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(54) **Silver halide color photographic light-sensitive material**

(57) There is disclosed a silver halide color photograph light-sensitive material comprising a specific hydrazine derivative, as a color-forming reducing agent (an agent for color-developing), a dye-forming coupler, and a sulfinic acid compound. The light-sensitive material comprises the color-forming reducing agent built therein, it is suitable for rapid processing, and it is suitable for remarkably reducing both the replenishment rate and the processing chemicals. Further, the light-sensitive material can restrain from stain to occur due to the long-term storage of the light-sensitive material, and it can keep the clarity of an image.

EP 0 777 153 A1

DescriptionFIELD OF THE INVENTION

5 The present invention relates to a silver halide color photographic light-sensitive material. The present invention further relates to a silver halide color photographic light-sensitive material that is excellent in processing stability and suitable for low-replenishment-rate processing.

The present invention also relates to a silver halide color photographic light-sensitive material that provides an image good in color-forming property and excellent in image stability and stained less in terms of long-term storage of the image.

BACKGROUND OF THE INVENTION

15 Generally, silver halide color photographic light-sensitive materials are processed through a color development step and a desilvering step, to form an image. In the color development step, silver halide grains that have been exposed to light are developed (reduced) with an aromatic primary amine developing agent, and the subsequent reaction of the oxidized product thereof, with couplers, gives a color-developed image.

For example, in the color printing paper processing, the color development is carried out in an alkali bath containing 4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)-aniline sulfate, as an aromatic primary amine developing agent.

20 When the above usual color-developing agent or the like is made into an alkaline solution, it is oxidized by air and is deteriorated considerably. As a result, a large amount of a preservative and a large amount of a replenisher are used, to keep the solution composition and the photographic performance constant.

In recent years, in this industry, a reduction of the burden on the environment, a reduction in the amount of waste, and recycling use are desired, and aims to reduce processing chemicals of the above color developer and to make the replenishment rate considerably low are now positively being promoted.

25 In order to keep the photographic performance good, both in continuous processing and intermittent processing, as well as to lower the replenishment rate, however, it is required to increase the concentrations of processing chemicals in the replenisher. Therefore, reduction in processing chemicals in number of their kinds and amounts to be used, has not yet been attained under the present conditions. Further, when a low replenishment rate is used, there arises the problem that stain and fluctuations of photographic performance, due to accumulated components, increase conspicuously.

30 As a proposed effective means of reducing processing chemicals and attaining a low replenishment rate, it is conceivable to build a color-developing agent or its precursor in a light-sensitive material and to process the light-sensitive material with an alkaline solution free of a developing agent, which is described, for example, in U.S. Patent No. 4,060,418. However, these aromatic primary amine developing agents and their precursors are unstable and are accompanied by the drawback that stain is formed when the unprocessed light-sensitive material is stored for a long period of time, or when the light-sensitive material is color-developed.

35 Further, in addition to the above-described color development methods, for example, a method described in European Patent Nos. 0545491 A1 and 0565165 A1 is known, wherein a sulfonylamidohydrazine-type compound and couplers are built in light-sensitive layers and a coupling image is formed when development is carried out. In this method, an image free of stain can be obtained relatively stably by building in, additionally, an auxiliary developing agent or its precursor, and the method is effective in view of reducing processing chemicals and processing solutions. However, it has become apparent that the stability of this light-sensitive material, wherein use is made of a sulfonylamidohydrazine-type compound, is not satisfactory and that the image preservability is poor. This is because, when the image is stored 45 for a long period of time, the color-forming reducing agent and the dye-forming coupler in the light-sensitive material are deteriorated, to form color in the white background. In particular, it has become apparent that when the image is stored under high-humidity conditions, stain in the white background increases considerably.

Further, the sulfonylamidohydrazine-type compound has the drawback that when a two-equivalent coupler is used, color is hardly formed. However, for example, in comparison with four-equivalent couplers, two-equivalent couplers 50 have the advantages that stain due to storage of couplers themselves can be reduced, and that coupling split-off groups can be made to have various functions. Herein, a coupling split-off group means a substituent which a coupler has at its coupling reactive position, and that is capable of being split-off upon coupling reaction with an oxidation product of a color-forming reducing agent (a developing agent).

In light of the above problems, development of a technique is desired in which the long-term preservability of an image 55 can be improved and two-equivalent couplers can be used.

In a conventional method wherein a color-formed dye image is obtained by using, in a light-sensitive material, the color-forming reducing agent according to the present invention, such as a sulfonylhydrazine or a carbamoylhydrazine, the storage preservability of the color-formed dye image obtained by processing is poor and formation of stain is conspicuous.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide color photographic light-sensitive material suitable for greatly reducing both the replenishment rate and processing chemicals.

Another object of the present invention is to provide a silver halide color photographic light-sensitive material improved in fastness of a dye image to the long-term storage of the light-sensitive material, and restrained from forming stain.

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

DETAILED DESCRIPTION OF THE INVENTION

In view of the above problems, the inventors of the present invention have studied intensively and have found that the above objects can be attained by the following means.

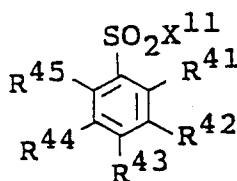
That is, the present invention provides:

(1) A silver halide color photographic light-sensitive material having at least one light-sensitive silver halide emulsion layer on a base, wherein at least one of the photographic constitutional layers contains at least one dye-forming coupler, and at least one color-forming reducing agent represented by formula (I):



wherein R^{11} represents an aryl group or a heterocyclic group; R^{12} represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group; and X represents a group selected from the group consisting of $-\text{SO}_2-$, $-\text{CO}-$, $-\text{COCO}-$, $-\text{CO-O}-$, $-\text{CO-N(R}^{13})-$, $-\text{COCO-O}-$, $-\text{COCO-N(R}^{13})-$, and $-\text{SO}_2\text{-N(R}^{13})-$, in which R^{13} represents a hydrogen atom or a group represented by R^{12} above; and at least one of the photographic constitutional layers contains a compound represented by formula (S):

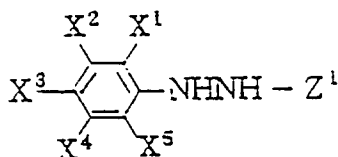
formula (S)



wherein X^{11} represents a hydrogen atom, some other atom, or a group of atoms, which atom or atoms form an inorganic or organic salt; and R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} , which are the same or different, each represent a hydrogen atom or a substituent, or the groups of R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} in the ortho-positions may bond together to form a 5- to 6-membered ring, provided that the sum total of the carbon atoms of R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} is 10 or more.

(2) The silver halide color photographic light-sensitive material as stated in the above (1), wherein the compound represented by formula (I) is represented by formula (II) or (III):

formula (II)





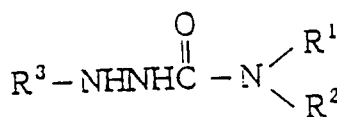
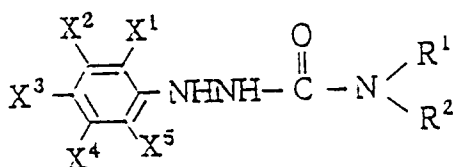
formula (III)

wherein Z^1 represents an acyl group, a carbamoyl group, an alkoxy carbonyl group, or an aryloxy carbonyl group; Z^2 represents a carbamoyl group, an alkoxy carbonyl group, or an aryloxy carbonyl group; X^1 , X^2 , X^3 , X^4 , and X^5 each represent a hydrogen atom or a substituent, provided that the sum of the Hammett substituent constant σ_p values of X^1 , X^3 , and X^5 , and the Hammett substituent constant σ_m values of X^2 and X^4 , is 0.80 or more but 3.80 or less; and R^3 represents a heterocyclic group.

(3) The silver halide color photographic light-sensitive material as stated in the above (2), wherein the compound represented by formula (II) or (III) is represented by formula (IV) or (V), respectively:

formula (IV)

formula (V)

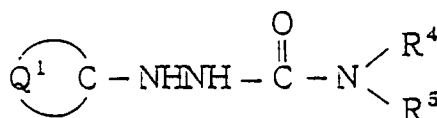
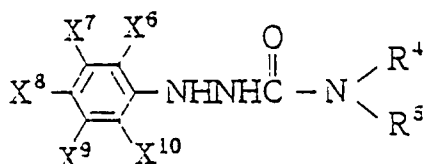


wherein R^1 and R^2 each represent a hydrogen atom or a substituent; X^1 , X^2 , X^3 , X^4 , and X^5 each represent a hydrogen atom or a substituent, provided that the sum of the Hammett substituent constant σ_p values of X^1 , X^3 , and X^5 , and the Hammett substituent constant σ_m values of X^2 and X^4 , is 0.80 or more but 3.80 or less; and R^3 represents a heterocyclic group.

(4) The silver halide color photographic light-sensitive material as stated in the above (3), wherein the compound represented by formula (IV) or (V) is represented by formula (VI) or (VII), respectively:

formula (VI)

formula (VII)



wherein R^4 and R^5 each represent a hydrogen atom or a substituent; X^6 , X^7 , X^8 , X^9 , and X^{10} each represent a hydrogen atom, a cyano group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, a carbamoyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, an acyl group, a trifluoromethyl group, a halogen atom, an acyloxy group, an acylthio group, or a heterocyclic group, provided that the sum of the Hammett substituent constant σ_p values of X^6 , X^8 , and X^{10} , and the Hammett substituent constant σ_m values of X^7 and X^9 , is 1.20 or more but 3.80 or less; and Q^1 represents a group of non-metal atoms required to form, together with the C, a 5- to 8-membered nitrogen-containing heterocyclic group.

(5) The silver halide color photographic light-sensitive material as stated in the above (1), (2), (3), or (4), comprising an auxiliary developing agent and/or its precursor.

(6) The silver halide color photographic light-sensitive material as stated in the above (1), (2), (3), (4), or (5), comprising a silver halide such that the total applied silver amount of all the applied layers is 0.003 to 0.3 g/m² in terms of silver.

(7) The silver halide color photographic light-sensitive material as stated in the above (1), (2), (3), (4), (5), or (6), wherein the said silver halide color photographic light-sensitive material is exposed to light by scanning exposure, with the exposure time per picture element being 10⁻⁸ to 10⁻⁴ sec.

The image obtained by using the color-forming reducing agent and the coupler for use in the present invention exhibits high color density and low minimum density and is excellent in long-term storage preservability. On the other hand, when the obtained image is stored for a long period of time under high temperature and high humidity, an increase in stain is observed, but stain that will occur during storage can be reduced greatly by using the sulfinic acid compound according to the present invention. When the color-forming reducing agent represented by formula (II) or (III) is used, the effect of suppressing stain by the sulfinic acid compound according to the present invention is particularly great. A combination of the color-forming reducing agent of formula (II) or (III) with a two-equivalent coupler gives a high-quality image with less stain.

Now, the specific constitution of the present invention will be described in detail.

The sulfinic acid compound represented by formula (S) according to the present invention is described in more detail.

X^{11} represents a hydrogen atom, some other atom, or a group of atoms, which atom or atoms forms an inorganic salt (e.g. Li, Na, K, Ca, and Mg) or an organic salt (e.g. NH_4^+ , $HN(C_2H_5)_3^+$, and $N(CH_3)_4^+$).

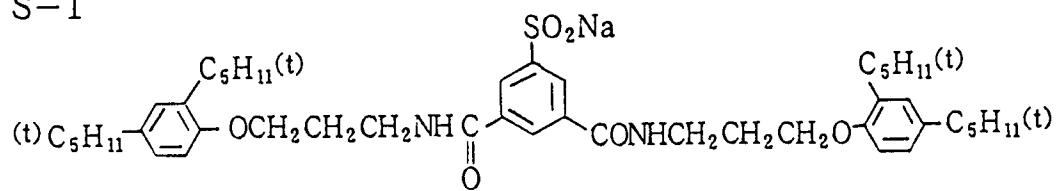
R^{41} to R^{45} , which are the same or different, each represent a hydrogen atom or a substituent. Examples of the substituent include an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, a halogen atom, a cyano group, a nitro group, a sulfo group, a sulfino group, a hydroxy group, an alkoxy group, an alkenoxy group, an aryloxy group, a heterocyclic oxy group, an alkylthio group, an alkenylthio group, an arylthio group, a heterocyclic thio group, an amino group, an alkylamino group, an alkenylamino group, an arylamino group, a heterocyclic amino group, an acylamino group, a sulfonamido group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, a silyloxy group, a carboxyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a carbamoyloxy group, and a ureido group. The above substituents may have a substituent, and example of such a substituent include those mentioned above.

The groups of R^{41} to R^{45} in the ortho-positions each other may bond together to form a 5- to 6-membered ring. Provided that the sum total of the carbon atoms of R^{41} to R^{45} is 10 or more.

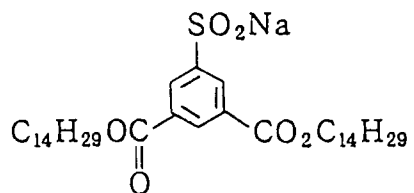
In the compound represented by formula (S), X^{11} preferably represents a hydrogen atom, Na, or K, and the sum total of the carbon atoms of R^{41} to R^{45} is preferably 12 or more, more preferably 15 or more. Preferable substituents represented by R^{41} to R^{45} include an alkyl group, an aryl group, a halogen atom, a cyano group, an alkoxy group, an aryloxy group, an alkylthio group, an acylamino group, a sulfonamido group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, and a ureido group.

Representative examples of the compound represented by formula (S) are listed below, but the present invention is not limited by these.

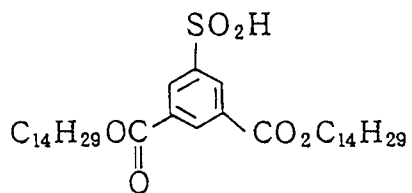
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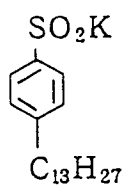
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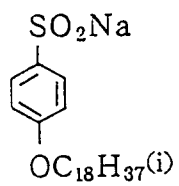
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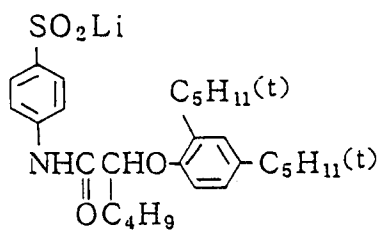
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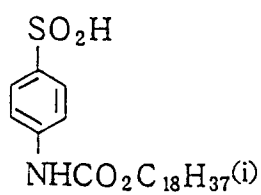
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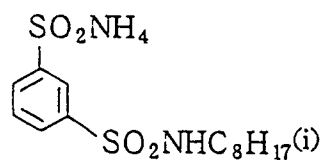
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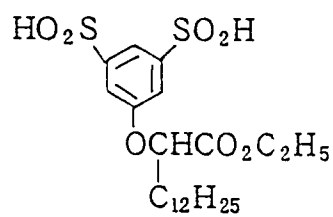
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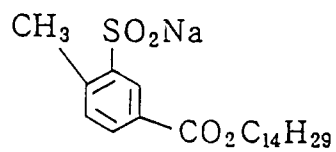
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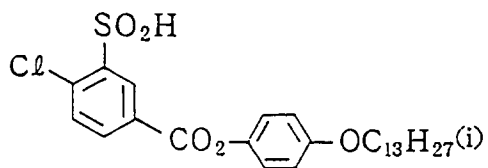
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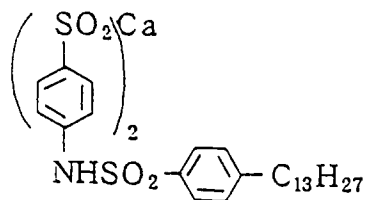
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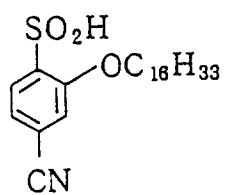
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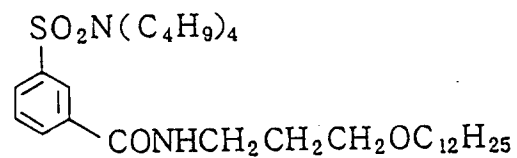
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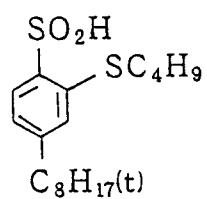
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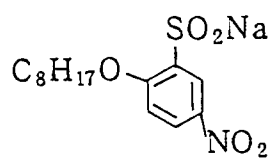
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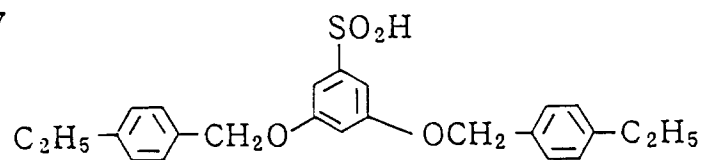
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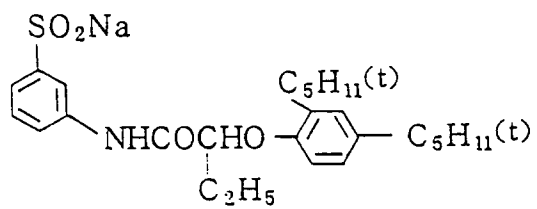
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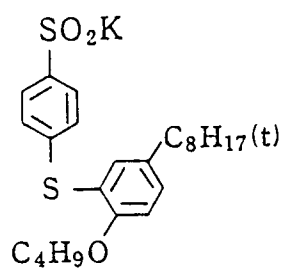
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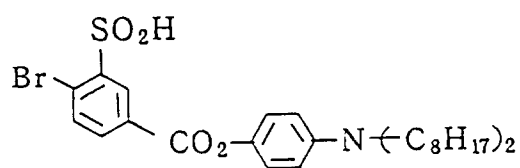
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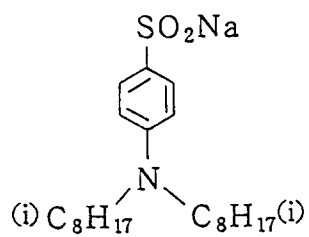
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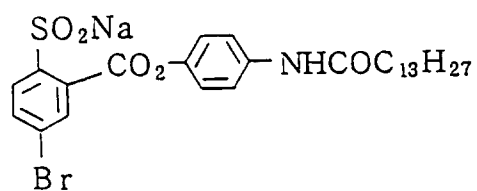
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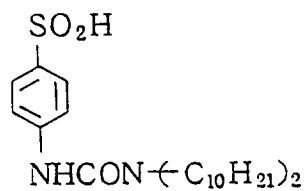
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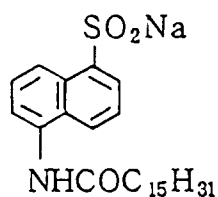
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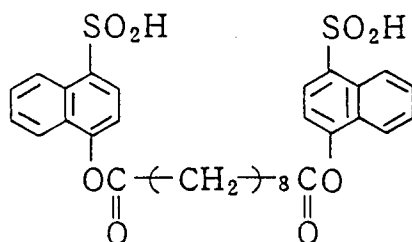
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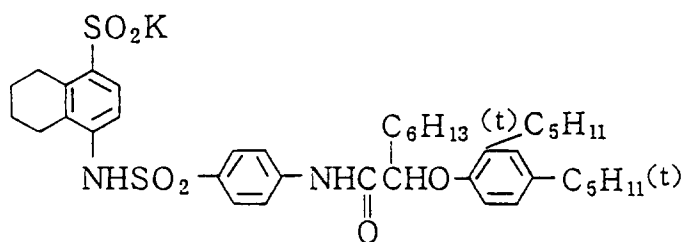
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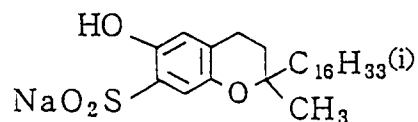
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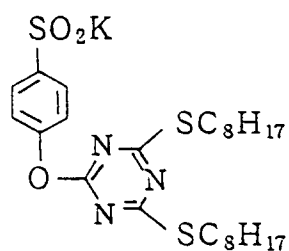
S-26



S-27



S-28



The usage amount of the compound represented by formula (S) according to the present invention is generally 0.01 to 10 times, preferably 0.05 to 2 times, and more preferably 0.1 to 1 times, the usage amount of the color-forming reducing agent to be used in a color-forming layer, in terms of mol.

Now, the color-forming reducing agent to be used in the present invention will be described in detail.

The color-forming reducing agent represented by formula (I) to be used in the present invention is a compound

characterized in that the compound is oxidized by reacting in an alkaline solution directly with a silver halide that has been exposed to light, or it is oxidized by undergoing a redox reaction with an auxiliary developing agent oxidized with a silver halide that has been exposed to light, and its oxidation product reacts with a dye-forming coupler, to form a dye.

The structure of the color-forming reducing agent represented by formula (I) is described in detail below.

