	I-18	II-1-9	0.14	1.00	1.04

* Dm value of Sample 201 was defined as 1.00.

From the results in Table 3, it can be understood that in Samples 202 and 203 using the compound of the present invention, asymmetric absorption at 400 nm is reduced to a great extent when compared with that of Sample 201, and also sufficient maximum color density can be obtained.

Example 4

On a paper support of which both surfaces were laminated with polyethylene, the following respective layers were provided by coating successively from a support side to prepare a polychromatic light-sensitive silver halide material Sample 301.

First layer: Blue-sensitive silver halide emulsion layer

The layer was so coated that 6.8 mg/100 cm^2 of a yellow coupler (Y-9), 3.2 mg/100 cm^2 calculated on silver of a blue-sensitive silver chlorobromide emulsion (containing 99.5 mole % of silver chloride), 3.5 mg/100 cm^2 of dibutyl phthalate and 13.5 mg/100 cm^2 of gelatin were attached.

Second layer: Intermediate layer

The layer was so coated that 0.75 mg/100 cm^2 of 2,5-di-t-octylhydroquinone (HQ-1), 0.5 mg/100 cm^2 of dibutyl phthalate and 9.0 mg/100 cm^2 of gelatin were attached.

Third layer: Green-sensitive silver halide emulsion layer

The layer was so coated that 5.5 mg/100 cm^2 of a magenta coupler (M-2), 2.5 mg/100 cm^2 calculated on silver of a green-sensitive silver chlorobromide emulsion (containing 99.5 mole % of silver chloride), 3.0 mg/100 cm^2 of dibutyl phthalate and 12.0 mg/100 cm^2 of gelatin were attached.

Fourth layer: Intermediate layer

The layer was so coated that 0.7 mg/100 cm^2 of a UV absorber (UV-1), 6.0 mg/100 cm^2 of dibutyl phthalate, 0.5 mg/100 cm^2 of HQ-1 and 12.0 mg/100 cm^2 of gelatin were attached.

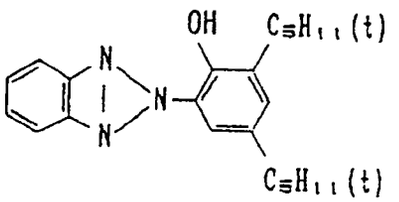
Fifth layer: Red-sensitive silver halide emulsion layer

The layer was so coated that 4.2 mg/100 cm^2 of a cyan coupler (C-3), 3.0 mg/100 cm^2 calculated on silver of a red-sensitive silver chlorobromide emulsion (containing 99.5 mole % of silver chloride), 3.5 mg/100 cm^2 of tricresyl phosphate and 11.5 mg/100 cm^2 of gelatin were attached.

Sixth layer: Protective layer

The layer was so coated that 8.0 mg/100 cm^2 of gelatin was attached.

UV-1



The procedures were carried out in the same manner as in Sample 301 except for replacing Magenta coupler M-2 in the third layer of Sample 301 thus prepared with an equimolar amount of Compound I-13 of the present invention and further adding 1.9 mg/100 cm^2 of II-1-10 to prepare Sample 302. The procedures were carried out in the same manner as in Sample 302 except for replacing I-13 in Sample 302 with an equimolar amount of I-3 and further replacing I-1-10 with an aquimolar amount of I-1-3 to prepare Sample 303.

The respective samples obtained as described above were subjected to wedge exposure by blue lights, and processing was carried out according to the following steps.

Processing step	Processing temperature	Processing time
Color development	35.0 ± 0.3 °C	45 sec
Bleach-fixing	35.0 ± 0.5 °C	45 sec
Stabilizing	30 to 34 °C	90 sec
Drying	natural drying at room temperature (25 °C)	

(Color developing solution)

Pure water	800 ml
Triethanolamine	10 g
N,N-Diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-Hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetic acid	1.0 g
Disodium catechol-3,5-disulfonnate	1.0 g
N-ethyl-N-β-methanesulfoamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Fluorescent brightener (4,4'-diaminostylbene disulfonic acid derivative)	1.0 g
Potassium carbonate	27 g

made up to 1 liter in total with addition of water, and adjusted pH to 10.10.