In formula (I), R^{11} represents an aryl group or a heterocyclic group, which may be substituted. The aryl group represented by R^{11} has preferably 6 to 14 carbon atoms, and examples are phenyl and naphthyl. The heterocyclic group represented by R^{11} is preferably a saturated or unsaturated, 5-membered, 6-membered, or 7-membered heterocyclic ring containing at least one of nitrogen, oxygen, sulfur, and selenium, to which a benzene ring or a heterocyclic ring may be condensed. Examples of the heterocyclic ring represented by R^{11} are furanyl, thienyl, oxazolyl, thiazolyl, imidazolyl, triazolyl, pyrrolidinyl, benzoxazolyl, benzthiazolyl, pyridyl, pyridazyl, pyrimidinyl, pyrazinyl, triazinyl, quinolinyl, isoquinolinyl, phthalazinyl, quinoxalinyl, quinazolinyl, purinyl, pteridinyl, azepinyl, and benzoxepinyl.

The substituent possessed by R^{11} includes, for example, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, an acyloxy group, an acylthio group, an alkoxy-carbonyloxy group, an aryloxy-carbonyloxy group, a carbamoyloxy group, an alkylsulfonyloxy group, an arylsulfonyloxy group, an amino group, an alkylamino group, an arylamino group, an amido group, an alkoxy-carbonylamino group, an aryloxy-carbonylamino group, a ureido group, a sulfonamido group, a sulfamoylamino group, an acyl group, an alkoxy-carbonyl group, an aryloxy-carbonyl group, a carbamoyl group, an acylcarbamoyl group, a carbamoylcarbamoyl group, a sulfonylcarbamoyl group, a sulfamoylcarbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkoxy-sulfonyl group, an aryloxy-sulfonyl group, a sulfamoyl group, an acylsulfamoyl group, a carbamoylsulfamoyl group, a halogen atom, a nitro group, a cyano group, a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group, a mercapto group, an imido group, and an azo group.

R^{12} represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, which may be substituted.

The alkyl group represented by R^{12} is a straight-chain, branched, or cyclic alkyl group having preferably 1 to 16 carbon atoms, such as methyl, ethyl, hexyl, dodecyl, 2-octyl, t-butyl, cyclopentyl, and cyclooctyl. The alkenyl group represented by R^{12} is a chain or cyclic alkenyl group having preferably 2 to 16 carbon atoms, such as vinyl, 1-octenyl, and cyclohexenyl.

The alkynyl group represented by R^{12} is an alkynyl group having preferably 2 to 16 carbon atoms, such as 1-butylnyl and phenylethylnyl. The aryl group and the heterocyclic group represented by R^{12} include those mentioned for R^{11} . The substituent possessed by R^{12} includes those mentioned for the substituent of R^{11} .

X is a $-SO_2-$, $-CO-$, $-COCO-$, $-CO-O-$, $-CON(R^{13})-$, $-COCO-O-$, $-COCO-N(R^{13})-$, or $-SO_2-N(R^{13})-$ group, in which R^{13} represents a hydrogen atom or a group represented by R^{12} that is defined above.

Among those groups, $-CO-$, $-CON(R^{13})-$, and $-CO-O-$ are preferable, and $-CON(R^{13})-$ is particularly preferable for giving the particularly excellent color-forming property.

Out of the compounds represented by formula (I), the compounds represented by formula (II) or (III) are preferable, the compounds represented by formula (IV) or (V) are more preferable, and the compounds represented by formula (VI) or (VII) are further more preferable.

Now, the compounds represented by formulae (II) to (VII) are described in detail.

In formulae (II) and (III), Z^1 represents an acyl group, a carbamoyl group, an alkoxy-carbonyl group, or an aryloxy-carbonyl group, and Z^2 represents a carbamoyl group, an alkoxy-carbonyl group, or an aryloxy-carbonyl group. The acyl group preferably has 1 to 50 carbon atoms, and more preferably 2 to 40 carbon atoms. Specific examples include an acetyl group, a 2-methylpropanoyl group, a cyclohexylcarbonyl group, an n-octanoyl group, a 2-hexyldecanoyl group, a dodecanoyl group, a chloroacetyl group, a trifluoroacetyl group, a benzoyl group, a 4-dodecyloxybenzoyl group, a 2-hydroxymethylbenzoyl group, and a 3-(N-hydroxy-N-methylaminocarbonyl)propanoyl group.

With respect to the case wherein Z^1 and Z^2 each represent a carbamoyl group, a description is made in detail in formulae (IV) to (VII).

Preferably the alkoxy-carbonyl group and the aryloxy-carbonyl group have 2 to 50 carbon atoms, and more preferably 2 to 40 carbon atoms. Specific examples include a methoxy-carbonyl group, an ethoxy-carbonyl group, an isobutyloxy-carbonyl group, a cyclohexyloxy-carbonyl group, a dodecyloxy-carbonyl group, a benzyloxy-carbonyl group, a phenoxy-carbonyl group, a 4-octyloxyphenoxy-carbonyl group, a 2-hydroxymethylphenoxy-carbonyl group, and a 2-dodecyloxyphenoxy-carbonyl group.

X^1 , X^2 , X^3 , X^4 , and X^5 each represent a hydrogen atom or a substituent. Examples of the substituent include a straight-chain or branched, chain or cyclic alkyl group having 1 to 50 carbon atoms (e.g. trifluoromethyl, methyl, ethyl, propyl, heptafluoropropyl, isopropyl, butyl, t-butyl, t-pentyl, cyclopentyl, cyclohexyl, octyl, 2-ethylhexyl, and dodecyl); a straight-chain or branched, chain or cyclic alkenyl group having 2 to 50 carbon atoms (e.g. vinyl, 1-methylvinyl, and cyclohexen-1-yl); an alkynyl group having 2 to 50 carbon atoms in all (e.g. ethynyl and 1-propynyl), an aryl group having 6 to 50 carbon atoms (e.g. phenyl, naphthyl, and anthryl), an acyloxy group having 1 to 50 carbon atoms (e.g. acetoxyl, tetradecanoyloxy, and benzoyloxy), a carbamoyloxy group having 1 to 50 carbon atoms (e.g. N,N-dimethylcarbamoyl-

loxy), a carbonamido group having 1 to 50 carbon atoms (e.g. formamido, N-methylacetamido, acetamido, N-methylformamido, and benzamido), a sulfonamido group having 1 to 50 carbon atoms (e.g. methanesulfonamido, dodecansulfonamido, benzenesulfonamido, and p-toluenesulfonamido), a carbamoyl group having 1 to 50 carbon atoms (e.g. N-methylcarbamoyl, N,N-diethylcarbamoyl, and N-mesylcarbamoyl), a sulfamoyl group having 0 to 50 carbon atoms (e.g. N-butylsulfamoyl, N,N-diethylsulfamoyl, and N-methyl-N-(4-methoxyphenyl)sulfamoyl), an alkoxy group having 1 to 50 carbon atoms (e.g. methoxy, propoxy, isopropoxy, octyloxy, t-octyloxy, dodecyloxy, and 2-(2,4-di-t-pentylphenoxy)ethoxy), an aryloxy group having 6 to 50 carbon atoms (e.g. phenoxy, 4-methoxyphenoxy, and naphthoxy), an aryloxy carbonyl group having 7 to 50 carbon atoms (e.g. phenoxycarbonyl and naphthoxycarbonyl), an alkoxycarbonyl group having 2 to 50 carbon atoms (e.g. methoxycarbonyl and t-butoxycarbonyl), an N-acylsulfamoyl group having 1 to 50 carbon atoms (e.g. N-tetradecanoylsulfamoyl and N-benzoylsulfamoyl), an alkylsulfonyl group having 1 to 50 carbon atoms (e.g. methanesulfonyl, octylsulfonyl, 2-methoxyethylsulfonyl, and 2-hexyldecylsulfonyl), an arylsulfonyl group having 6 to 50 carbon atoms (e.g. benzenesulfonyl, p-toluenesulfonyl, and 4-phenylsulfonylphenylsulfonyl), an alkoxy carbonylamino group having 2 to 50 carbon atoms (e.g. ethoxycarbonylamino), an aryloxy carbonylamino group having 7 to 50 carbon atoms (e.g. phenoxycarbonylamino and naphthoxycarbonylamino), an amino group having 0 to 50 carbon atoms (e.g. amino, methylamino, diethylamino, diisopropylamino, anilino, and morpholino), a cyano group, a nitro group, a carboxyl group, a hydroxy group, a sulfo group, a mercapto group, an alkylsulfinyl group having 1 to 50 carbon atoms (e.g. methanesulfinyl and octanesulfinyl), an arylsulfinyl having 6 to 50 carbon atoms (e.g. benzenesulfinyl, 4-chlorophenylsulfinyl, and p-toluenesulfinyl), an alkylthio group having 1 to 50 carbon atoms (e.g. methylthio, octylthio, and cyclohexylthio), an arylthio group having 6 to 50 carbon atoms (e.g. phenylthio and naphthylthio), a ureido group having 1 to 50 carbon atoms (e.g. 3-methylureido, 3,3-dimethylureido, and 1,3-diphenylureido), a heterocyclic group having 2 to 50 carbon atoms (e.g. a 3-membered to 12-membered, monocyclic ring or condensed ring having at least one hetero atom(s), such as nitrogen, oxygen, and sulfur, for example, 2-furyl, 2-pyranyl, 2-pyridyl, 2-thienyl, 2-imidazolyl, morpholino, 2-quinolyl, 2-benzimidazolyl, 2-benzothiazolyl, and 2-benzoxazolyl), an acyl group having 1 to 50 carbon atoms (e.g. acetyl, benzoyl, and trifluoroacetyl), a sulfamoylamino group having 0 to 50 carbon atoms (e.g. N-butylsulfamoylamino and N-phenylsulfamoylamino), a silyl group having 3 to 50 carbon atoms (e.g. trimethylsilyl, dimethyl-t-butylsilyl, and triphenylsilyl), and a halogen atom (e.g. a fluorine atom, a chlorine atom, and a bromine atom). The above substituents may have a substituent, and examples of such a substituent include those mentioned above. Further, X^1 , X^2 , X^3 , X^4 , and X^5 may bond together to form a condensed ring. As condensed ring, 5-membered to 7-membered ring is preferable, and 5-membered to 6-membered ring is more preferable.

The number of carbon atoms of the substituent is preferably 50 or below, more preferably 42 or below, and most preferably 34 or below, and there is preferably 1 or more carbon atom(s).

With respect to X^1 , X^2 , X^3 , X^4 , and X^5 in formulae (II) and (IV), the sum of the Hammett substituent constant σ_p values of X^1 , X^3 , and X^5 and the Hammett substituent constant σ_m values of X^2 and X^4 is 0.80 or more but 3.80 or below. X^6 , X^7 , X^8 , X^9 , and X^{10} in formula (VI) each represent a hydrogen atom, a cyano group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, an acyl group, a trifluoromethyl group, a halogen atom, an acyloxy group, an acylthio group, or a heterocyclic group, which may have a substituent and may bond together to form a condensed ring. Specific examples are the same as those described for X^1 , X^2 , X^3 , X^4 , and X^5 . In formula (VI), the sum of the Hammett substituent constant σ_p values of X^6 , X^8 , and X^{10} and the Hammett substituent constant σ_m values of X^7 and X^9 is 1.20 or more but 3.80 or below, preferably 1.50 or more but 3.80 or below, and more preferably 1.70 or more but 3.80 or below.

Herein, if the sum of the σ_p values and the σ_m values is too small, the problem arises that the color formation is unsatisfactory, while if the sum of the σ_p values and the σ_m values is over 3.80, the synthesis and availability of the compounds themselves become difficult.

Parenthetically, Hammett substituent constants σ_p and σ_m are described in detail in such books as "Hammett no Hosoku/Kozo to Hannousei," written by Naoki Inamoto (Maruzen); "Shin-jikken Kagaku-koza 14/Yukikagoubutsu no Gosei to Hanno V," page 2605 (edited by Nihonkagakukai, Maruzen); "Riron Yukikagaku Kaisetsu," written by Tadao Nakaya, page 217 (Tokyo Kagakudojin); and "Chemical Review" (Vol. 91), pages 165 to 195 (1991).

R^1 and R^2 in formulae (IV) and (V), and R^4 and R^5 in formulae (VI) and (VII), each represent a hydrogen atom or a substituent, and examples of the substituent are the same as those described for X^1 , X^2 , X^3 , X^4 , and X^5 ; preferably each represent a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 50 carbon atoms, a substituted or unsubstituted aryl group having 6 to 50 carbon atoms, or a substituted or unsubstituted heterocyclic group having 1 to 50 carbon atoms, and more preferably at least one of R^1 and R^2 , and at least one of R^4 and R^5 , are each a hydrogen atom.

In formulae (III) and (V), R^3 represents a heterocyclic group. Herein, a preferable heterocyclic group has 1 to 50 carbon atoms, and the heterocyclic group contains at least one hetero atom, such as a nitrogen atom, an oxygen atom, and a sulfur atom, and further the heterocyclic group is a saturated or unsaturated 3-membered to 12-membered (preferably 3-membered to 8-membered) monocyclic or condensed ring. Specific examples of the heterocyclic ring are furan, pyran, pyridine, thiophene, imidazole, quinoline, benzimidazole, benzothiazole, benzoxazole, pyrimidine, pyrazine, 1,2,4-thiadiazole, pyrrole, oxazole, thiazole, quinazoline, isothiazole, pyridazine, indole, pyrazole, triazole, and qui-

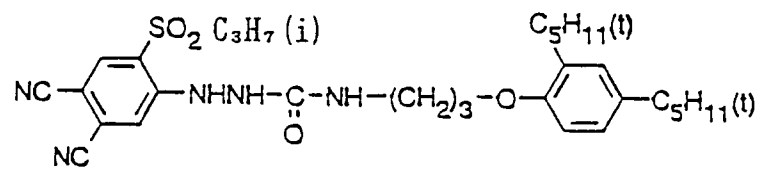
noxaline. These heterocyclic groups may have a substituent, and preferably they have one or more electron-attracting groups. Herein, the term "an electron-attracting group" means one wherein the Hammett σ_p value is a positive value.

In formula (VII), the 5- to 8-membered nitrogen-containing heterocyclic group formed by Q^1 and the C may contain other hetero atom such as a sulfur atom and an oxygen atom, and may be condensed with another ring such as a benzene ring. The heterocyclic group formed by Q^1 and the C preferably contains 1 to 3 nitrogen atoms and is preferably a 5- to 6-membered heterocyclic group. These heterocyclic groups formed by Q^1 and the C may have a substituent, which are described in detail for the above R^3 .

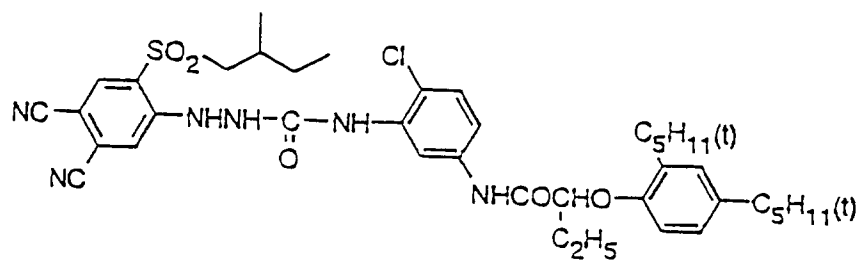
When the color-forming reducing agent according to the present invention is built in a light-sensitive material, preferably at least one of Z^1 , Z^2 , R^1 to R^5 , and X^1 to X^{10} , has a ballasting group. Herein, a "ballasting group" means a group, having 5 to 50, preferably 8 to 40 carbon atoms, which makes the color-forming reducing agent that has a ballasting group, easily-soluble in a high-boiling organic solvent, and been hardly deposited even after emulsifying and dispersing, and which makes the color-forming reducing agent immobilized in a hydrophilic colloid.

Now, novel color-forming reducing agents used in the present invention are described specifically, but the scope of the present invention is not limited to them.

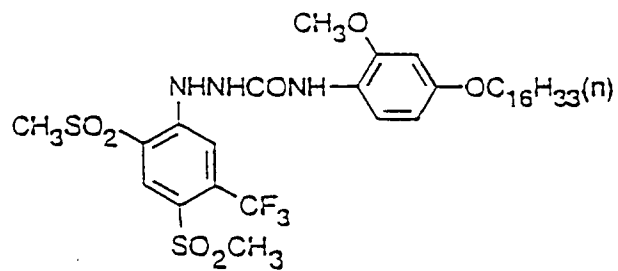
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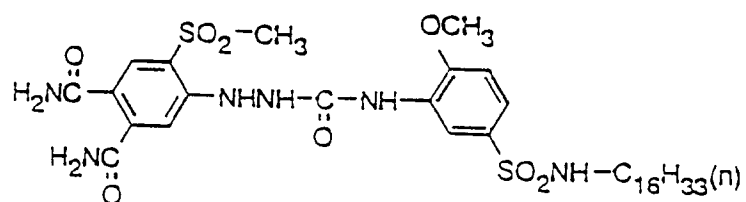
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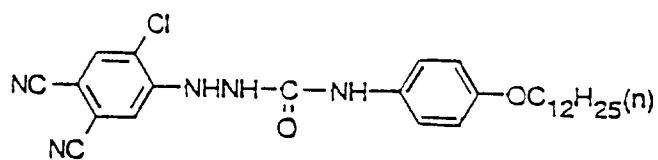
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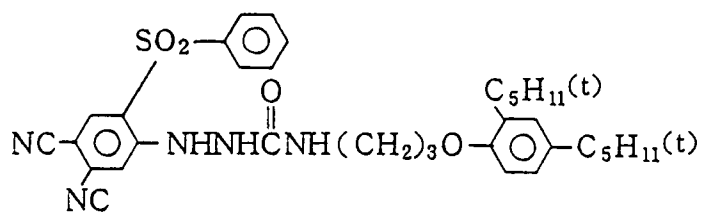
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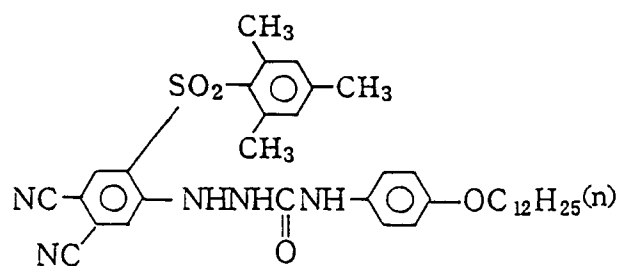
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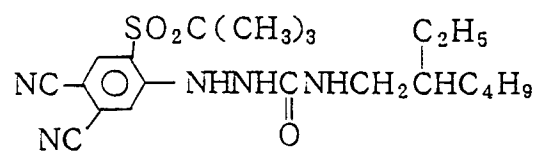
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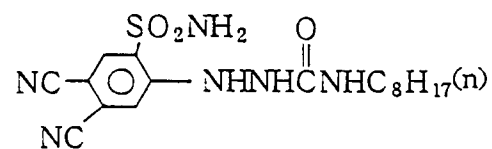
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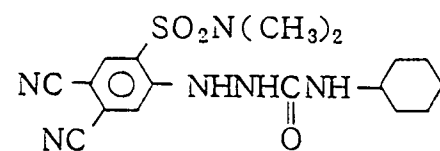
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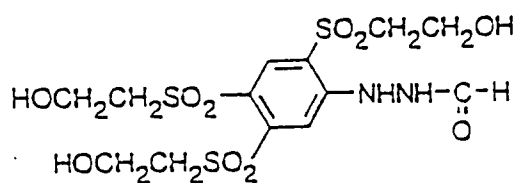
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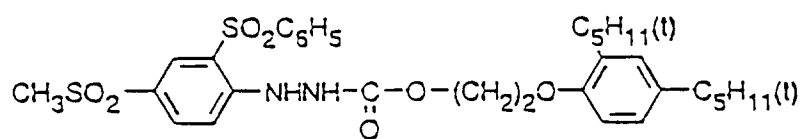
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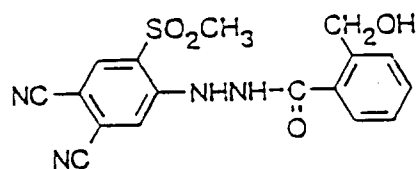
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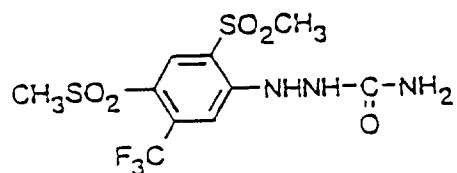
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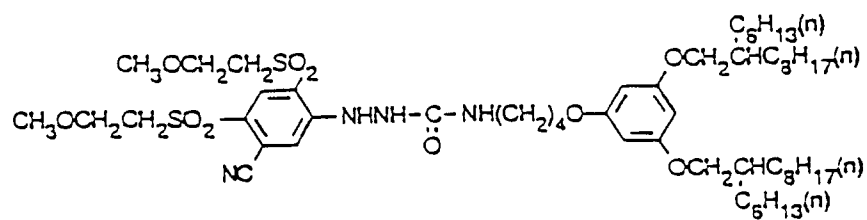
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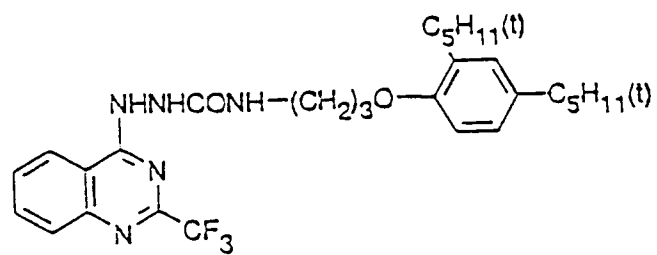
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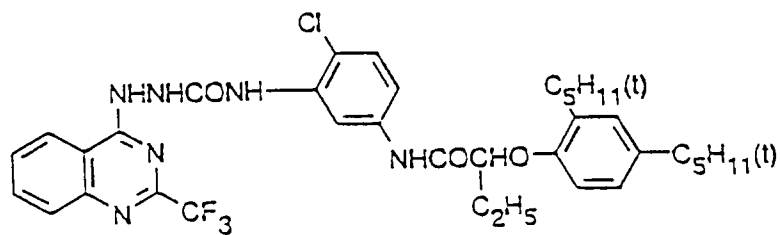
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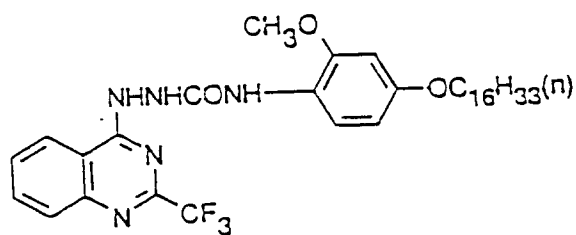
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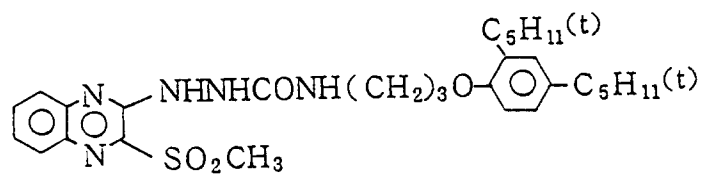
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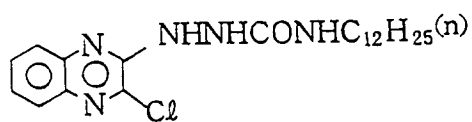