(Bleach-fixing solution)

Ferric ammonium ethylenediaminetetra-acetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70 % aqueous solution)	100 ml
Ammonium sulfite (40 % aqueous solution)	27.5 ml

made up to 1 liter in total with addition of water, and adjusted pH to 6.2 with potassium carbonate or glacial acetic acid.

(Stabilizing solution)

5-Chloro-2-methyl-4-isothiazolin-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide (20 % aqueous solution)	3.0 g
Ammonium sulfite	3.0 g
Fluorescent brightener (4,4'-diaminostyl-bene disulfonic acid derivative)	1.5 g

made up to l liter in total with addition of water, and adjusted pH to 7.0 with sulfuric acid or potassium hydroxide.

For the respective samples processed as described above, absorption spectrum at a reflection density of 1.0 was measured, and reflection densities at 420 nm and 555 nm were determined.

The results are shown in Table 4.

Table 4

	Magenta coupler	Compound II-1	Reflection density at 420 nm	Reflection density at 555 nm
Sample 301 (Comparative)	M-2	-	0.18	1.00
Sample 302 (Present invention)	I-13	II-1-10	0.13	1.00
Sample 303 (Present invention)	I-13	II-1-12	0.12	1.00

From the results in Table 4, it can be understood that in Samples 302 and 303 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 301, and therefore color reproducibility is good.

Example 5

The respective samples used in Example 4 were left to stand for 3 days in a dark place under high temperature and high humidity conditions of a temperature of 60 °C and a relative humidity of 80 %, and then the

samples were subjected to exposure and processed according to the same method as in Example 4. When fog, sensitivity, γ and Dm were measured according to a conventional method, it was found that the measured values of Samples 302 and 303 of the present invention were substantially the same as those of Comparative sample 301.

Example 6

The procedures were carried out in the same manner as in Sample 101 of Example 1 except for changing Cyan coupler C-1 to I-19 (the same equimolar amount as that of Cyan coupler C-1 was added), and further adding 9.1×10^{-4} mole of II-1-1 to prepare Sample 402 of the present invention. The sample obtained as described above was processed in the same manner as in Sample 101 of Example 1, and evaluated.

The results are shown in Table 5.

Table 5

	Cyan coupler	Compound II-2	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	-	2.84	0.38	1.00
Sample 402 (Present invention)	I-19	II-2-1	2.80	0.23	1.00

From the results in Table 5, it can be understood that in Sample 402 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 101, and also sufficient maximum color density can be obtained.

Example 7-1

The procedures were carried out in the same manner as in Sample 402 of Example 6 except for excluding Compound II-2-1 of the present invention used in Sample 402 to prepare Sample 403. This sample and Comparative sample No. 101 were subjected to wedge exposure according to a conventional method, and then development processing was carried out according to the same steps as in Example 6. However, a color developing solution used in Example 6 to which 2.0 g of Compound II-2-13 of the present invention was added was used as a color developing solution.

For the samples processed, entirely the same measurement as in Example 6 was conducted

The results are shown in Table 6.

Table 6

	Cyan coupler	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	2.83	0.40	1.0
Sample 403 (Present invention)	I-19	2.77	0.28	1.0

As shown in the results in Table 6, it can be understood that even when the compound represented by the formula (II-2) of the present invention is added in a color developing solution, the same effect as in Example 6 can be exhibited.

Example 7-2

The procedures were carried out in the same manner as in Sample 402 of Example 6 except for excluding Compound I-19 of the present invention used in Sample 402 to prepare Sample 404. When this sample was subjected to exposure in the same manner as in Example 6 and then development processing was carried out by a color developing solution in which Compound I-23 of the present invention was added, the same effect as in Example 6 was obtained.

Example 7-3

The procedures were carried out in the same manner as in Sample 402 of Example 6 except for excluding Compounds I-19 and II-2-1 of the present invention used in Sample 402 to prepare Sample 405. When this sample was subjected to exposure in the same manner as in Example 6 and then development processing was carried out by a color developing solution in which Compounds I-23 and II-2-13 of the present invention were added, the same effect as in Example 6 was obtained.

Example 8

The procedures were carried out in the same manner as in Sample 201 of Example 3 except for replacing Cyan coupler C-17 in RL layer and RH layer of Sample 201 with an equimolar amount of Compound I-18 of the present invention, and further adding 0.21 g and 0.10 g of II-1-2 to RL layer and RH layer, respectively, to prepare Sample 502. The procedures were carried out in the same manner as in Sample 502 except for replacing II-1-2 with an equimolar amount of II-2-11 to prepare Sample 503.