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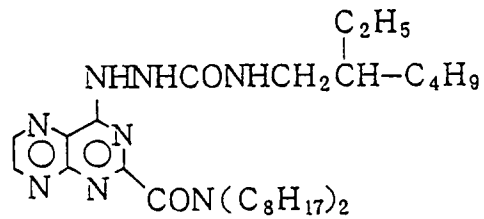
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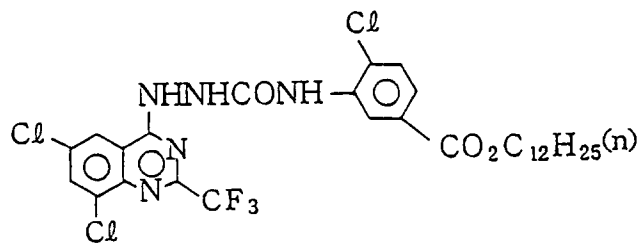
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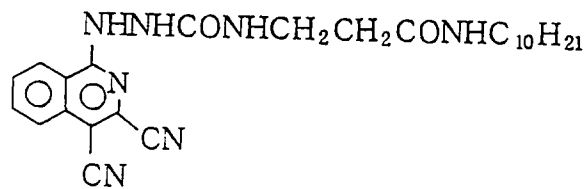
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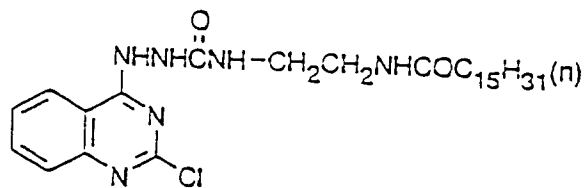
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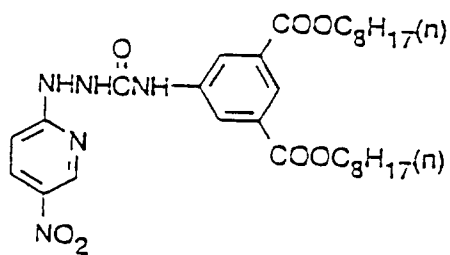
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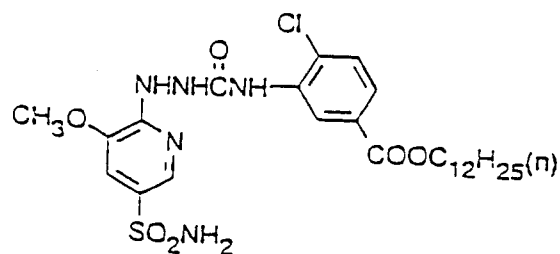
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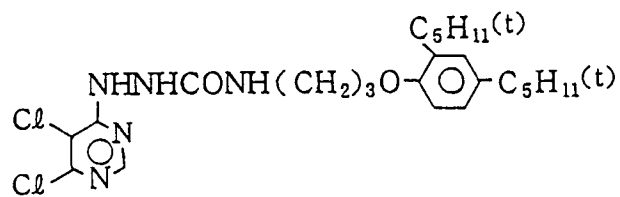
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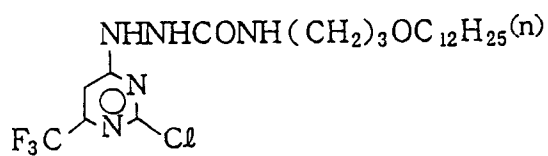
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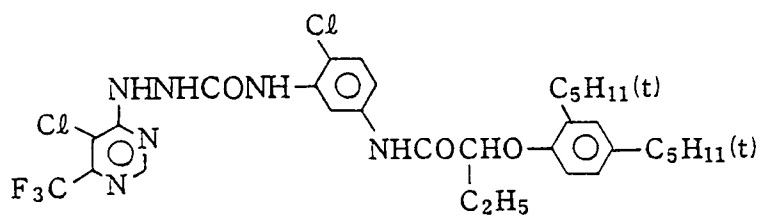
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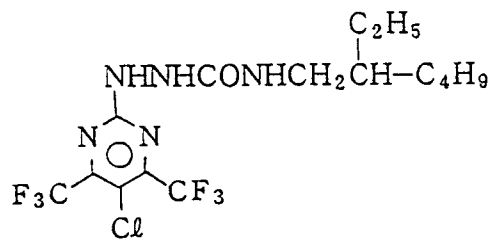
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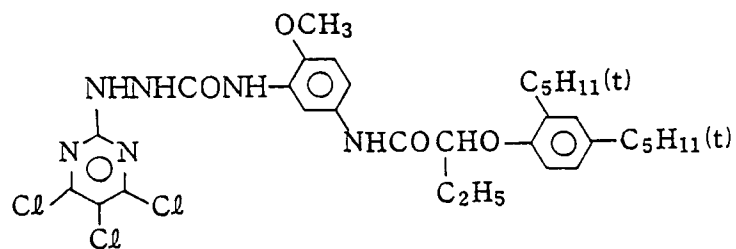
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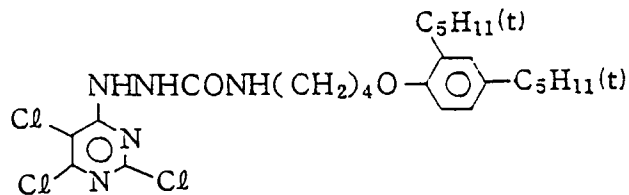
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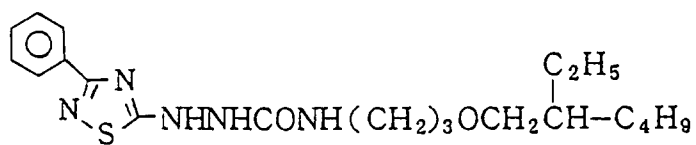


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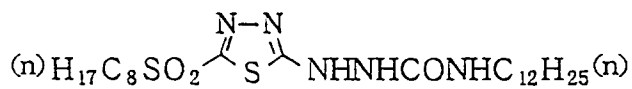
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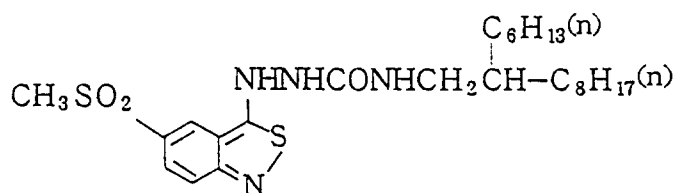
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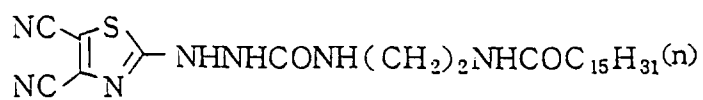
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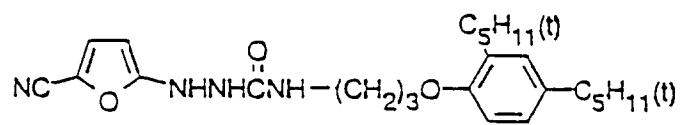
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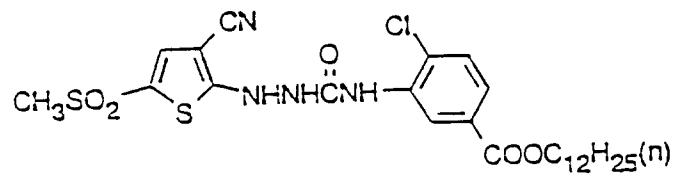
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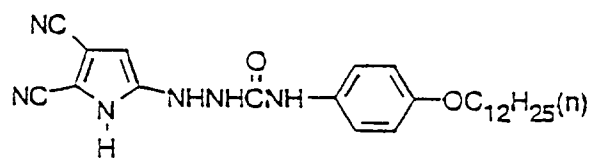
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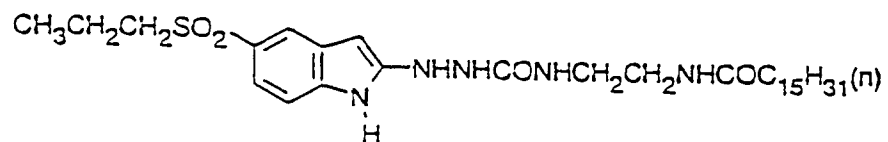
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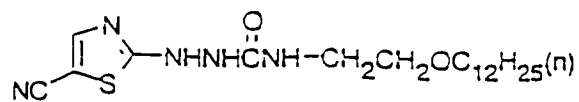
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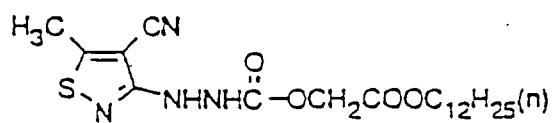
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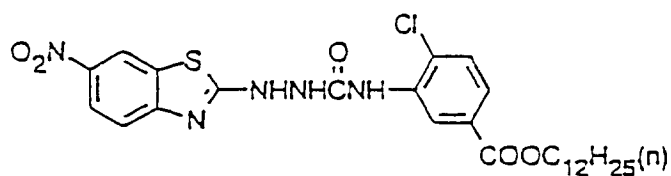
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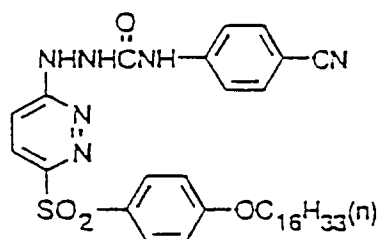
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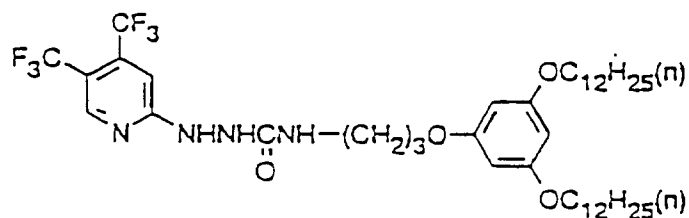
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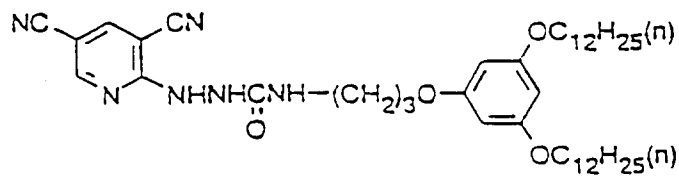
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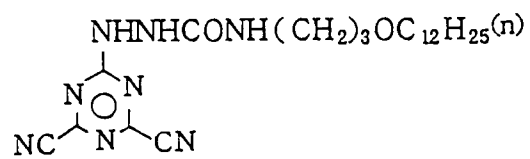
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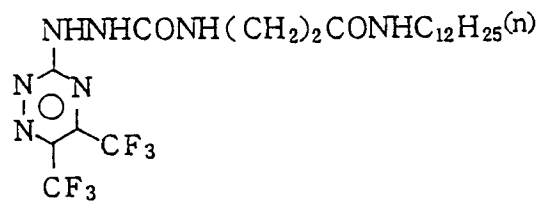
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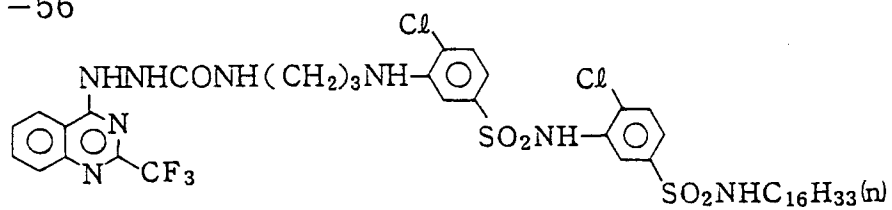
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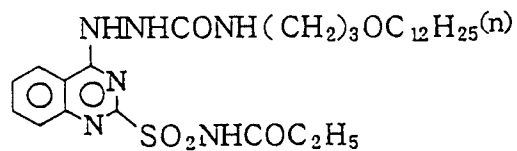
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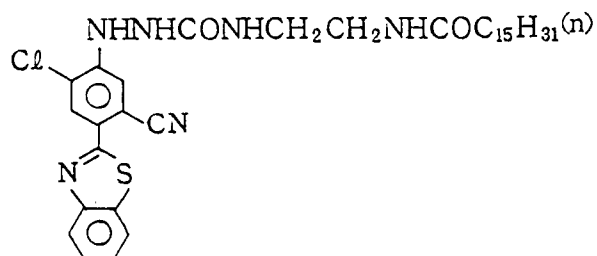
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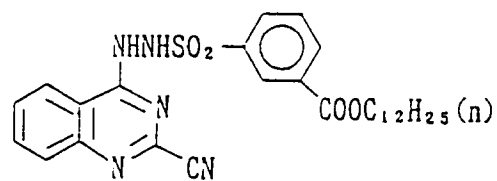
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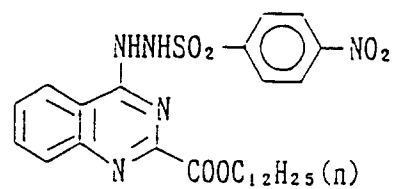
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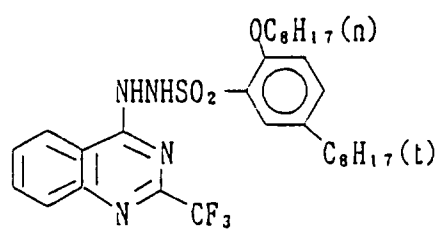
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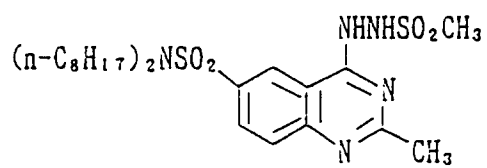
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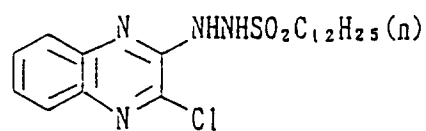
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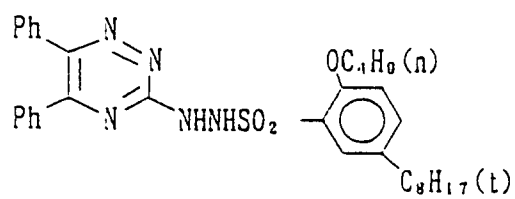
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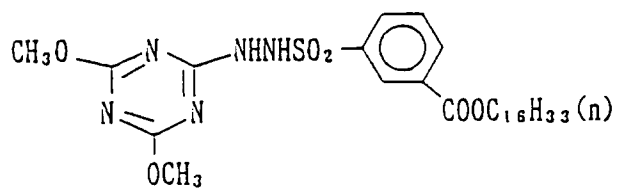
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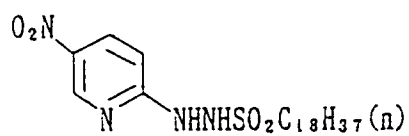
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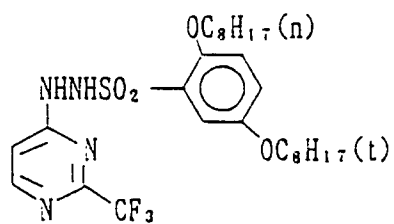
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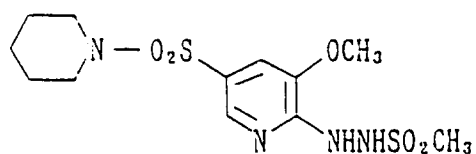
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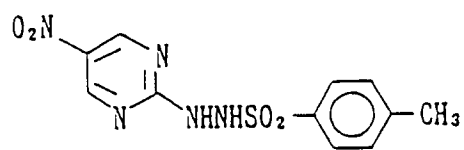
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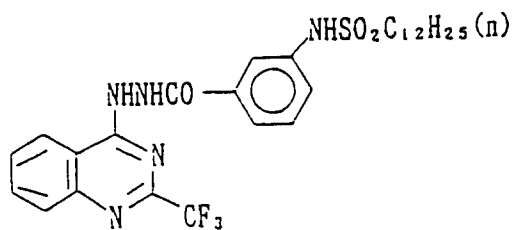
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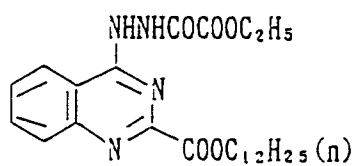
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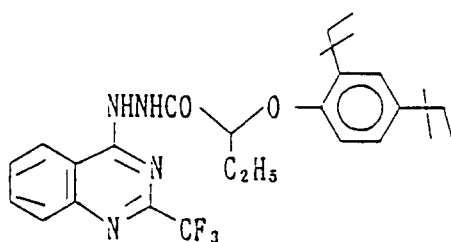
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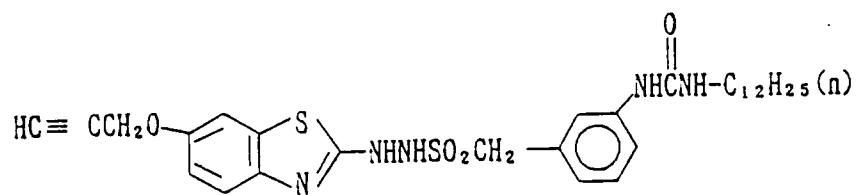


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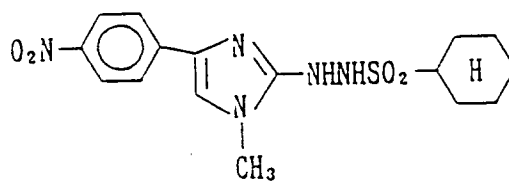


() represents a $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}-\text{C}_2\text{H}_5 \\ | \\ \text{CH}_3 \end{array}$ group.)