In Samples 201, 502 and 503, a hardener, an activator and an antifungal agent (a mixture of 2-methyl-isothiazol-3-one and 5-chloro-2-methyl-isothiazol-3-one) were added.

The respective samples were subjected to color development processing according to the same steps as in Example 3, and evaluated in the same manner..

The results are shown in Table 7.

Table 7

	Cyan coupler	Compound II-2	Reflection density at 400 nm	Reflection density at 700 nm	Maximum color density (Dm rate)*
Sample 201 (Comparative)	C-17	-	0.22	1.00	1.00
Sample 502 (Present invention)	I-18	II-2-2	0.10	1.00	1.03
Sample 503 (Present invention)	I-18	II-2-11	0.13	1.00	1.03

* Dm value of Sample 201 was defined as 1.00.

From the results in Table 7, it can be understood that in Samples 502 and 503 using the compound of the present invention, asymmetric absorption at 400 nm is reduced to a great extent when compared with that of Sample 201, and also sufficient maximum color density can be obtained.

Example 9

The procedures were carried out in the same manner as in Sample 301 prepared in Example 4 except for replacing Magenta coupler M-2 in the third layer of Sample 301 with an equimolar amount of Compound I-13 of the present invention, and further adding 1.7 mg/100 cm^2 of II-2-12 to prepare Sample 602. The procedures were carried out in the same manner as in Sample 602 except for replacing II-2-12 with an equimolar amount

of II-2-3 to prepare Sample 603.

In the respective samples, a hardener, an activator and an antifungal agent (a mixture of 2-methyl-isothiazol-3-one and 5-chloro-2-methyl-isothiazol-3-one) were added.

The respective samples obtained as described above were processed according to the same steps as in Example 4, and evaluated in the same manner.

The results are shown in Table 8.

Table 8

	Magenta coupler	Compound II-2	Reflection density at 420 nm	Reflection density at 555 nm
Sample 301 (Comparative)	M-2	-	0.18	1.00
Sample 602 (Present invention)	I-13	II-2-12	0.11	1.00
Sample 603 (Present invention)	I-3	II-2-3	0.14	1.00

From the results in Table 8, it can be understood that in Samples 602 and 603 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 301, and therefore color reproducibility is good.

Example 10

The respective samples used in Example 9 were left to stand for 3 days in a dark place under high temperature and high humidity conditions of a temperature of 60 °C and a relative humidity of 80 %, and then the samples were subjected to exposure and processed according to the same method as in Example 9. When fog, sensitivity, γ and Dm were measured according to a conventional method, it was found that the measured values of Samples 602 and 603 of the present invention were substantially the same as those of Comparative sample 301.

Example 11

The procedures were carried out in the same manner as in Sample 101 of Example 1 except for changing Cyan coupler C-6 to II-17 (the same equimolar amount as that of Cyan coupler C-6 was added) and further adding 9.4×10^{-4} mole of III-1 to prepare Sample 702 of the present invention.

Sample 702 obtained as described above was subjected to wedge exposure and development processing was carried out in the same manner as in Sample 101 of Example 1, and then evaluated.

The results are shown in Table 9.

Table 9

	Cyan coupler	Compound III	Maximum color density (Dm)	Reflection density at 410 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-6	-	2.62	0.33	1.00
Sample 702 (Present invention)	I-17	III-1	2.60	0.23	1.00

From the results in Table 9, it can be understood that in Sample 702 using the compound of the present

invention, asymmetric absorption at 410 nm is reduced to a great extent when compared with that of Sample 101, and also sufficient maximum color density can be obtained.

Example 12-1

The procedures were carried out in the same manner as in Sample 702 of Example 11 except for excluding Compound III-1 of the present invention used in Sample 702 to prepare Sample 703. This sample and Comparative sample 101 were subjected to wedge exposure according to a conventional manner, and then development processing was carried out according to the same steps as in Example 11. However, a color developing solution used in Example 11 to which 3.5 g of Compound III-3 of the present invention was added was used as a color developing solution.

For the samples processed, entirely the same measurement as in Example 11 was conducted

The results are shown in Table 10.