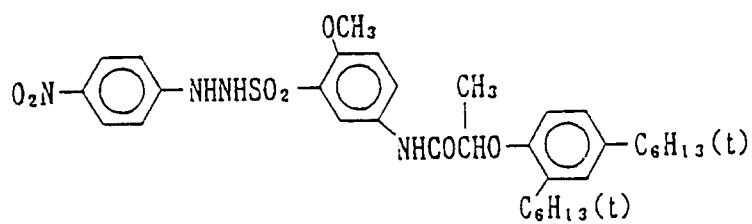
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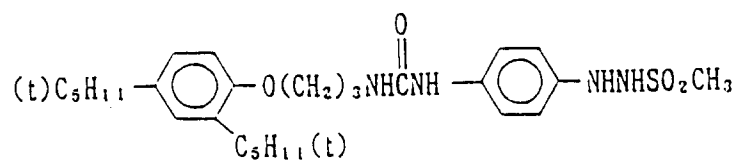
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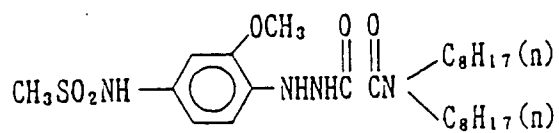
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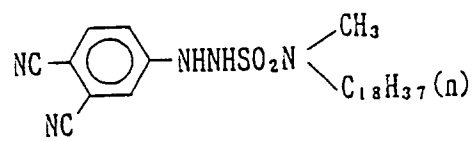
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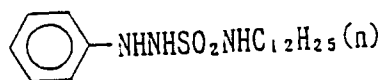
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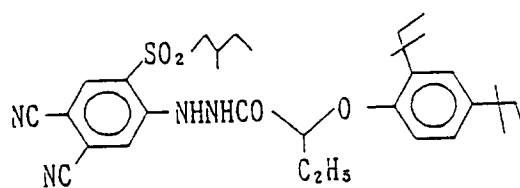
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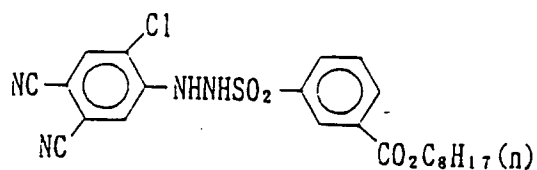
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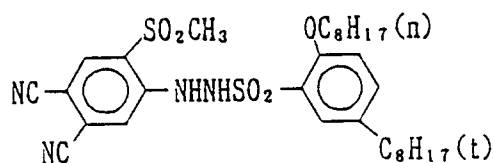
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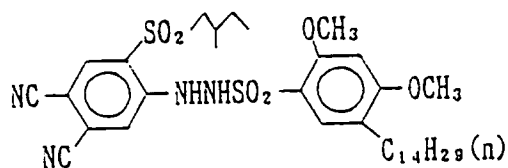
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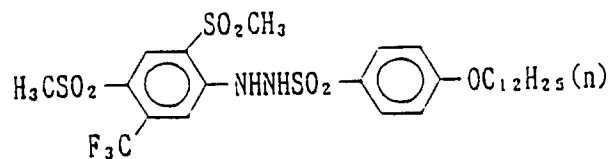
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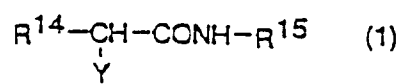
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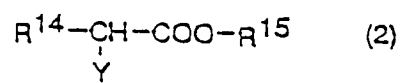
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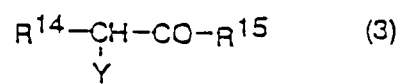
As couplers that are preferably used in the present invention, compounds having structures described by the following formulae (1) to (12) are mentioned. They are compounds collectively generally referred to as active methylenes, pyrazoloolones, pyrazoloazoles, phenols, naphthols, and pyrrolotriazoles, respectively, which are compounds known in the art.



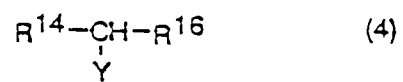
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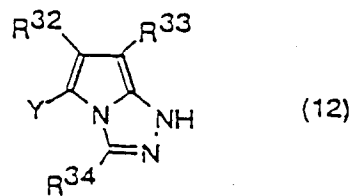
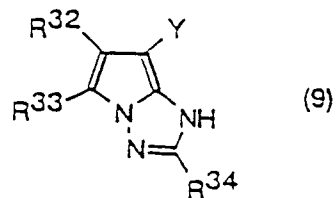
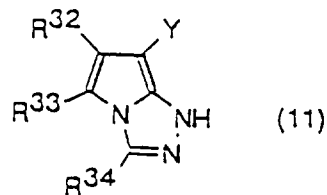
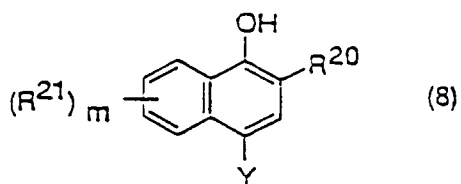
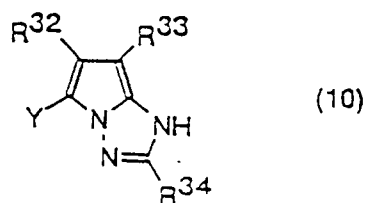
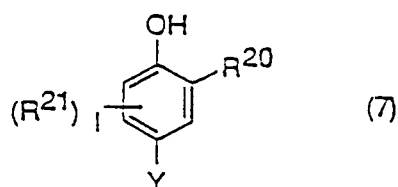
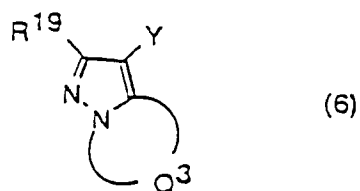
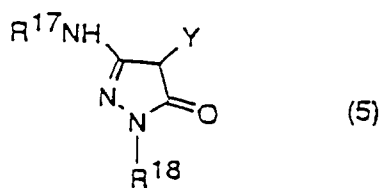
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Formulae (1) to (4) represent couplers that are called active methylene-seires couplers, and, in the formulae, R¹⁴ represents an acyl group, a cyano group, a nitro group, an aryl group, a heterocyclic residue, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, a sulfamoyl group, an alkylsulfonyl group, or an arylsulfonyl group, optionally substituted.

In formulae (1) to (3), R¹⁵ represents an optionally substituted alkyl group, aryl group, or heterocyclic residue. In formula (4), R¹⁶ represents an optionally substituted aryl group or heterocyclic residue. Examples of the substituent that

may be possessed by R^{14} , R^{15} , and R^{16} include those mentioned for X^1 to X^5 .

In formulae (1) to (4), Y represents a hydrogen atom or a group capable of coupling split-off by coupling reaction with the oxidation product of the color-forming reducing agent. Examples of Y are a heterocyclic group (a saturated or unsaturated 5-membered to 7-membered monocyclic or condensed ring having, as a hetero atom, at least one nitrogen atom, oxygen atom, sulfur atom, or the like, e.g. succinimido, maleinimido, phthalimido, diglycolimido, pyrrole, pyrazole, imidazole, 1,2,4-triazole, tetrazole, indole, benzopyrazole, benzimidazole, benzotriazole, imidazolin-2,4-dione, oxazolidin-2,4-dione, thiazolidin-2,4-dione, imidazolidin-2-one, oxazolin-2-one, thiazolin-2-one, benzimidazolin-2-one, benzoxazolin-2-one, benzthiazolin-2-one, 2-pyrrolin-5-one, 2-imidazolin-5-one, indolin-2,3-dione, 2,6-dioxypurine, parabic acid, 1,2,4-triazolidin-3,5-dione, 2-pyridone, 4-pyridone, 2-pyrimidone, 6-pyridazine, 2-pyrazone, 2-amino-1,3,4-thiazolidine, and 2-imino-1,3,4-thiazolidin-4-one), a halogen atom (e.g. a chlorine atom and a bromine atom), an aryloxy group (e.g. phenoxy and 1-naphthoxy), a heterocyclic oxy group (e.g. pyridyloxy and pyrazolyloxy), an acyloxy group (e.g. acetoxy and benzyloxy), an alkoxy group (e.g. methoxy and dodecyloxy), a carbamoyloxy group (e.g. N,N-diethylcarbamoyloxy and morpholinocarbonyloxy), an aryloxy carbonyloxy group (e.g. phenylcarbonyloxy), an alkoxy carbonyloxy group (e.g. methoxycarbonyloxy and ethoxycarbonyloxy), an arylthio group (e.g. phenylthio and naphthylthio), a heterocyclic thio group (e.g. tetrazolylthio, 1,3,4-thiadiazolylthio, 1,3,4-oxadiazolylthio, and benzimidazolylthio), an alkylthio group (e.g. methylthio, octylthio, and hexadecylthio), an alkylsulfonyloxy group (e.g. methanesulfonyloxy), an arylsulfonyloxy group (e.g. benzenesulfonyloxy and toluenesulfonyloxy), a carbonamido group (e.g. acetamido and trifluoroacetamido), a sulfonamido group (e.g. methanesulfonamido and benzenesulfonamido), an alkylsulfonyl group (e.g. methanesulfonyl), an arylsulfonyl group (e.g. benzenesulfonyl), an alkylsulfinyl group (e.g. methanesulfinyl), an arylsulfinyl group (e.g. benzenesulfinyl), an arylazo group (e.g. phenylazo and naphthylazo), and a carbamoylamino group (e.g. N-methylcarbamoylamino).

Y may be substituted, and examples of the substituent that may be possessed by Y include those mentioned for X^1 to X^5 .

Preferably Y represents a halogen atom, an aryloxy group, a heterocyclic oxy group, an acyloxy group, an aryloxy carbonyloxy group, an alkoxy carbonyloxy group, or a carbamoyloxy group.

In formulae (1) to (4), R^{14} and R^{15} , and R^{14} and R^{16} , may bond together to form a ring.

Formula (5) represents a coupler that is called a 5-pyrazolone-series coupler, and in the formula, R^{17} represents an alkyl group, an aryl group, an acyl group, or a carbamoyl group. R^{18} represents a phenyl group or a phenyl group that is substituted by one or more halogen atoms, alkyl groups, cyano groups, alkoxy groups, alkoxy carbonyl groups, or acylamino groups.

Preferable 5-pyrazolone-series couplers represented by formula (5) are those wherein R^{17} represents an aryl group or an acyl group, and R^{18} represents a phenyl group that is substituted by one or more halogen atoms.

With respect to these preferable groups, more particularly, R^{17} is an aryl group, such as a phenyl group, a 2-chlorophenyl group, a 2-methoxyphenyl group, a 2-chloro-5-tetradecaneamidophenyl group, a 2-chloro-5-(3-octadecenyl-1-succinimido)phenyl group, a 2-chloro-5-octadecylsulfonamidophenyl group, and a 2-chloro-5-[2-(4-hydroxy-3-*t*-butylphenoxy)tetradecaneamido]phenyl group; or R^{17} is an acyl group, such as an acetyl group, a 2-(2,4-di-*t*-pentylphenoxy)butanoyl group, a benzoyl group, and a 3-(2,4-di-*t*-amylphenoxyacetamido)benzoyl group, any of which may have a substituent, such as a halogen atom or an organic substituent that is bonded through a carbon atom, an oxygen atom, a nitrogen atom, or a sulfur atom. Y has the same meaning as defined above.

Preferably R^{18} represents a substituted phenyl group, such as a 2,4,6-trichlorophenyl group, a 2,5-dichlorophenyl group, and a 2-chlorophenyl group.

Formula (6) represents a coupler that is called a pyrazoloazole-series coupler, and, in the formula, R^{19} represents a hydrogen atom or a substituent. Q^3 represents a group of nonmetal atoms required to form a 5-membered azole ring containing 2 to 4 nitrogen atoms, which azole ring may have a substituent (including a condensed ring).

Preferable pyrazoloazole-series couplers represented by formula (6), in view of spectral absorption characteristics of the color-formed dyes, are imidazo[1,2-*b*]pyrazoles described in U.S. Patent No. 4,500,630, pyrazolo[1,5-*b*]-1,2,4-triazoles described in U.S. Patent No. 4,500,654, and pyrazolo[5,1-*c*]-1,2,4-triazoles described in U.S. Patent No. 3,725,067.

Details of substituents of the azole rings represented by the substituents R^{19} and Q^3 are described, for example, in U.S. Patent No. 4,540,654, the second column, line 41, to the eighth column, line 27. Preferable pyrazoloazole couplers are pyrazoloazole couplers having a branched alkyl group directly bonded to the 2-, 3-, or 6-position of the pyrazolotriazole group, as described in JP-A ("JP-A" means unexamined published Japanese patent application) No. 65245/1986; pyrazoloazole couplers containing a sulfonamido group in the molecule, as described in JP-A No. 65245/1986; pyrazoloazole couplers having an alkoxyphenylsulfonamido ballasting group, as described in JP-A No. 147254/1986; pyrazolotriazole couplers having an alkoxy group or an aryloxy group at the 6-position, as described in JP-A No. 209457/1987 or 307453/1988; and pyrazolotriazole couplers having a carbonamido group in the molecule, as described in JP-A No. 201443/1990. Y has the same meaning as defined above.

Formulae (7) and (8) are respectively called phenol-series couplers and naphthol-series couplers, and in the formulae R^{20} represents a hydrogen atom or a group selected from the group consisting of $-\text{CONR}^{22}\text{R}^{23}$, $-\text{SO}_2\text{NR}^{22}\text{R}^{23}$,

-NHCOR²², -NHCONR²²R²³, and -NHSO₂NR²²R²³. R²² and R²³ each represent a hydrogen atom or a substituent. In formulae (7) and (8), R²¹ represents a substituent, l is an integer selected from 0 to 2, and m is an integer selected from 0 to 4. When l and m are 2 or more, R²¹'s may be different. The substituents of R²¹ to R²³ include those mentioned above as examples for X¹ to X⁵ of formulae (II) and (IV). Y has the same meaning as defined above.

Preferable examples of the phenol-series couplers represented by formula (7) include 2-acylamino-5-alkylphenol couplers described, for example, in U.S. Patent Nos. 2,369,929, 2,801,171, 2,772,162, 2,895,826, and 3,772,002; 2,5-diacylaminophenol couplers described, for example, in U.S. Patent Nos. 2,772,162, 3,758,308, 4,126,396, 4,334,011, and 4,327,173, West Germany Patent Publication No. 3,329,729, and JP-A No. 166956/1984; and 2-phenylureido-5-acylamino-phenol couplers described, for example, in U.S. Patent Nos. 3,446,622, 4,333,999, 4,451,559, and 4,427,767. Y has the same meaning as defined above.

Preferable examples of the naphthol-series couplers represented by formula (8) include 2-carbamoyl-1-naphthol couplers described, for example, in U.S. Patent Nos. 2,474,293, 4,052,212, 4,146,396, 4,282,233, and 4,296,200; and 2-carbamoyl-5-amido-1-naphthol couplers described, for example, in U.S. Patent No. 4,690,889. Y has the same meaning as defined above.

Formulas (9) to (12) are couplers called pyrrolotriazoles, and R³², R³³, and R³⁴ each represent a hydrogen atom or a substituent. Y has the same meaning as defined above. Examples of the substituent of R³², R³³, and R³⁴ include those mentioned for X¹, X², X³, X⁴, and X⁵. Preferable examples of the pyrrolotriazole-series couplers represented by formulae (9) to (12) include those wherein at least one of R³² and R³³ is an electron-attracting group, which specific couplers are described in European Patent Nos. 488,248A1, 491,197A1, and 545,300. Y has the same meaning as defined above.

Further, a fused-ring phenol, imidazole, pyrrole, 3-hydroxypyridine, active methylene (other than those mentioned above), active methine, 5,5-ring-fused heterocyclic, and 5,6-ring-fused heterocyclic coupler, can be used.

As the fused-ring phenol-series couplers, those described, for example, in U.S. Patent Nos. 4,327,173, 4,564,586, and 4,904,575, can be used.

As the imidazole-series couplers, those described, for example, in U.S. Patent Nos. 4,818,672 and 5,051,347, can be used.

As the 3-hydroxypyridine-series couplers, those described, for example, in JP-A No. 315736/1989, can be used.

As the active methylene-series and active methine-series couplers, those described, for example, in U.S. Patent Nos. 5,104,783 and 5,162,196, can be used.

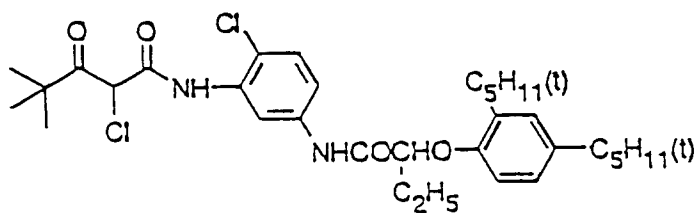
As the 5,5-ring-fused heterocyclic couplers, for example, pyrrolopyrazole couplers described in U.S. Patent No. 5,164,289, and pyrroloimidazole couplers described in JP-A No. 174429/1992, can be used.

As the 5,6-ring-fused heterocyclic couplers, for example, pyrazolopyrimidine couplers described in U.S. Patent No. 4,950,585, pyrrolotriazine couplers described in JP-A No. 204730/1992, and couplers described in European Patent No. 556,700, can be used.

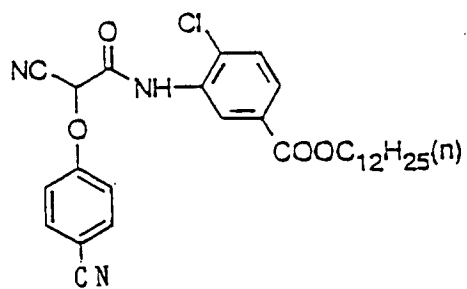
In the present invention, in addition to the above couplers, use can be made of couplers described, for example, in West Germany Patent Nos. 3,819,051A and 3,823,049, U.S. Patent Nos. 4,840,883, 5,024,930, 5,051,347, and 4,481,268, European Patent Nos. 304,856A2, 329,036, 354,549A2, 374,781A2, 379,110A2, and 386,930A1, and JP-A Nos. 141055/1988, 32260/1989, 32261/1989, 297547/1990, 44340/1990, 110555/1990, 7938/1991, 160440/1991, 172839/1991, 172447/1992, 179949/1992, 182645/1992, 184437/1992, 188138/1992, 188139/1992, 194847/1992, 204532/1992, 204731/1992, and 204732/1992.

Specific examples of the couplers that can be used in the present invention are shown below, but, of course, the present invention is not limited to them:

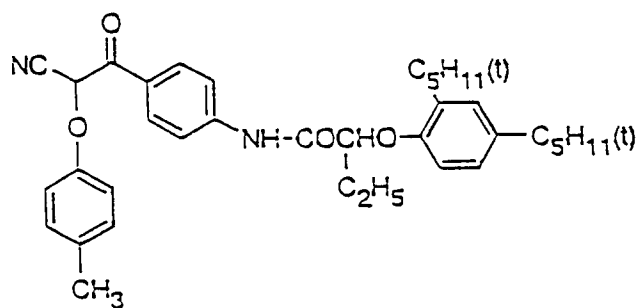
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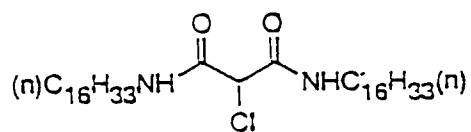
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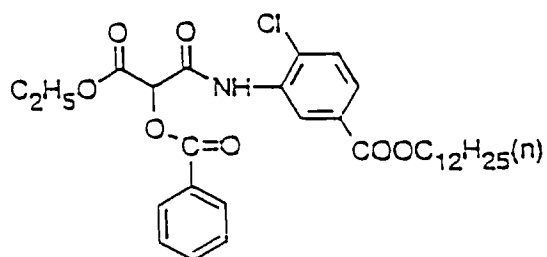
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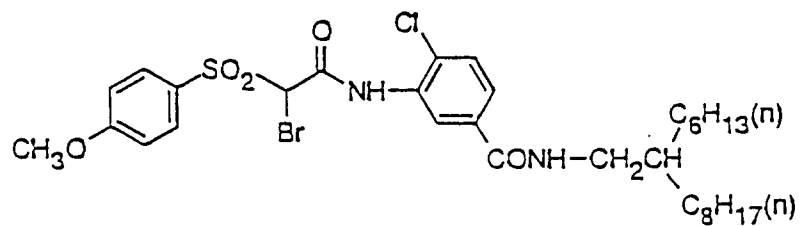
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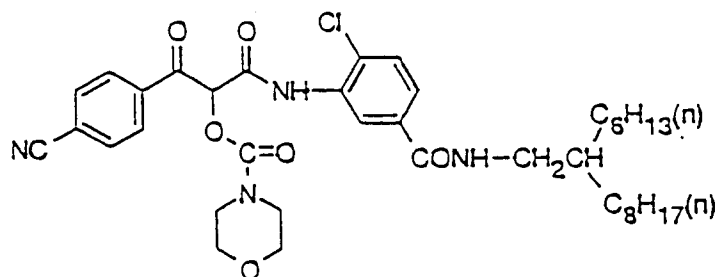
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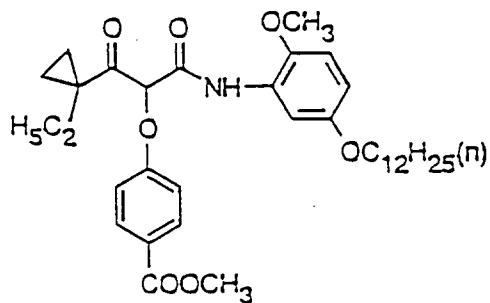
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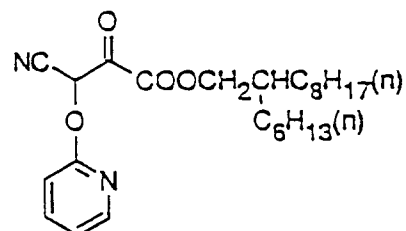
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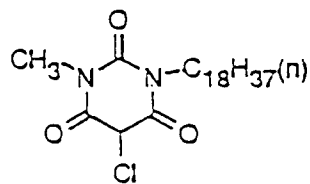
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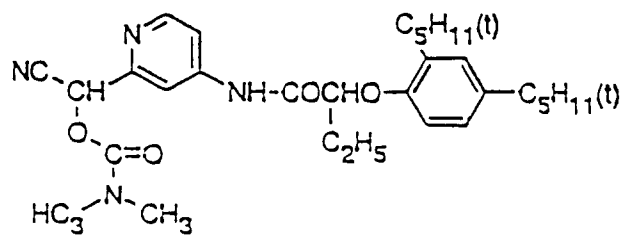
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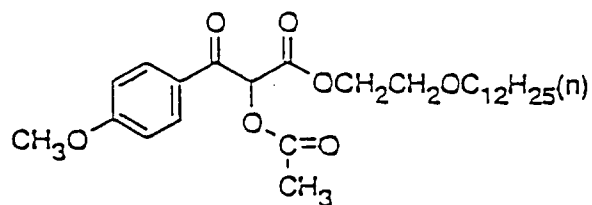
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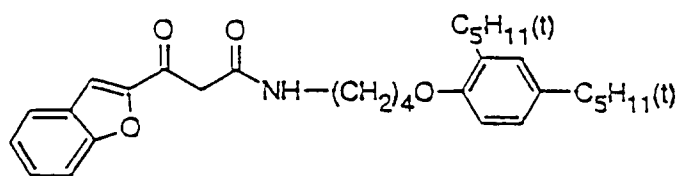
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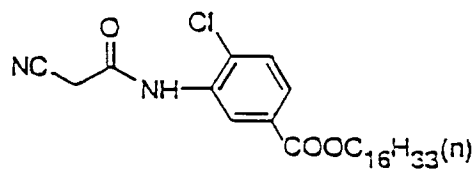
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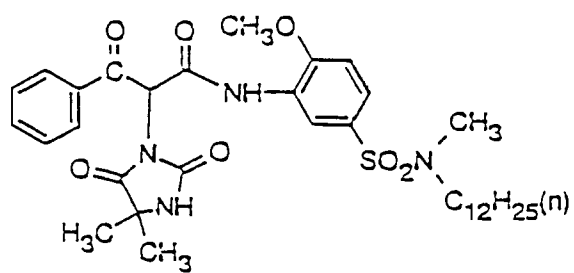
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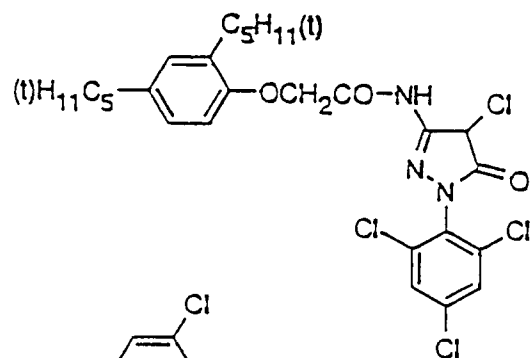
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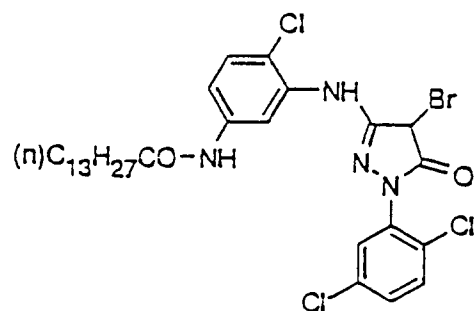
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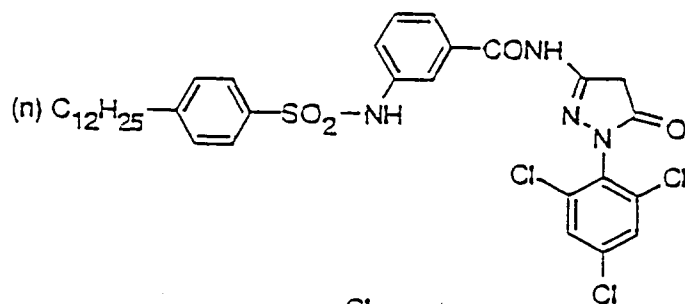
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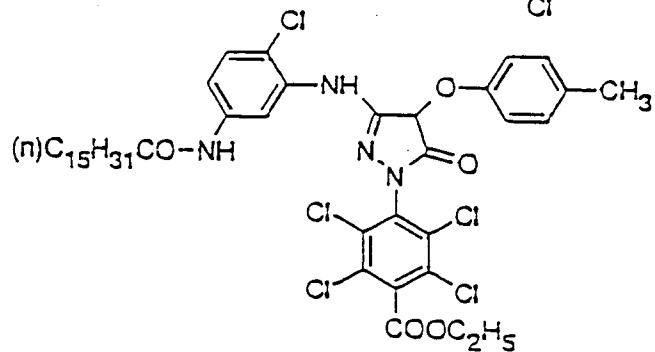
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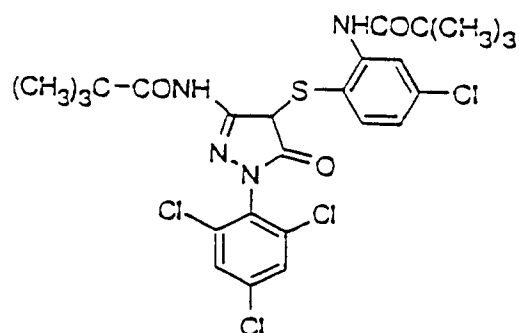
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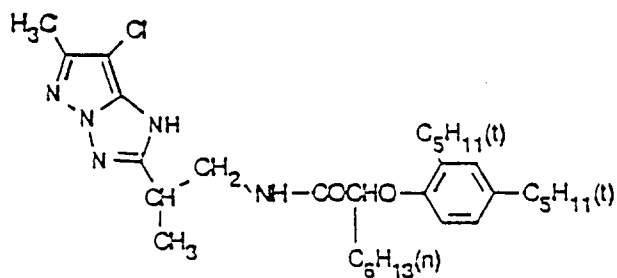
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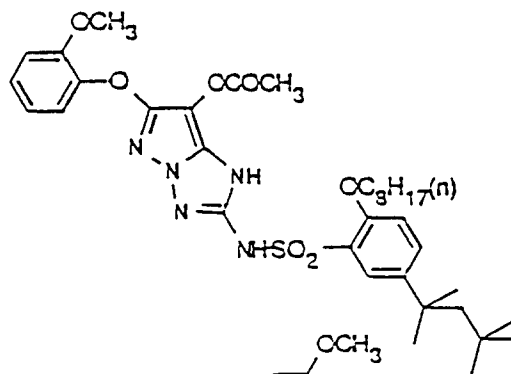
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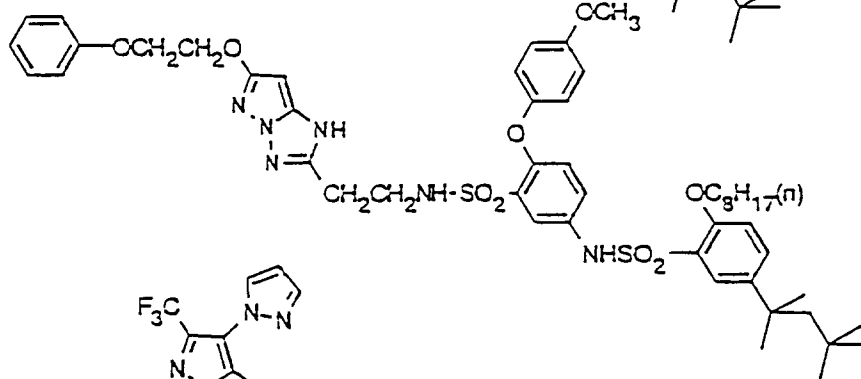
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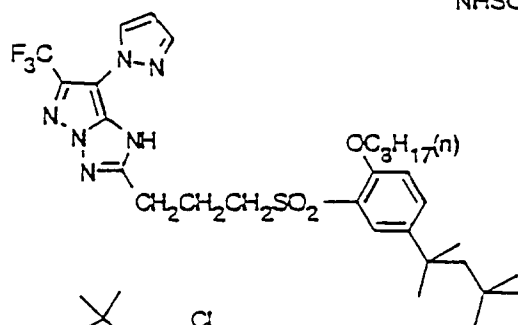
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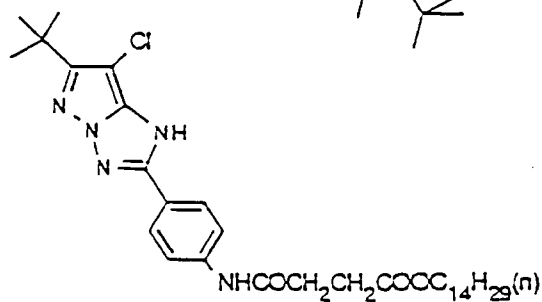
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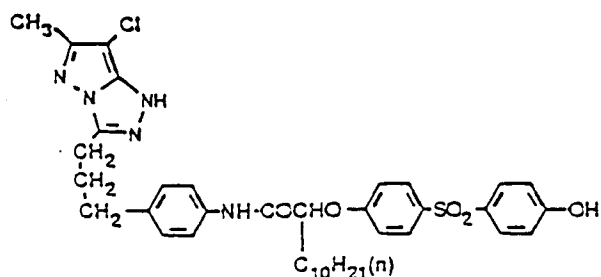
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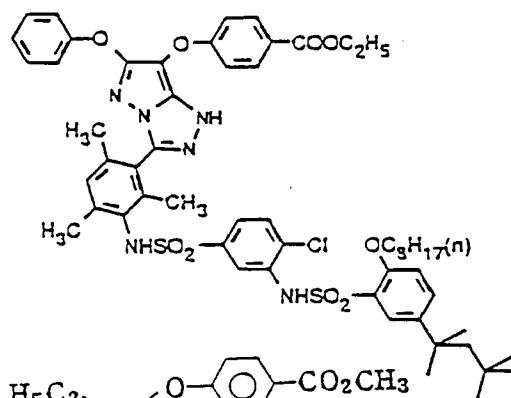
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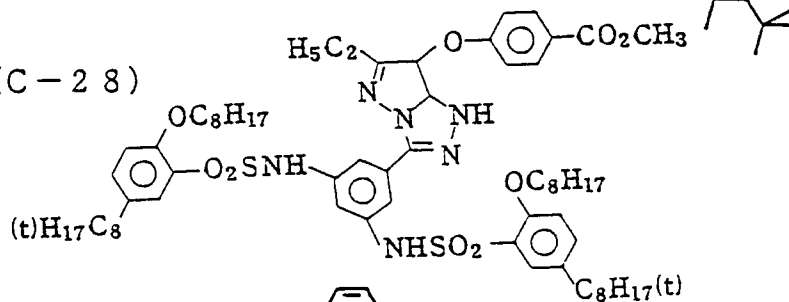
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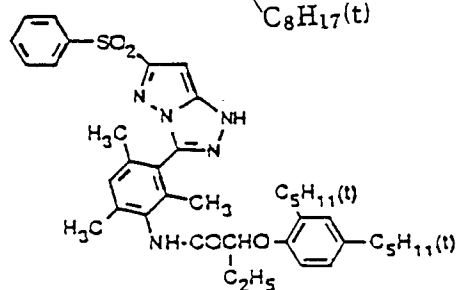
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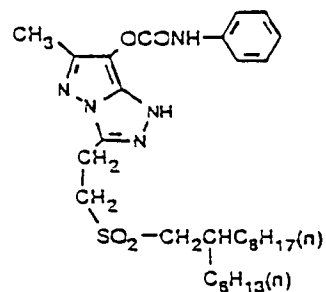
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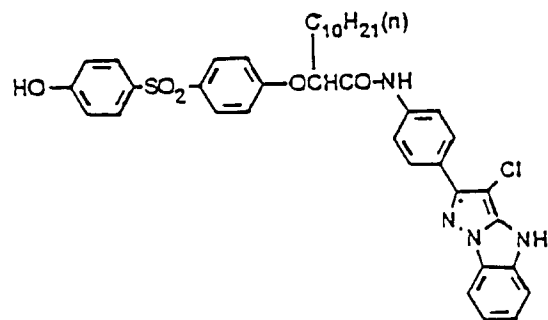
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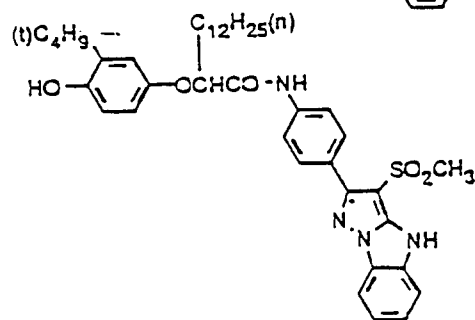
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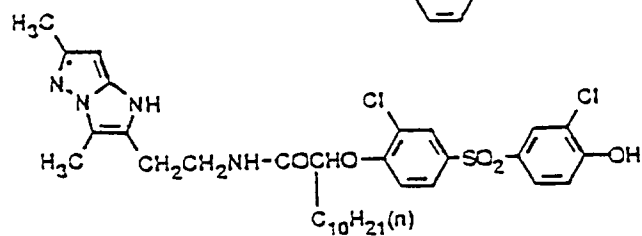
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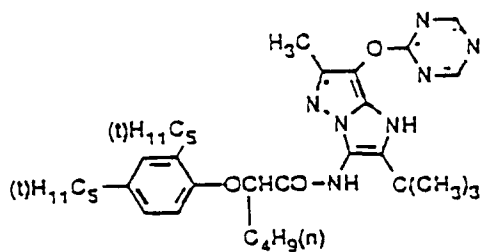
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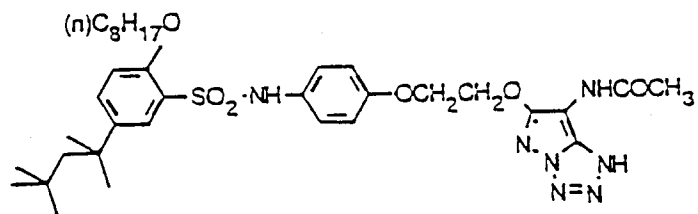
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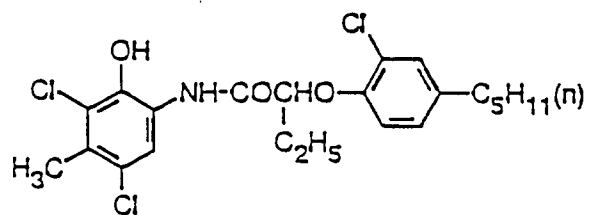
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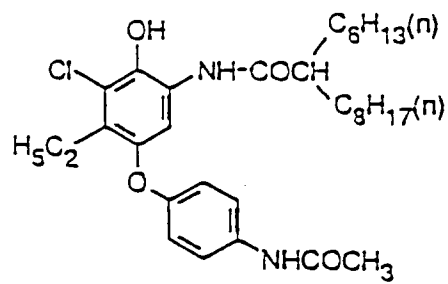
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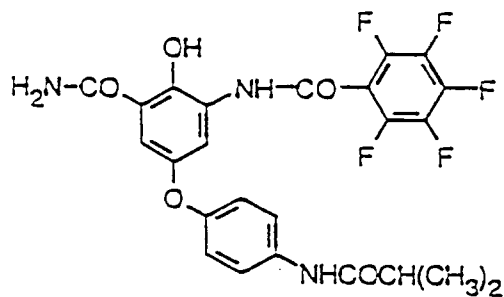
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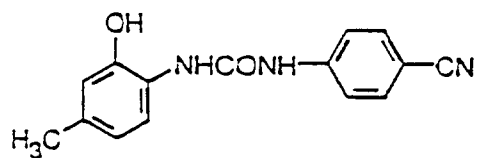
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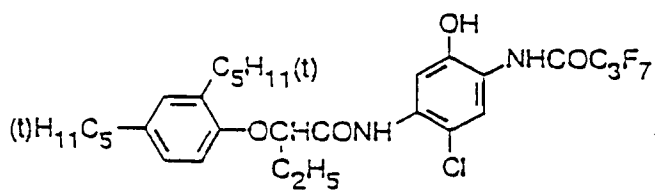
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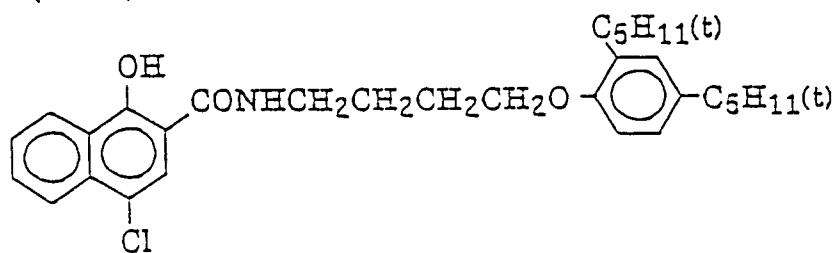
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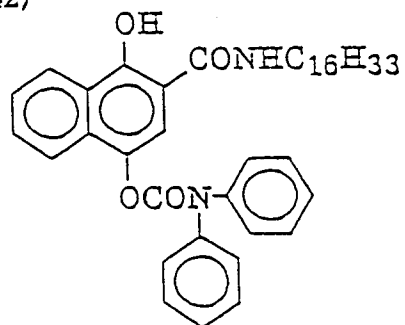
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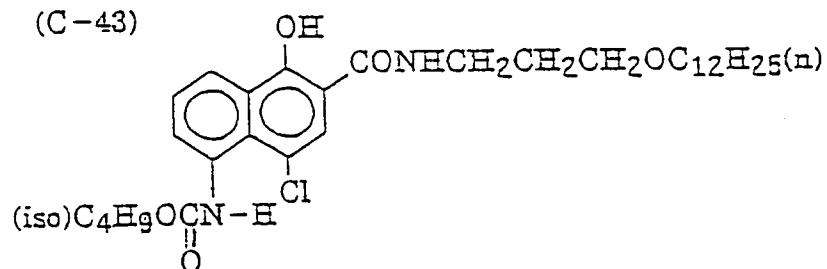
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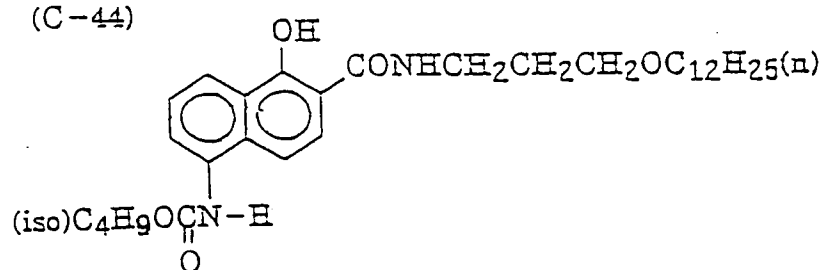
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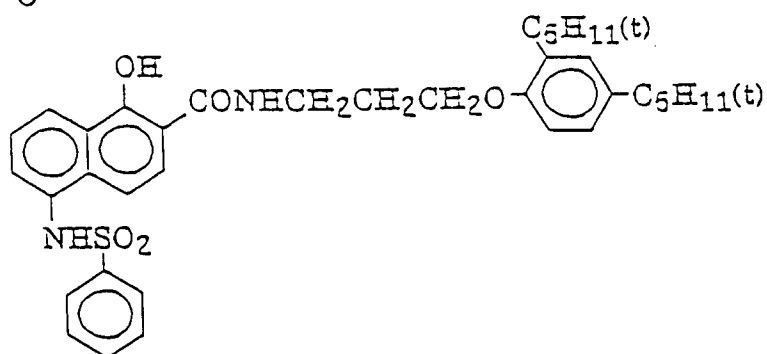
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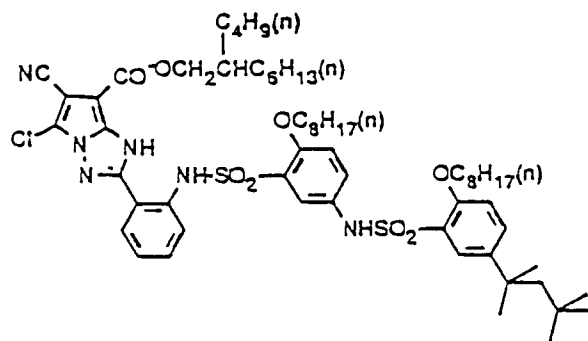
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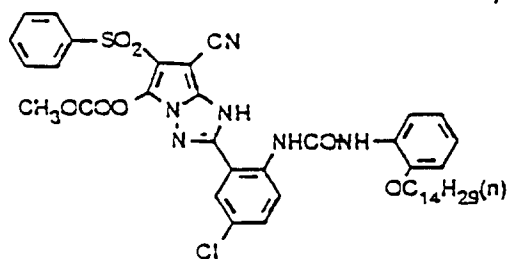
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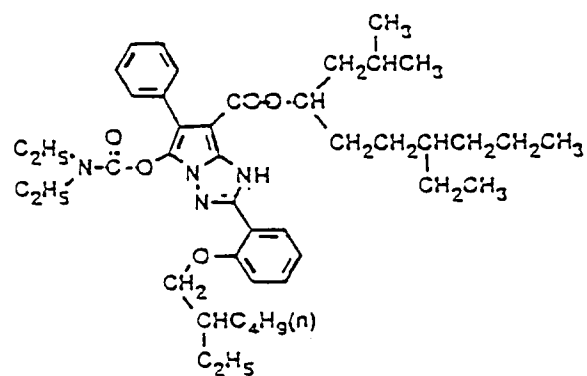
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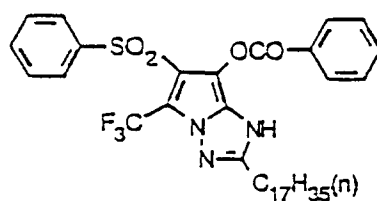
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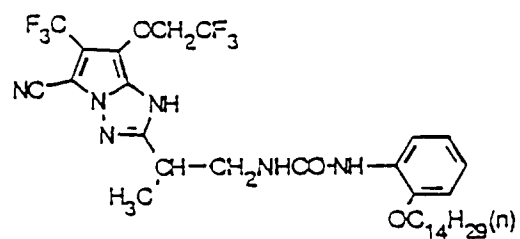
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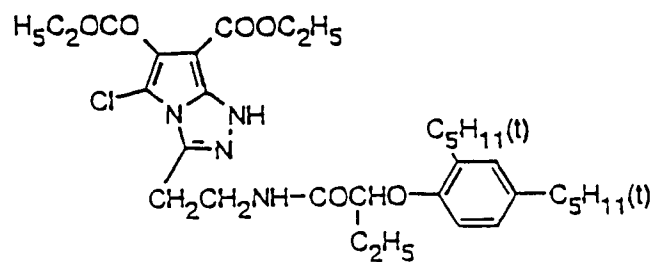
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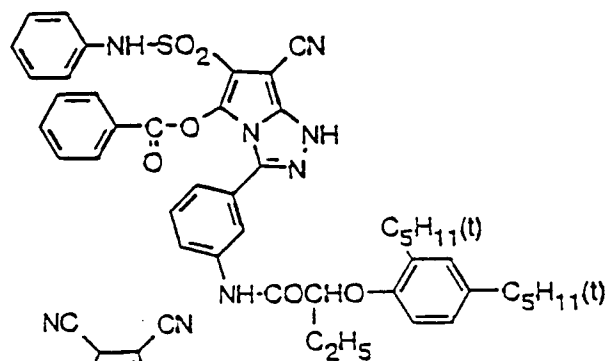
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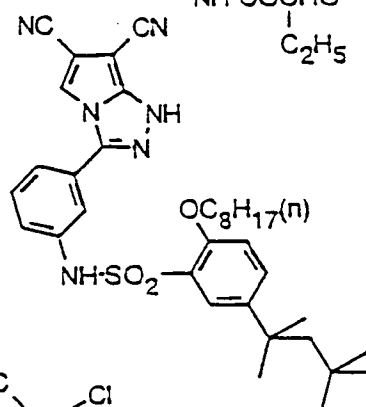
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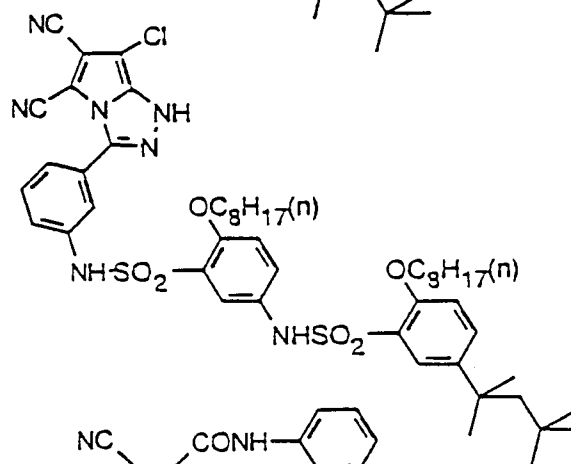
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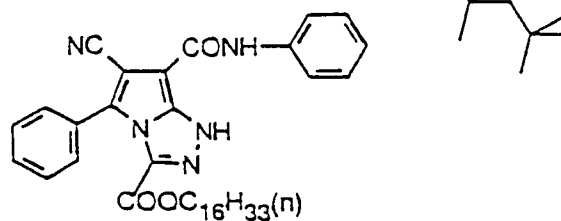
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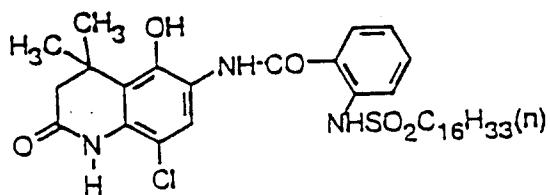
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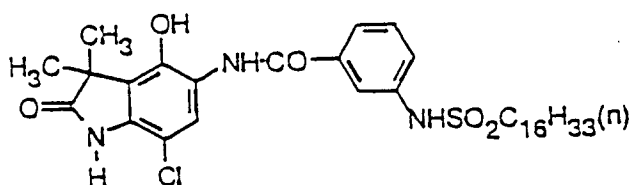
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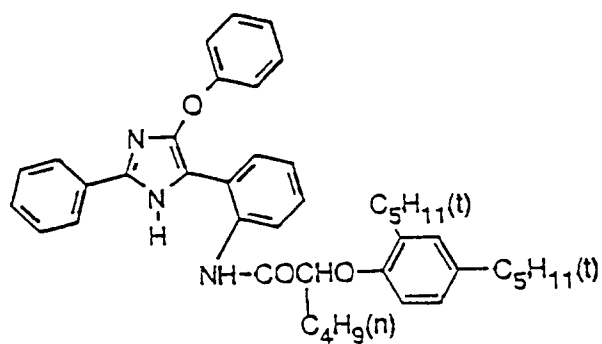
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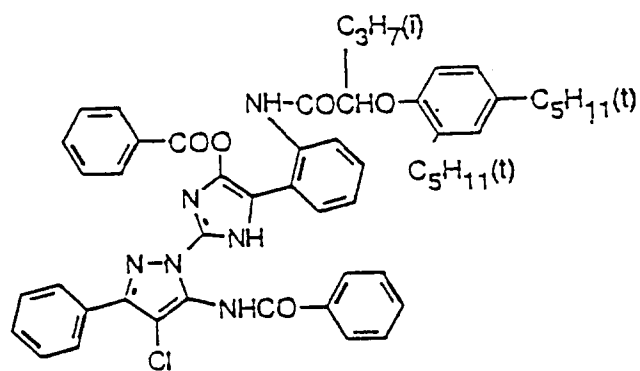
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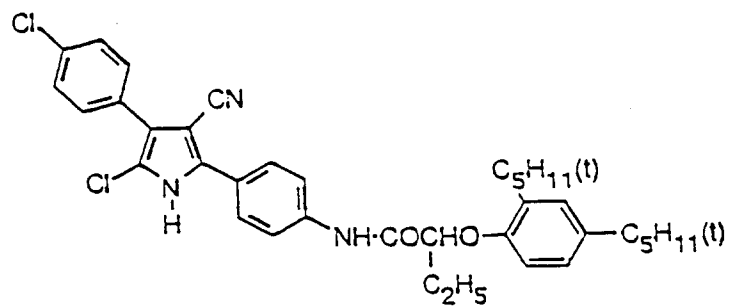
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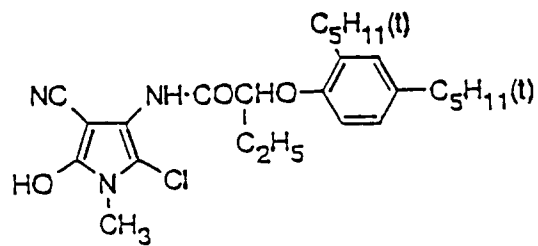
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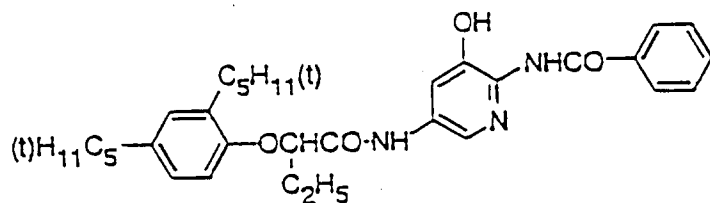
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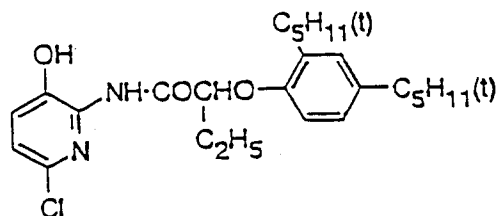
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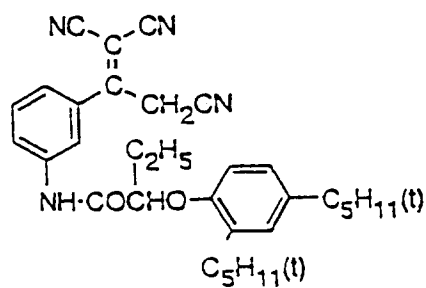
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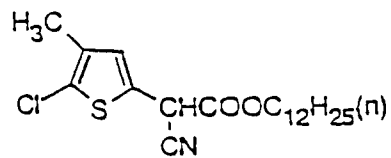
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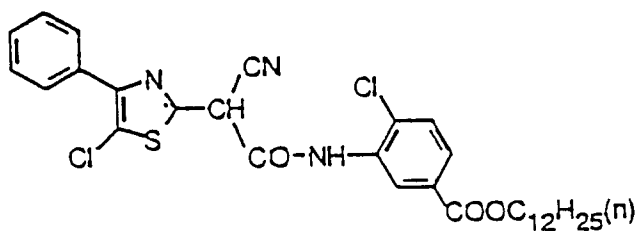
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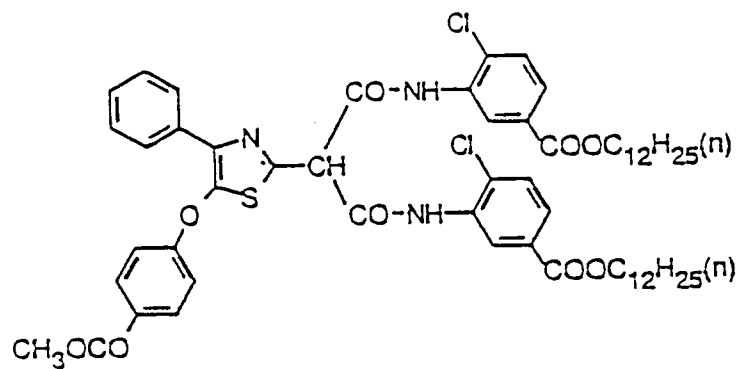
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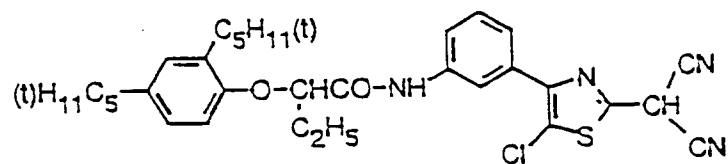
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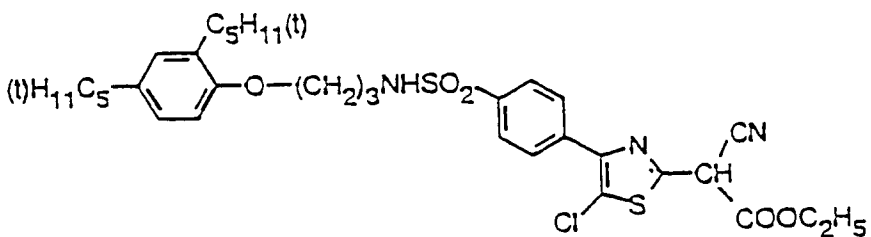
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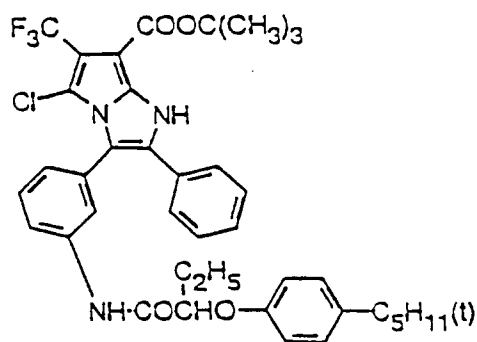
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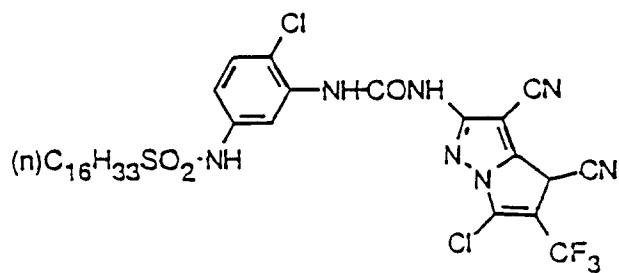
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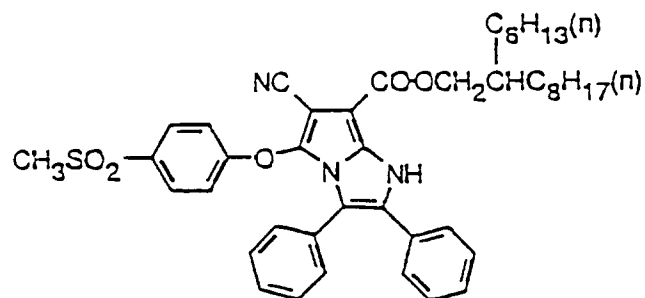
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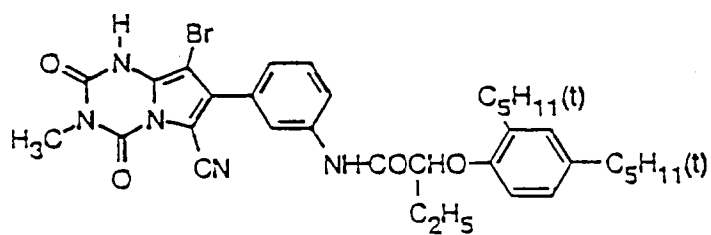
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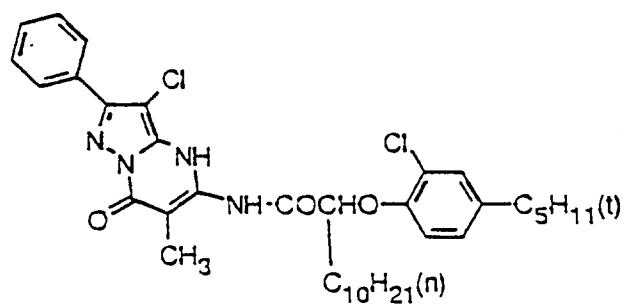
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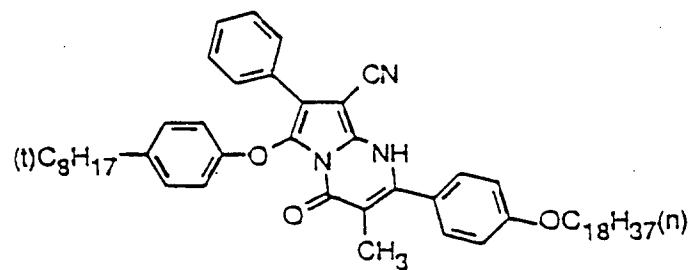
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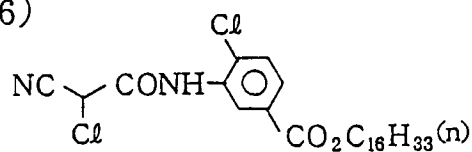
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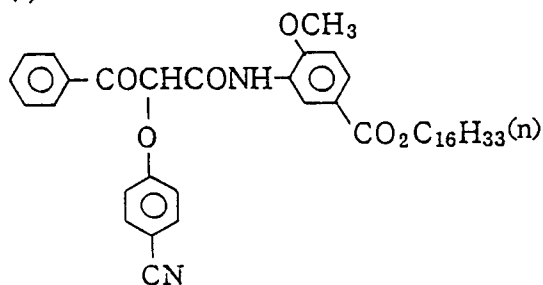
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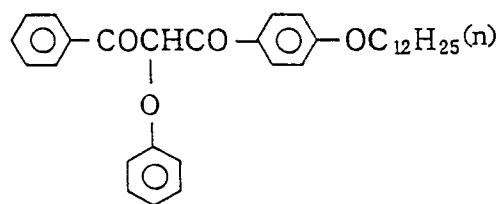
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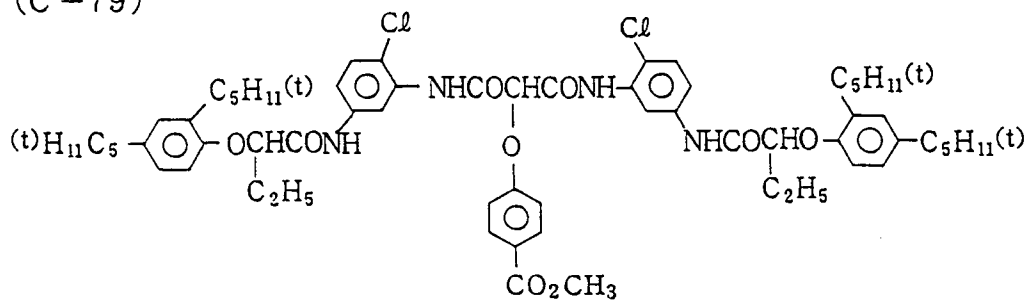
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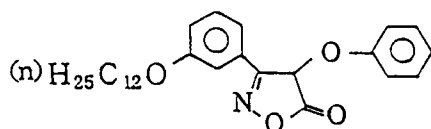
(C-78)