Table 10

	Cyan coupler	Maximum color density (Dm)	Reflection density at 410 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-6	2.60	0.33	1.0
Sample 703 (Present invention)	I-17	2.57	0.24	1.0

As shown in the results in Table 10, it can be understood that even when the compound represented by the formula (III) of the present invention is added in a color developing solution, the same effect as in Example 11 can be exhibited.

Example 12-2

The procedures were carried out in the same manner as in Sample 702 of Example 11 except for excluding Compound I-17 of the present invention used in Sample 702 to prepare Sample 704. When this sample was subjected to exposure in the same manner as in Example 11 and then development processing was carried out by a color developing solution in which Compound I-23 of the present invention was added, the same effect as in Example 11 was obtained.

Example 12-3

The procedures were carried out in the same manner as in Sample 702 of Example 11 except for excluding Compounds I-17 and III-1 of the present invention used in Sample 702 to prepare Sample 705. When this sample was subjected to exposure in the same manner as in Example 11 and then development processing was carried out by a color developing solution in which Compounds I-23 and III-3 of the present invention were added, the same effect as in Example 11 was obtained.

Example 13

The procedures were carried out in the same manner as in Sample 201 of Example 3 except for replacing Cyan coupler C-17 in RL layer and RH layer of Sample 201 with an equimolar amount of Compound I-18 of the present invention, and further adding 0.38 g and 0.19 g of III-4 to RL layer and RH layer, respectively, to prepare Sample 802. The procedures were carried out in the same manner as in Sample 802 except for replacing III-4 with an equimolar amount of III-11 to prepare Sample 803.

The respective samples were subjected to color development processing according to the same steps as in Example 3, and evaluated in the same manner..

The results are shown in Table 11.

Table 11

	Cyan coupler	Compound III	Reflection density at 400 nm	Reflection density at 700 nm	Maximum color density (Dm rate)*
Sample 201 (Comparative)	C-17	-	0.23	1.00	1.00
Sample 802 (Present invention)	I-18	III-4	0.14	1.00	1.04
Sample 803 (Present invention)	I-18	III-11	0.16	1.00	1.05

* Dm value of Sample 201 was defined as 1.00.

From the results in Table 11, it can be understood that in Samples 802 and 803 using the compound of the present invention, asymmetric absorption at 400 nm is reduced to a great extent when compared with that of Sample 201, and also sufficient maximum color density can be obtained.

Example 14

The procedures were carried out in the same manner as in Sample 301 prepared in Example 4 except for replacing Magenta coupler M-2 in the third layer of Sample 301 with an equimolar amount of Compound I-13 of the present invention, and further adding 3.3 mg/100 cm^2 of III-5 to prepare Sample 902. The procedures were carried out in the same manner as in Sample 902 except for replacing I-13 with an equimolar amount of I-3, and further replacing III-5 with an equimolar amount of III-12 to prepare Sample 903.

The respective samples obtained as described above were processed according to the same steps as in Example 4, and evaluated in the same manner.

The results are shown in Table 12.

Table 12

	Magenta coupler	Compound III	Reflection density at 420 nm	Reflection density at 555 nm
Sample 301 (Comparative)	M-2	-	0.19	1.00
Sample 902 (Present invention)	I-13	III-5	0.13	1.00
Sample 903 (Present invention)	I-3	III-12	0.14	1.00

From the results in Table 12, it can be understood that in Samples 902 and 903 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 301, and therefore color reproducibility is good.

Example 15

The respective samples used in Example 14 were left to stand for 3 days in a dark place under high temperature and high humidity conditions of a temperature of 60 °C and a relative humidity of 80 %, and then the samples were subjected to exposure and processed according to the same method as in Example 14. When

fog, sensitivity, γ and Dm were measured according to a conventional method, it was found that the measured values of Samples 902 and 903 of the present invention were substantially the same as those of Comparative sample 301.

Example 16

The procedures were carried out in the same manner as in Sample 101 of Example 1 except for changing Cyan coupler C-1 to I-19 (the same equimolar amount as that of Cyan coupler C-1 was added) and further adding 9.1 x 10^{-4} mole of IV-3 to prepare Sample 1002 of the present invention.

Samples 101 and 1002 obtained as described above were processed in the same manner as in Sample 101 of Example 1, and evaluated.

The results are shown in Table 13.