(C-79)



(C-80)



The color-forming reducing agent according to the present invention is preferably used in an amount of 0.01 to 10 mmol/m² in one color-forming layer, in order to obtain satisfactory color density. More preferably the amount to be used is 0.05 to 5 mmol/m², and particularly preferably 0.1 to 1 mmol/m².

A preferable amount of the coupler to be used in the color-forming layer in which the color-forming reducing agent

according to the present invention is used, is 0.05 to 20 times, more preferably 0.1 to 10 times, and particularly preferably 0.2 to 5 times, the amount of the color-forming reducing agent in terms of mol.

The color light-sensitive material of the present invention comprises, basically, at least one photographic constitutional layer comprising a hydrophilic colloid layer coated on a support (base), and in at least one photographic constitutional layer is contained a photosensitive silver halide, a coupler for forming a dye (also referred to as a dye-forming coupler or a coupler), a color-forming reducing agent, and a sulfinic acid compound.

The dye-forming coupler, the color-forming reducing agent and the sulfinic acid compound to be used in the present invention are added to the same layer, which is the most general mode, but they may be added separately to separate layers if they are placed in the reactive state. Preferably these components are added to a silver halide emulsion layer of the light-sensitive material or a layer adjacent to it, and particularly preferably all of these components are added to a silver halide emulsion layer.

The color-forming reducing agent, the sulfinic acid compound, and the coupler according to the present invention can be introduced into the light-sensitive material by various known dispersion methods. Preferably the oil-in-water dispersion method is used, in which they are dissolved in a high-boiling organic solvent (and, if necessary, together with a low-boiling organic solvent), the solution is emulsified and dispersed in an aqueous gelatin solution, and the emulsified dispersion is added to a silver halide emulsion. The high-boiling organic solvent to be used in the present invention is preferably a compound nonmiscible with water, and having a melting point of 100 °C or below and a boiling point of 140 °C or over, that is a good solvent for the color-forming reducing agents, sulfinic acid compounds, and couplers. The melting point of the high-boiling organic solvent is preferably 80 °C or below. The boiling point of the high-boiling organic solvent is more preferably 160 °C or over, and even further preferably 170 °C or over. Details of these high-boiling organic solvents are described in JP-A No. 215272/1987, page 137, lower right column, to page 144, upper right column. In the present invention, the amount of the high-boiling organic solvent to be used may be any amount, but preferably the amount is such that the weight ratio of the high-boiling organic solvent to the color-forming reducing agent is from 20 or less : 1, more preferably from 0.02 to 5 : 1, and particularly preferably from 0.2 to 4 : 1.

Further, in the present invention, known polymer dispersion methods can be used. Specific examples of steps, effects, and latexes for impregnation of the latex dispersion method, which is one polymer dispersion method, are described, for example, in U.S. Patent No. 4,199,363, West Germany Patent Application (OLS) Nos. 2,541,274 and 2,541,230, JP-B ("JP-B" means examined Japanese patent publication) No. 41091/1978, and European Patent Publication No. 029104, and as a more preferable method, a dispersion method using a polymer which is water-insoluble and organic solvent-soluble is described in PCT International Publication No. WO 88/00723.

The lipophilic fine particles containing the color-forming reducing agent according to the present invention may have any average grain size. In light of color-forming property, the average particle size is preferably 0.05 to 0.3 µm, and further preferably 0.05 to 0.2 µm.

To make the average particle size of lipophilic fine particles small is generally accomplished, for example, by choosing a type of surface-active agent, by increasing the amount of the surface-active agent to be used, by elevating the viscosity of the hydrophilic colloid solution, by lowering the viscosity of the lipophilic organic layer, through use of an additional low-boiling organic solvent, by increasing the rotational frequency of the stirring blades of an emulsifying apparatus, to increase the shearing force, or by prolonging the emulsifying time.

The particle size of lipophilic fine particles can be measured by an apparatus, such as a Nanosizer (trade name, manufactured by British Coulter Co.).

In the present invention, when the dye that is produced from the color-forming reducing agent and the dye-forming coupler is a diffusible dye, preferably a mordant is added to the light-sensitive material. If the present invention is applied to such a mode, it is not required to dip the material in an alkali to form color, and therefore image stability after processing is remarkably improved. Although the mordant according to the present invention can be used in any layer, if the mordant is added to a layer containing the color-forming reducing agent according to the present invention, the stability of the color-forming reducing agent is deteriorated. Therefore preferably the mordant is used in a layer that does not contain the color-forming reducing agent according to the present invention. Further, the dye that is produced from a color-forming reducing agent and a coupler diffuses into the gelatin film that has been swelled during the processing, to dye the mordant. Therefore, in order to obtain good sharpness, the shorter the diffusion distance is, the more preferred it is. Accordingly, the layer to which the mordant is added is preferably a layer adjacent to the layer containing the color-forming reducing agent.

Further, since the dye that is produced from the color-forming reducing agent according to the present invention and the coupler for use in the present invention is a water-soluble dye, there is a possibility that the dye may flow out into the processing solution. Therefore, to prevent this, preferably the layer to which the mordant is added is situated on the same side of the base and opposite to (more remote from the base than) the layer containing the color-forming reducing agent. However, when a barrier layer, as described in JP-A No. 168335/1995, is provided on the same side of the base and opposite to (more remote from the base than) a layer in which the mordant is added, also preferably the layer in which the mordant is added, is situated on the same side of the base and nearer the base than the layer containing the color-forming reducing agent.

Further, the mordant for use in the present invention may also be added to several layers, and in particular, when several layers contain the color-forming reducing agent, also preferably the mordant is added to each layer adjacent thereto.

The coupler that forms a diffusible dye may be any coupler that results in a diffusible dye formed by coupling with the color-forming reducing agent according to the present invention, the resultant diffusible dye being capable of reaching the mordant. Preferably the coupler is a coupler that results in a diffusible dye having one or more dissociable groups with a pKa (an acid dissociation constant) of 12 or less, more preferably 8 or less, and particularly preferably 6 or less. Preferably the molecular weight of the diffusible dye that will be formed is 200 or more but 2,000 or less. Further, preferably the ratio (the molecular weight of the dye that will be formed/the number of dissociable groups with a pKa of 12 or less) is 100 or more but 2,000 or less, and more preferably 100 or more but 1,000 or less. Herein the value of pKa is the value measured by using, as a solvent, dimethylformamide/water (1 : 1).

The coupler that forms a diffusible dye is preferably one that results in a diffusible dye formed by coupling with the color-forming reducing agent according to the present invention, the resultant diffusible dye being dissolvable, in an alkali solution having a pH of 11, in an amount of 1×10^{-6} mol/liter or more, more preferably 1×10^{-5} mol/liter or more, and particularly preferably 1×10^{-4} mol/liter or more, at 25 °C. Further, the coupler that forms a diffusible dye is preferably one that results in a diffusible dye formed by coupling with the color-forming reducing agent according to the present invention, the resultant diffusible dye having a diffusion constant of 1×10^{-8} m²/s⁻¹ or more, more preferably 1×10^{-7} m²/s⁻¹ or more, and particularly preferably 1×10^{-6} m²/s⁻¹ or more, at 25 °C when dissolved in an alkali solution of pH 11, at a concentration of 10^{-4} mol/liter.

The mordant that can be used in the present invention can be suitably chosen from among mordants that are usually used, and among them, in particular, polymer mordants are preferable. Herein, by polymer mordant is meant a polymer containing a tertiary amino group, polymers having a nitrogen-containing heterocyclic moiety, polymers containing a quaternary cation group thereof, etc.

Preferable specific examples of homopolymers and copolymers containing vinyl monomer units with a tertiary imidazole group are described, for example, in U.S. Patent Nos. 4,282,305, 4,115,124, and 3,148,061 and JP-A Nos. 118834/1985, 122941/1985, 244043/1987, and 244036/1987.

Preferable specific examples of homopolymers and copolymers containing vinyl monomer units with a quaternary imidazolium salt are described, for example, in British Patent Nos. 2,056,101, 2,093,041, and 1,594,961, U.S. Patent Nos. 4,124,386, 4,115,124, and 4,450,224, and JP-A No. 28325/1973.

Further, preferable specific examples of homopolymers and copolymers having vinyl monomer units with a quaternary ammonium salt are described, for example, in U.S. Patent Nos. 3,709,690, 3,898,088, and 3,958,995, and JP-A Nos. 57836/1985, 60643/1985, 122940/1985, 122942/1985, and 235134/1985.

Further, vinylpyridine polymers and vinylpyridinium cation polymers, as disclosed, for example, in U.S. Patent Nos. 2,548,564, 2,484,430, 3,148,161, and 3,756,814; polymer mordants capable of being crosslinked to gelatin or the like, as disclosed, for example, in U.S. Patent Nos. 3,625,694, 3,859,096, and 4,128,538, and British Patent No. 1,277,453; aqueous soltype mordants disclosed, for example, in U.S. Patent Nos. 3,958,995, 2,721,852, and 2,798,063, and JP-A Nos. 115228/1979, 145529/1979, and 26027/1979; water-insoluble mordants disclosed in U.S. Patent No. 3,898,088; reactive mordants capable of covalent bonding to dyes, as disclosed in U.S. Patent No. 4,168,976 (JP-A No. 137333/1979); and mordants disclosed in U.S. Patent Nos. 3,709,690, 3,788,855, 3,642,482, 3,488,706, 3,557,066, and 3,271,147, and JP-A Nos. 71332/1975, 30328/1978, 155528/1977, 125/1978, and 1024/1978, can all be mentioned.

Still further, mordants described in U.S. Patent Nos. 2,675,316 and 2,882,156 can be mentioned.

The molecular weight of the polymer mordants for use in the present invention is suitably 1,000 to 1,000,000, and particularly preferably 10,000 to 200,000.

The above polymer mordants are used generally by mixing them with a hydrophilic colloid. As the hydrophilic colloid, a hydrophilic colloid and/or a highly hygroscopic polymer can be used, and gelatin is most typically used. The mixing ratio of the polymer mordant to the hydrophilic colloid, and the coating amount of the polymer mordant, can be determined easily by those skilled in the art in accordance with the amount of the dye to be mordanted, the type and composition of the polymer mordant, and the image formation process to be used. Preferably the mordant/hydrophilic colloid ratio is from 20/80 to 80/20 (by weight), and the coating amount of the mordant is suitably 0.2 to 15 g/m², and preferably 0.5 to 8 g/m², for use.

In the present invention, preferably an auxiliary developing agent and/or its precursor are used in the light-sensitive material. These compounds are described below.

By the auxiliary developing agent that may be used in the present invention, is meant a compound having a function for promoting the transfer of electrons from a color-forming reducing agent to a silver halide, in the process of development of silver halide grains. Preferably the auxiliary developing agent is a compound that can develop silver halide grains that have been exposed to light, and its oxidation product can oxidize (hereinafter referred to as cross-oxidize) a color-forming reducing agent.

As the auxiliary developing agent that may be used in the present invention, preferably pyrazolidones, dihydroxy-

benzenes, reductones, or aminophenols are used, with particular preference given to pyrazolidones. Preferably the diffusibility of these compounds in hydrophilic colloid layers is low, and, for example, the solubility (25 °C) in water is preferably 0.1% or less, more preferably 0.05% or less, and particularly preferably 0.01% or less.

The precursor of the auxiliary developing agent that may be used in the present invention is a compound that can exist stably in the light-sensitive material, but it can quickly release the above auxiliary developing agent, upon processing with a processing solution. When this compound is used, preferably the diffusibility in hydrophilic colloid layers is low. For example, the solubility (25 °C) in water is preferably 0.1% or less, more preferably 0.05% or less, and particularly preferably 0.01% or less. There is no particular restriction on the solubility of the auxiliary developing agent that will be released from the precursor, but preferably the solubility of the auxiliary developing agent itself is low.

Preferably the auxiliary developing agent precursor for use in the present invention is represented by formula (A):



wherein A represents a blocking group whose bond to $(L)_n-PUG$ will be split upon development processing, L represents a linking group whose bond to PUG will be split off after the split of the bond between L and A in formula (A), n is an integer of 0 to 3, and PUG represents an auxiliary developing agent.

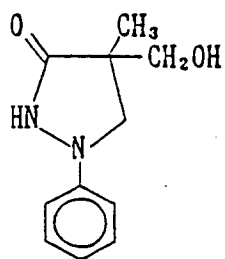
As the auxiliary developing agent, use can be made of compounds that can emit electrons in accordance with the Kendall-Pelz's rule, excluding p-phenylenediamine compounds, and preferably pyrazolidones mentioned above are used.

As the blocking group represented by A, the following known blocking groups can be used, for example: blocking groups, such as an acyl group and a sulfonyl group, as described, for example, in U.S. Patent No. 3,311,476; blocking groups that use the reverse Michael reaction, as described, for example, in JP-A No. 105642/1984; blocking groups that use quinonemethide or compounds similar to quinonemethide by intramolecular electron transfer, as described, for example, in JP-A No. 280140/1990; blocking groups that use an intramolecular nucleophilic substitution reaction, as described, for example, in JP-A No. 318555/1988 (European Patent Publication No. 0295729); blocking groups that use an addition reaction of a nucleophilic agent to a conjugated unsaturated bond, as described, for example, in JP-A No. 186344/1992; blocking groups that use a β -elimination reaction, as described in JP-A No. 163051/1987; blocking groups that use a nucleophilic substitution reaction of diarylmethanes, as described in JP-A No. 188540/1986; blocking groups that use a Lossen rearrangement reaction, as described in JP-A No. 187850/1987; blocking groups that use a reaction of an N-acyl product of thiazolidin-2-thione with an amine, as described in JP-A No. 147457/1987; and blocking groups that have two electrophilic groups and react with two nucleophilic agents, as described in International Publication Patent No. 93/03419.

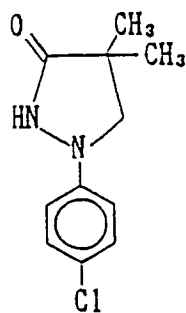
The group represented by L is a linking group that can be split from the group represented by A, upon development processing, and that then can split $(L)_{n-1}-PUG$. There are no particular restrictions on the linking group, as long as that function is attained.

Specific examples of the auxiliary developing agent and its precursor are shown below, but compounds that may be used in the present invention are not restricted to these examples.

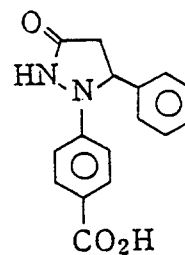
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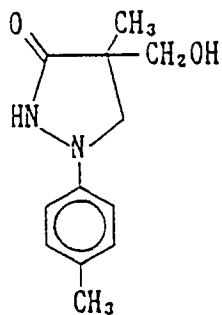
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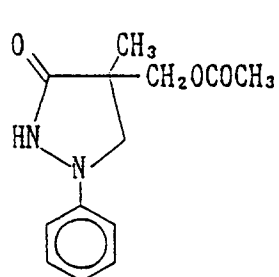
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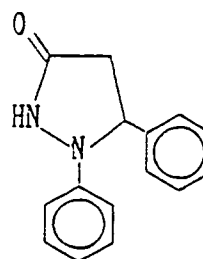
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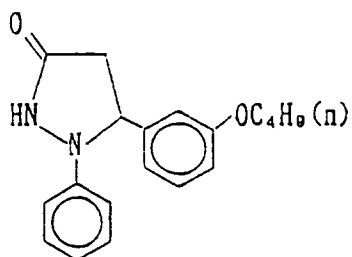
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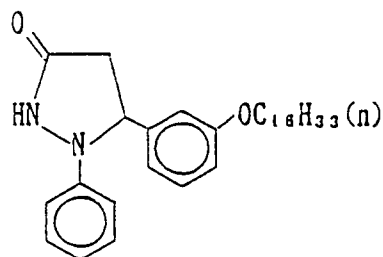
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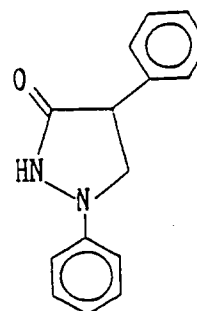
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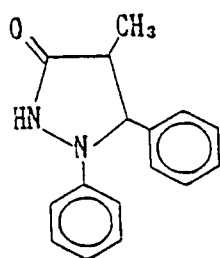
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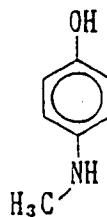
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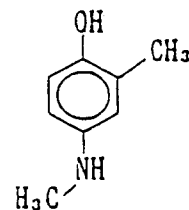
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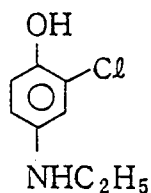
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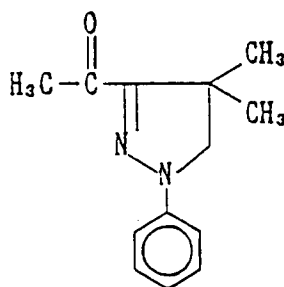
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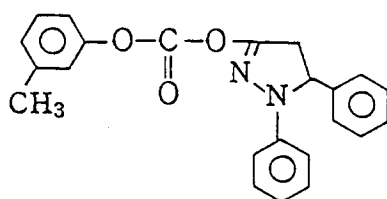
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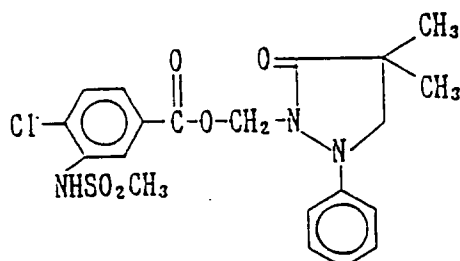
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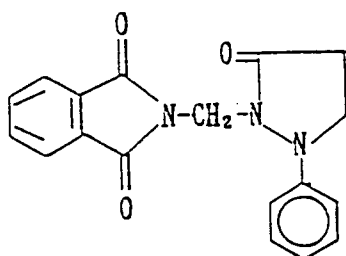
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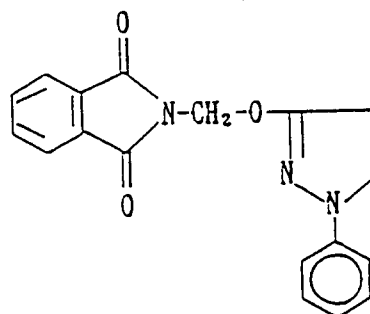
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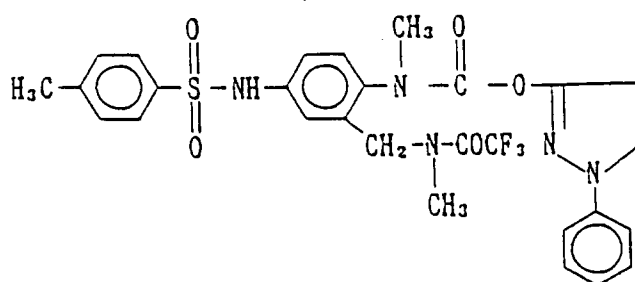
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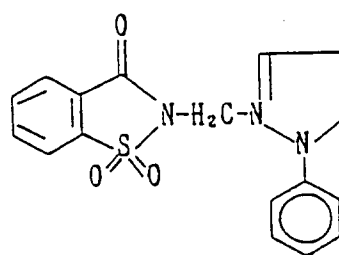
(E T A - 18)



(E T A - 19)



(E T A - 20)



These compounds may be added to any of light-sensitive layers, intermediate layers, undercoat layers, and protective layers. When the auxiliary developing agent is contained, it is preferably added to non-light-sensitive layers, for use.

To incorporate these compounds into the light-sensitive material, use can be made of, for example, a method wherein the compound is dissolved in an organic solvent miscible with water, such as methanol, and the solution is added directly to a hydrophilic colloid layer; a method wherein an aqueous solution or colloid dispersion of the compound prepared in the presence of a surface-active agent, is added; a method wherein the compound is dissolved in a

solvent or oil substantially immiscible with water, the solution is dispersed in water or a hydrophilic colloid, and the dispersion is added; or a method wherein the compound in the state of a solid fine particle dispersion is added, and these conventionally known methods can be applied alone or in combination. Details of a method of preparing a solid fine particle dispersion are described in JP-A No. 235044/1992, page 20.

5 The amount to be added to the light-sensitive material is generally 1 to 200 mol%, preferably 5 to 100 mol %, and more preferably 10 to 50 mol%, based on the color-forming reducing agent.

As the support to be used in the present invention, any support can be used if it is a transmissible support or a reflective support, on which a photographic emulsion layer can be coated, such as glass, paper, and plastic film. As the plastic film to be used in the present invention, for example, polyester films made, for example, of polyethylene terephthalates, polyethylene naphthalates, cellulose triacetate, or cellulose nitrate; polyamide films, polycarbonate films, and polystyrene films can be used.

10 "The reflective support" that can be used in the present invention refers to a support that increases the reflecting properties to make bright the dye image formed in the silver halide emulsion layer, and such a reflective support includes a support coated with a hydrophilic resin containing a light-reflecting substance, such as titanium oxide, zinc oxide, calcium oxide, and calcium sulfate, dispersed therein, or a support made of a hydrophilic resin itself containing a dispersed light-reflecting substance. Examples are a polyethylene-coated paper, a polyester-coated paper, a polypropylene-series synthetic paper, a support having a reflective layer or using a reflecting substance, such as a glass sheet; a polyester film made, for example, of a polyethylene terephthalate, cellulose triacetate, or cellulose nitrate; a polyamide film, a polycarbonate film, a polystyrene film, and a vinyl chloride resin. As the polyester-coated paper, particularly a
20 polyester-coated paper whose major component is a polyethylene terephthalate, as described in European Patent EP 0,507,489, is preferably used.

The reflective support to be used in the present invention is preferably a paper support, both surfaces of which are coated with a water-resistant resin layer, and at least one of the water-resistant resin layers contains fine particles of a white pigment. Preferably the particles of a white pigment are contained in a density of 12% or more by weight, and
25 more preferably 14% or more by weight. Preferably the light-reflecting white pigment is kneaded well in the presence of a surface-active agent, and the surface of the pigment particles is treated with a dihydric to tetrahydric alcohol.

In the present invention, a support having the second kind diffuse reflective surface can also be used, preferably. "The second kind diffuse reflectivity" means diffuse reflectivity obtained by making a specular surface uneven, to form finely divided specular surfaces facing different directions. The unevenness of the second kind diffuse reflective surface has a three-dimensional average coarseness of generally 0.1 to 2 μm , and preferably 0.1 to 1.2 μm , for the center surface. Details about such a support are described in JP-A No. 239244/1990.

In order to obtain colors ranging widely on the chromaticity diagram by using three primary colors: yellow, magenta, and cyan, use is made of a combination of at least three silver halide emulsion layers photosensitive to respectively different spectral regions. For examples, a combination of three layers of a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, and a combination of a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive layer, and the like can be coated on the above support. The photosensitive layers can be arranged in various orders known generally for color light-sensitive materials. Further, each of these light-sensitive layers can be divided into two or more layers if necessary.

In the light-sensitive material, photographic constitutional layers comprising the above photosensitive layers and various non-light-sensitive layers, such as a protective layer, an underlayer, an intermediate layer, an antihalation layer, and a backing layer, can be provided. Further, in order to improve the color separation, various filter dyes can be added to the photographic constitutional layer.

As a binder or a protective colloid that can be used in the light-sensitive material according to the present invention, a gelatin is advantageously used, and other hydrophilic colloids can be used alone or in combination with a gelatin. The calcium content of gelatin is preferably 800 ppm or less, more preferably 200 ppm or less, and the iron content of the gelatin is preferably 5 ppm or less, more preferably 3 ppm or less. Further, in order to prevent the proliferation of various molds and fungi that will proliferate in a hydrophilic colloid layer, to deteriorate an image, preferably mildew-proofing agents, as described in JP-A No. 271247/1988, are added.