Table 13

	Cyan coupler	Compound IV	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	-	2.80	0.30	1.00
Sample 1002 (Present invention)	I-19	IV-3	2.72	0.21	1.00

From the results in Table 13, it can be understood that in Sample 1002 using the compound of the present invention, asymmetric absorption at 420 nm is reduced to a great extent when compared with that of Sample 101, and also sufficient maximum color density can be obtained.

Example 17-1

The procedures were carried out in the same manner as in Sample 1002 of Example 16 except for excluding Compound IV-3 of the present invention used in Sample 1002 to prepare Sample 1003. This sample and Comparative sample 101 were subjected to wedge exposure according to a conventional manner, and then development processing was carried out according to the same steps as in Example 16. However, a color developing solution used in Example 16 to which 1.1 g of Compound IV-2 of the present invention was added was used as a color developing solution.

For the samples processed, entirely the same measurement as in Example 16 was conducted.

The results are shown in Table 14.

Table 14

	Cyan coupler	Maximum color density (Dm)	Reflection density at 420 nm	Reflection density at 650 nm
Sample 101 (Comparative)	C-1	2.75	0.39	1.0
Sample 1003 (Present invention)	I-19	2.74	0.23	1.0

As shown in the results in Table 14, it can be understood that even when the compound represented by the formula (IV) of the present invention is added in a color developing solution, the same effect as in Example 16 can be exhibited.

Example 17-2

The procedures were carried out in the same manner as in Sample 1002 of Example 16 except for excluding Compound I-19 of the present invention used in Sample 1002 to prepare Sample 1004. When this sample was subjected to exposure in the same manner as in Example 16 and then development processing was carried out by a color developing solution in which Compound I-23 of the present invention was added, the same effect as in Example 16 was obtained.

Example 17-3

The procedures were carried out in the same manner as in Sample 1002 of Example 16 except for excluding Compounds I-19 and IV-3 of the present invention used in Sample 1002 to prepare Sample 1005. When this sample was subjected to exposure in the same manner as in Example 16 and then development processing was carried out by a color developing solution in which Compounds I-23 and IV-2 of the present invention were added, the same effect as in Example 16 was obtained.

Example 18

The procedures were carried out in the same manner as in Sample 201 of Example 3 except for replacing Magenta coupler M-19 in GL layer and GH layer of Sample 201 with an equimolar amount of Compound I-14 of the present invention, and further adding 0.18 g of IV-14 to GL layer and GH layer, respectively, to prepare Sample 1102. The procedures were carried out in the same manner as in Sample 1102 except for replacing I-14 with an equimolar amount of I-20, and further replacing IV-14 with an equimolar amount of IV-4 to prepare Sample 1103.

The respective samples were subjected to color development processing according to the same steps as in Example 3, and evaluated in the same manner.

The results are shown in Table 15.

Table 15

	Magenta coupler	Compound IV	Reflection density at 430 nm	Reflection density at 555 nm	Maximum color density (Dm rate)*
Sample 201 (Comparative)	M-19	-	0.17	1.00	1.00
Sample 1102 (Present invention)	I-14	IV-14	0.12	1.00	1.05
Sample 1103 (Present invention)	I-20	IV-4	0.10	1.00	0.98

* Dm value of Sample 201 was defined as 1.00.

From the results in Table 15, it can be understood that in Samples 1102 and 1103 using the compound of the present invention, asymmetric absorption at 430 nm is reduced to a great extent when compared with that of Sample 201, and also sufficient maximum color density can be obtained.

Example 19

The procedures were carried out in the same manner as in Sample 301 prepared in Example 4 except for replacing Yellow coupler Y-9 in the first layer of Sample 301 with an equimolar amount of Compound I-9 of the present invention, and further adding 2.5 mg/100 cm^2 of IV-13 to prepare Sample 1202. The procedures were carried out in the same manner as in Sample 1202 except for replacing I-9 with an equimolar amount of I-21, and further replacing I-13 with an equimolar amount of I-10 to prepare Sample 1203.

The respective samples obtained as described above were processed according to the same steps as in Example 4, and evaluated in the same manner.

The results are shown in Table 16.

Table 16

	Yellow coupler	Compound IV	Reflection density at 440 nm	Reflection density at 500 nm
Sample 301 (Comparative)	Y-9	-	1.00	0.43
Sample 1202 (Present invention)	I-9	IV-13	1.00	0.38
Sample 1203 (Present invention)	I-21	IV-10	1.00	0.39

From the results in Table 16, it can be understood that in Samples 1202 and 1203 using the compound of the present invention, reflective density at 500 nm is low when compared with that of Sample 301, and therefore the upstand at a short wavelength side is good.

Example 20

The respective samples used in Example 19 were left to stand for 3 days in a dark place under high temperature and high humidity conditions of a temperature of 60 °C and a relative humidity of 80 %, and then the samples were subjected to exposure and processed according to the same method as in Example 19. When fog, sensitivity, γ and Dm were measured according to a conventional method, it was found that the measured values of Samples 1202 and 1203 of the present invention were substantially the same as those of Comparative sample 301.

As clearly seen from the above results, by using the compound of the present invention, a light-sensitive silver halide color photographic material excellent in color reproducibility and small in change of photographic performances during storage could be provided.

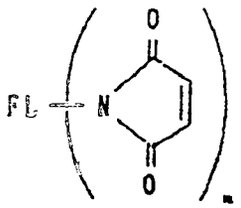
Claims

1. A light-sensitive silver halide color photographic material having at least one silver halide emulsion layer on a support, which comprises at least one coupler represented by the following formula (I) and a fluorescent substance precursor which can form a fluorescent substance from an eliminated component released from the above coupler at the time of color development, or from an eliminated component released from the above coupler and a color developing solution component at the time of color development.

$$Cp\text{-}SR_1 \qquad (I)$$

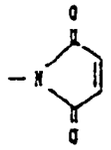
wherein Cp represents a coupler residue; SR_1 represents a group eliminated at the time of coupling with an oxidized product of a color developing agent during development processing; and R_1 represents an alkyl group, an aryl group, a heterocyclic group, a substituted alkyl group, a substituted aryl group and a substituted heterocyclic group.

2. The material of Claim 1 wherein the above fluorescent substance precursor is a compound represented by the following formula (II):



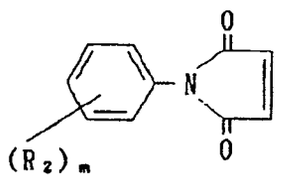
(II)

wherein FL represents a fluorescent compound;



represents a compound with which a chromophore portion of the fluorescent compound is directly substituted; and n represents an integer of 1 or more.

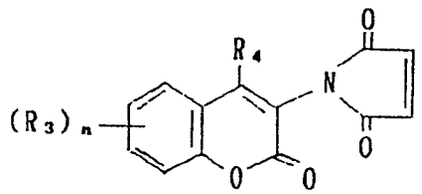
3. The material of Claim 2 wherein the compound represented by the above formula (II) is a compound represented by the following formula (II-1):



(II-1)

wherein R_2 represents a substituent group with which a benzene ring can be substituted; m represents an integer of 0 to 5; when m is 2 or more, plural R_2 may be the same or different; and R_2 which are adjacent to each other may be condensed mutually to form a ring.

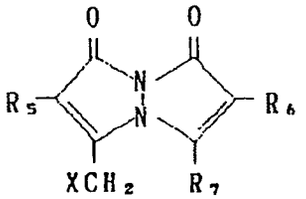
4. The material of Claim 2 wherein the compound represented by the above formula (II) is a compound represented by the following formula (II-2):



(II-2)

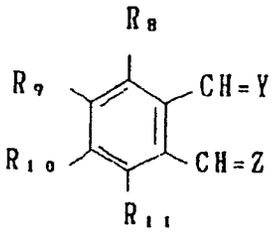
wherein R_3 represents a substituent group with which a benzene ring can be substituted; n represents an integer of 0 to 4; when n is 2 or more, plural R_3 may be the same or different; R_3 which are adjacent to each other may be condensed mutually to form a ring; and R_4 represents a hydrogen atom or a substituent group.

5. The material of Claim 1 wherein the above fluorescent substance precursor is at least one compound selected from the oompounds represented by the following formuale (III) and (IV):



(III)

wherein R_5, R_6 and R_7 each represent a hydrogen atom or a substituent group; X represents a halogen atom; and R_5, R_6 and R_7 cannot represent a hydrogen atom at the same time.



(IV)

wherein R_8, R_9, R_{10} and R_{11} each represent a hydrogen atom and a substituent group with which a benzene ring can be substituted; R_8 and R_9, R_9 and R_{10}, and R_{10} and R_{11} which are adjacent to each other, respectively, may be condensed mutually to form a hydrocarbon ring or a hetero ring; and Y and Z each represent 0 or N-R_{12} where R_{12} represents a substituent group.

6. The material of Claim 5 wherein the above fluorescent substance precursor is a compound represented by the above formula (III).

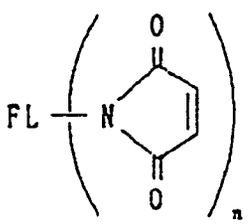
7. The material of Claim 5 wherein the above fluorescent substanoe precursor is a compound represented by the above formula (IV).

8. A method for processing a light-sensitive silver halide photographic material, which comprises color development of a light-sensitive silver halide photographic material under the presence of a coupler represented by the following formula (I) and a fluorescent substance precursor which can form a fluorescent substance from an eliminated component released from the above coupler at the time of color development, or from an eliminated component released from the above coupler and a color developing solution component at the time of color development.

$$Cp\text{-}SR_1 \qquad (I)$$

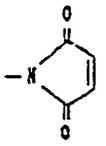
wherein Cp represents a coupler residue; SR_1 represents a group eliminated at the time of coupling with an oxidized product of a color developing agent during development processing; and R_1 represents an alkyl group, an aryl group, a heterocyclic group, a substituted alkyl group, a substituted aryl group and a substituted heterocyclic group.

9. The method of Claim 8 wherein the above fluorescent substance precursor is a compound represented by the following formula (II):



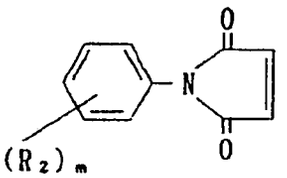
(II)

wherein FL represents a fluorescent compound;



represents a compound with which a chromophore portion of the fluorescent compound is directly substituted; and n represents an integer of 1 or more.

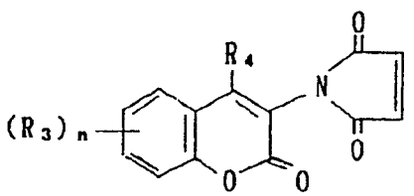
10. The method of Claim 9 wherein the compound represented by the above formula (II) is a compound represented by the following formula (II-1):



(II-1)

wherein R_2 represents a substituent group with which a benzene ring can be substituted; m represents an integer of 0 to 5; when m is 2 or more, plural R_2 may be the same or different; and R_2 which are adjacent to each other may be condensed mutually to form a ring.

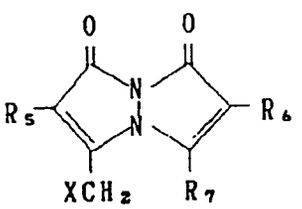
11. The method of Claim 9 wherein the compound rerpesented by the above formula (II) is a compound represented by the following formula (II-2):



(II-2)

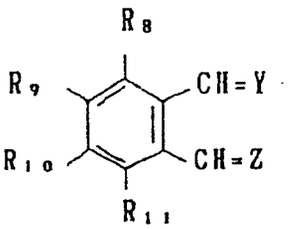
wherein R_3 represents a substituent group with which a benzene ring can be substituted; n represents an integer of 0 to 4; when n is 2 or more, plural R_3's may be the same or different; R_3 which are adjacent to each other may be condensed mutually to form a ring; and R_4 represents a hydrogen atom or a substituent group.

12. The method of Claim 8 wherein the above fluorescent substance precursor is at least one compound selected from the compounds represented by the following formulae (III) and (IV):



(III)

wherein R_5, R_6 and R_7 each represent a hydrogen atom or a substituent group; X represents a halogen atom; and R_5, R_6 and R_7 cannot represent a hydrogen atom at the same time.



(IV)

wherein R_8, R_9, R_{10} and R_{11} each represent a hydrogen atom and a substituent group with which a benzene ring can be substituted; R_8 and R_9, R_9 and R_{10}, and R_{10} and R_{11} which are adjacent to each other, respectively, may be condensed mutually to form a hydrocarbon ring or a hetero ring; and Y and Z each represent O or N-R_{12} where R_{12} represents a substituent group.

13. The method of Claim 12 wherein the above fluorescent substance precursor is a compound represented by the above formula (III).

14. The method of Claim 12 wherein the above fluorescent substance precursor is a compound represented by the above formula (IV).