When the light-sensitive material of the present invention is subjected to printer exposure to light, it is preferable to use a band stop filter described in U.S. Patent No. 4,880,726, by which light color-mixing is removed, to noticeably improve color reproduction.

The light-sensitive material of the present invention is used in a print system using usual negative printers, and also it is preferably used for digital scanning exposure that uses monochromatic high-density light, such as a second harmonic generating light source (SHG) that comprises a combination of a nonlinear optical crystal with a semiconductor laser or a solid state laser using a semiconductor laser as an excitation light source, a gas laser, a light-emitting diode, or a semiconductor laser. To make the system compact and inexpensive, it is preferable to use a semiconductor laser or a second harmonic generating light source (SHG) that comprises a combination of a nonlinear optical crystal with a semiconductor laser or a solid state laser. Particularly, to design an apparatus that is compact, inexpensive, long in life, and high in stability, the use of a semiconductor laser is preferable, and it is desired to use a semiconductor laser for at
55

least one of the exposure light sources.

If such a scanning exposure light source is used, the spectral sensitivity maximum of the light-sensitive material of the present invention can arbitrarily be set by the wavelength of the light source for the scanning exposure to be used. In an SHG light source obtained by combining a nonlinear optical crystal with a semiconductor laser or a solid state laser that uses a semiconductor laser as an excitation light source, since the emitting wavelength of the laser can be halved, blue light and green light can be obtained. Therefore, the spectral sensitivity maximum of the light-sensitive material can be present in each of the usual three regions, the blue region, the green region and the red region. In order to use a semiconductor laser as a light source to make the apparatus inexpensive, high in stability, and compact, preferably each of at least two layers has a spectral sensitivity maximum at 670 nm or over. This is because the emitting wavelength range of the available, inexpensive, and stable III-V group semiconductor laser is present now only in from the red region to the infrared region. However, on the laboratory level, the oscillation of a II-VI group semiconductor laser in the green or blue region is confirmed and it is highly expected that these semiconductor lasers can be used inexpensively and stably if production technique for the semiconductor lasers is developed. In that event, the necessity that each of at least two layers has a spectral sensitivity maximum at 670 nm or over becomes lower.

In such scanning exposure, the time for which the silver halide in the light-sensitive material is exposed is the time for which a certain very small area is required to be exposed. As the very small area, the minimum unit that controls the quantity of light from each digital data is generally used and is called a picture element. Therefore, the exposure time per picture element is changed depending on the size of the picture element. The size of the picture element is dependent on the density of the picture element, and the actual range is from 50 to 2,000 dpi. If the exposure time is defined as the time for which a picture size is exposed with the density of the picture element being 400 dpi, preferably the exposure time is 10^{-4} sec or less, more preferably 10^{-6} sec or less. The lower limit is not particularly restricted, but it is preferably 10^{-8} sec. More preferably, the exposure time per picture element is in a range between 10^{-8} to 10^{-4} sec.

The silver halide grains used in the present invention are made of silver bromide, silver chloride, silver iodide, silver chlorobromide, silver chloriodide, silver iodobromide, or silver chloriodobromide. Other silver salts, such as silver rhodanate, silver sulfide, silver selenide, silver carbonate, silver phosphate, or a silver salt of an organic acid, may be contained in the form of independent grains or as part of silver halide grains. If it is desired to make the development/desilvering (bleaching, fixing, and bleach-fix) step rapid, a so-called high-silver-chloride grains having a silver chloride content of 90 mol% or more are desirable. Further, if the development is to be restrained moderately, it is preferable to contain silver iodide. The preferable silver iodide content varies depending on the intended light-sensitive material.

A high-silver-chloride emulsion used in the present invention preferably has a structure having a silver bromide localized phase in a layered manner, or a non-layered manner, in the silver halide grains, and/or on the surface of the silver halide grains. The halogen composition of said localized phase preferably has a silver bromide content of at least 10 mol%, and more preferably of more than 20 mol%. The silver bromide content of the silver bromide localized layer can be analyzed, for example, by using X-ray diffractometry (e.g. described in "Shinjikken Kagaku-koza 6, Kozo Kaiseki", edited by Nihonkagaku-kai, Maruzen). The localized phase can be present in the grains, or on the edges, corners, or planes of the surfaces of the grains. As a preferable example, a localized phase grown epitaxially on the corners of grains, can be mentioned.

Further, for the purpose of reducing the replenishment rate of a development processing solution, it is also effective to further increase the silver chloride content of the silver halide emulsion. In such a case, an emulsion comprising nearly pure silver chloride, for example having a silver chloride content of 98 to 100 mol%, is also preferably used.

The grains of the silver halide emulsion for use in the present invention preferably have a distribution or a structure with respect to the halogen composition. Typical examples thereof are disclosed, for example, in JP-B No. 13162/1968, JP-A Nos. 215540/1986, 222845/1985, 143331/1985, 75337/1986 and 222844/1985.

In order to make the inside of grains have a structure, not only the enclosing structure, as mentioned above, but also a so-called junctioned structure can be used to form grains. Examples thereof are disclosed, for example, in JP-A Nos. 133540/1984 and 108526/1983, European Patent No. 199,290A2, JP-B No. 24772/1983, and JP-A No. 16254/1984.

In the case of a junctioned structure, not only a combination of silver halides but also a combination of a silver halide with a silver salt compound having no rock salt structure, such as silver rhodanate and silver carbonate, can be used for the junctioned structure.

In the case of grains of silver iodobromide or the like having these structures, a preferable mode is one wherein the core part has higher silver iodide content than the shell part. Reversely, in some cases, grains having a lower silver iodide content in the core part than in the shell part are preferable. Similarly, in the case of grains having a junctioned structure, the silver iodide content of the host crystals is relatively higher than that of the junctioned crystals, or this may be reversed. The boundary part of the grains having these structures in which different halogen compositions are present, may be distinct or indistinct. Also preferable is a mode wherein the composition is continuously changed positively.

It is important that in the case of that two or more silver halides are present as mixed crystals, or as silver halide

grains having structures, the halogen composition distribution between grains is controlled. The method of measuring the halogen composition distribution between grains is described in JP-A No. 254032/1985. In particular, a highly uniform emulsion having a deviation coefficient of halogen composition distribution of 20% or below is preferable.

It is important to control the silver halide composition near the surface of grains. An increase in the silver iodide content or the silver chloride content at the part near the surface changes the adsorption of a dye or the developing speed, and in accordance with the purpose, this can be chosen.

In the silver halide grains used in the present invention, in accordance with the purpose, any of regular crystals having no twin plane, those described in "Shashin Kogyo no Kiso, Ginen Shashin-hen", edited by Nihon Shashin-gakkai (Corona Co.), page 163 (1979), parallel multiple twins having two or more parallel twin planes, and nonparallel multiple twins having two or more nonparallel twin planes, can be chosen and used. An example in which grains different in shape are mixed is disclosed in U.S. Patent No. 4,865,964. In the case of regular crystals, cubes having (100) planes, octahedrons having (111) planes, and dodecahedral grains having (110) planes, as disclosed in JP-B No. 42737/1980 and JP-A No. 222842/1985, can be used. Further, (hlm) plane grains, as reported in "Journal of Imaging Science", Vol. 30, page 247 (1986), can be chosen and used in accordance with the purpose. Grains having two or more planes in one grain, such as tetradecahedral grains having (100) and (111) planes in one grain, grains having (100) and (110) planes in one grain, or grains having (111) and (110) planes in one grain, can also be chosen and used in accordance with the purpose.

The value obtained by dividing the diameter of the projected area, which is assumed to be a circle, by the thickness of the grain, is called an aspect ratio, which defines the shape of tabular grains. Tabular grains having an aspect ratio of greater than 1 can be used in the present invention. Tabular grains can be prepared by methods described, for example, by Cleve in "Photography Theory and Practice" (1930), page 131; by Gutoff in "Photographic Science and Engineering", Vol. 14, pages 248 to 257 (1970); and in U.S. Patent Nos. 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent No. 2,112,157. When tabular grains are used, such merits are obtained that the covering power is increased and the color sensitization efficiency due to a sensitizing dye is increased, as described in detail in the above-mentioned U.S. Patent No. 4,434,226. The average aspect ratio of 80% or more of all the projected areas of grains is desirably 1 or more but less than 100, more preferably 2 or more but less than 20, and particularly preferably 3 or more but less than 10. As the shape of tabular grains, a triangle, a hexagon, a circle, and the like can be chosen. A regular hexagonal shape having six approximately equal sides, described in U.S. Patent No. 4,797,354, is a preferable mode.

In many cases, the grain size of tabular grains is expressed by the diameter of the projected area assumed to be a circle, and grains having an average diameter of 0.6 microns or below, as described in U.S. Patent No. 4,748,106, are preferable, because the quality of the image is made high. An emulsion having a narrow grain size distribution, as described in U.S. Patent No. 4,775,617, is also preferable. It is preferable to restrict the shape of tabular grains so that the thickness of the grains may be 0.5 microns or below, and more preferably 0.3 microns or below, because the sharpness is increased. Further, an emulsion in which the grains are highly uniform in thickness, with the deviation coefficient of grain thickness being 30% or below, is also preferable. Grains in which the thickness of the grains and the plane distance between twin planes are defined, as described in JP-A No. 163451/1988, are also preferable.

In accordance with the purpose, it is preferable to choose grains having no dislocation lines, grains having several dislocation lines, or grains having many dislocation lines. Dislocation introduced straight in a special direction in the crystal orientation of grains, or curved dislocation, can be chosen, and it is possible to choose from, for example, dislocation introduced throughout grains, dislocation introduced in a particular part of grains, and dislocation introduced limitedly to a particular part such as fringes of grains. In addition to the case of introduction of dislocation lines into tabular grains, also preferable is the case of introduction of dislocation lines into regular crystalline grains or irregular grains, represented by potato grains.

The silver halide emulsion used in the present invention may be subjected to a treatment for making grains round, as disclosed, for example, in European Patent Nos. 96,727B1 and 64,412B1, or it may be improved in the surface, as disclosed in West German Patent No. 2,306,447C2 and JP-A No. 221320/1985.

Generally, the grain surface has a flat structure, but it is also preferable in some cases to make the grain surface uneven intentionally. Examples are described, for example, in JP-A Nos. 106532/1983 and 221320/1985, and U.S. Patent No. 4,643,966.

The grain size of the emulsion used in the present invention is evaluated, for example, by the diameter of the projected area equivalent to a circle using an electron microscope; by the diameter of the grain volume equivalent to a sphere, calculated from the projected area and the grain thickness; or by the diameter of a volume equivalent to a sphere, using the Coulter Counter method. A selection can be made with wide range of grains from ultrafine grains having a sphere-equivalent diameter of 0.01 microns or below, to coarse grains having a sphere-equivalent diameter of 10 microns or more. Preferably grains of 0.1 microns or more but 3 microns or below are used as photosensitive silver halide grains.

As the emulsion used in the present invention, an emulsion having a wide grain size distribution, that is, a so-called polydisperse emulsion, or an emulsion having a narrow grain size distribution, that is, a so-called monodisperse emulsion, can be chosen and used in accordance with the purpose. As the scale for representing the size distribution, the

diameter of the projected area of the grain equivalent to a circle, or the deviation coefficient of the diameters of the grain volume equivalent to a sphere, can be used. If a monodisperse emulsion is used, it is preferable to use an emulsion having such a size distribution that the deviation coefficient is 25% or below, more preferably 20% or below, and further more preferably 15% or below.

Further, in order to allow the light-sensitive material to satisfy the intended gradation, in an emulsion layer having substantially the same color sensitivity, two or more monodisperse silver halide emulsions different in grain size are mixed and applied to the same layer or are applied as overlaid layers. Further, two or more polydisperse silver halide emulsions can be used as a mixture; or they can be used to form overlaid layers; or a combination of a monodisperse emulsion and a polydisperse emulsion can be used as a mixture; or the combination can be used to form overlaid layers.

The photographic emulsion for use in the present invention can be prepared by a method described, for example, by P. Glafkides in "Chemie et Physique Photographique," Paul Montel, 1967; by G. F. Duffin in "Photographic Emulsion Chemistry," Focal Press, 1966; or by V. L. Zelikman et al. in "Making and Coating Photographic Emulsion," Focal Press, 1964. A method wherein grains are formed in the presence of excess silver ions (the so-called reverse precipitation process) can also be used. As one type of the double-jet method, a method wherein pAg in the liquid phase, in which a silver halide will be formed, is kept constant, that is, the so-called controlled double-jet method, can also be used. According to this method, a silver halide emulsion wherein the crystals are regular in shape and whose grain size is approximately uniform, can be obtained.

A method in which previously precipitated and formed silver halide grains are added to a reaction vessel for the preparation of an emulsion, and the methods described, for example, in U.S. Patent Nos. 4,334,012, 4,301,241, and 4,150,994, are preferable in some cases. These can be used as seed crystals, or they are effective when they are supplied as a silver halide for growth. Further, in some cases, it is also effective to add fine grains having different halogen compositions in order to modify the surface.

The method in which a large part or only a small part of the halogen composition of silver halide grains is converted by the halogen conversion method is disclosed, for example, in U.S. Patent Nos. 3,477,852 and 4,142,900, European Patent Nos. 273,429 and 273,430, and West German Publication Patent No. 3,819,241. To convert to a more hardly soluble silver salt, it is possible to add a solution of a soluble halogen or to add silver halide grains.

In addition to the method in which the grain growth is made by adding a soluble silver salt and a halogen salt at constant concentrations and at constant flow rates, grain formation methods wherein the concentration is changed or the flow rate is changed, as described in British Patent No. 1,469,480 and U.S. Patent Nos. 3,650,757 and 4,242,445, are preferable methods. By increasing the concentration or increasing the flow rate, the amount of the silver halide to be supplied can be changed as a linear function, a quadratic function, or a more complex function, of the addition time.

A mixing vessel that is used when a solution of a soluble silver salt and a solution of a soluble halogen salt are reacted can be selected for use from methods described in U.S. Patent Nos. 2,996,287, 3,342,605, 3,415,650, and 3,785,777, and West German Publication Patent Nos. 2,556,885 and 2,555,364.

For the purpose of promoting the ripening, a silver halide solvent is useful. For example, it is known to allow an excess amount of halide ions to be present in the reaction vessel, to promote the ripening. Further, other ripening agent can be used. All of the amount of these ripening agents may be blended in the dispersion medium in the reaction vessel before silver salts and halide salts are added, or their introduction into the reaction vessel may be carried out together with the addition of a halide salt, a silver salt, or a peptizer.

As examples of these, ammonia, thiocyanates (e.g. potassium rhodanate and ammonium rhodanate), organic thioether compounds (e.g. compounds described, for example, in U.S. Patent Nos. 3,574,628, 3,021,215, 3,057,724, 3,038,805, 4,276,374, 4,297,439, 3,704,130, and 4,782,013, and JP-A No. 104926/1982), thion compounds (e.g. tetra-substituted thioureas described, for example, in JP-A Nos. 82408/1978 and 77737/1980, and U.S. Patent No. 4,221,863; and compounds described in JP-A No. 144319/1978), mercapto compounds capable of promoting the growth of silver halide grains, as described in JP-A No. 202531/1982, and amine compounds (e.g. described in JP-A No. 100717/1979), can be mentioned.

As a protective colloid and as a binder of other hydrophilic colloid layers that are used when the emulsion according to the present invention is prepared, gelatin is used advantageously, but another hydrophilic colloid can also be used.

Use can be made of, for example, a gelatin derivative, a graft polymer of gelatin with another polymer, a protein, such as albumin and casein; a cellulose derivative, such as hydroxyethyl cellulose, carboxymethyl cellulose, and cellulose sulfates; a saccharide derivative, such as sodium alginate, a starch derivative; and many synthetic hydrophilic polymers, including homopolymers and copolymers, such as a polyvinyl alcohol, a polyvinyl alcohol partial acetal, a poly-N-vinylpyrrolidone, a polyacrylic acid, a polymethacrylic acid, a polyacrylamide, a polyvinylimidazole, and a polyvinylpyrazole.

As the gelatin, in addition to lime-processed gelatin, acid-processed gelatin, and enzyme-processed gelatin described in Bull. Soc. Sci. Photo. Japan, No. 16, page 30 (1966), can be used. Further a hydrolyzate or enzymolyzate of gelatin can also be used. For the preparation of tabular grains, it is preferable to use a low-molecular-weight gelatin described in JP-A No. 158426/1989.

Preferably, the silver halide emulsion according to the present invention is washed with water for desalting and is dispersed in a freshly prepared protective colloid. The temperature at which the washing with water is carried out can be selected in accordance with the purpose, and preferably the temperature is selected in the range of 5 to 50 °C. The pH at which the washing is carried out can be selected in accordance with the purpose, and preferably the pH is selected in the range of 2 to 10, and more preferably in the range of 3 to 8. The pAg at which the washing is carried out can be selected in accordance with the purpose, and preferably the pAg is selected in the range of 5 to 10. As a method of washing with water, one can be selected from the noodle washing method, the dialysis method using a diaphragm, the centrifugation method, the coagulation settling method, and the ion exchange method. In the case of the coagulation settling method, selection can be made from, for example, the method wherein sulfuric acid salt is used, the method wherein an organic solvent is used, the method wherein a water-soluble polymer is used, and the method wherein a gelatin derivative is used.

When the silver halide emulsion according to the present invention is prepared, in accordance with the purpose, it is preferable to allow a salt of a metal ion to be present, for example, at the time when grains are formed, in the step of desalting, at the time when the chemical sensitization is carried out, or before the application. When the grains are doped, the addition is preferably carried out at the time when the grains are formed; or after the formation of the grains but before the completion of the chemical sensitization, when the surface of the grains is modified or when the salt of a metal ion is used as a chemical sensitizer. As to the doping of grains, selection can be made from a case in which the whole grains are doped, one in which only the core parts of the grains are doped, one in which only the shell parts of the grains are doped, one in which only the epitaxial parts of the grains are doped, and one in which only the substrate grains are doped. For example, Mg, Ca, Sr, Ba, Al, Sc, Y, La, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ru, Rh, Pd, Re, Os, Ir, Pt, Au, Cd, Hg, Tl, In, Sn, Pb, and Bi can be used. These metals can be added if they are in the form of a salt that is soluble at the time when grains are formed, such as an ammonium salt, an acetate, a nitrate, a sulfate, a phosphate, a hydroxide, a six-coordinate complex, and a four-coordinate complex. Examples include CdBr_2 , CdCl_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$, K_3IrCl_6 , $(\text{NH}_4)_3\text{RhCl}_6$, and $\text{K}_4\text{Ru}(\text{CN})_6$. As a ligand of the coordination compound, one can be preferably selected from halogen, H_2O , cyano, cyanate, thiocyanate, nitrosyl, thionitrosyl, oxo, and carbonyl. With respect to these metal compounds, only one can be used, but two or more can also be used in combination.

In some cases, a method wherein a chalcogen compound is added during the preparation of the emulsion, as described in U.S. Patent No. 3,772,031, is also useful. In addition to S, Se, and Te, a cyanate, a thiocyanate, a selenocyanate, a carbonate, a phosphate, or an acetate may be present.

The silver halide grains for used in the present invention can be subjected to at least one of sulfur sensitization, selenium sensitization, tellurium sensitization (these three are called chalcogen sensitization, collectively), noble metal sensitization, and reduction sensitization, in any step of the production for the silver halide emulsion. A combination of two or more sensitizations is preferable. Various types of emulsions can be produced, depending on the steps in which the chemical sensitization is carried out. There are a type wherein chemical sensitizing nuclei are embedded in grains, a type wherein chemical sensitizing nuclei are embedded at parts near the surface of grains, and a type wherein chemical sensitizing nuclei are formed on the surface. In the emulsion for use in the present invention, the location at which chemical sensitizing nuclei are situated can be selected in accordance with the purpose.

Chemical sensitizations that can be carried out preferably in the present invention are chalcogen sensitization and noble metal sensitization, which may be used singly or in combination; and the chemical sensitization can be carried out by using active gelatin, as described by T. H. James in "The Theory of the Photographic Process," 4th edition, Macmillan, 1997, pages 67 to 76, or by using sulfur, selenium, tellurium, gold, platinum, palladium, or iridium, or a combination of these sensitizing agents, at a pAg of 5 to 10, a pH of 5 to 8, and a temperature of 30 to 80 °C, as described in Research Disclosure, Item 12008 (April 1974); Research Disclosure, Item 13452 (June 1975); Research Disclosure, Item 307105 (November 1989); U.S. Patent Nos. 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018, and 3,904,415, and British Patent No. 1,315,755.

In the sulfur sensitization, an unstable sulfur compound is used, and specifically, thiosulfates (e.g. hypo), thioureas (e.g. diphenylthiourea, triethylthiourea, and allylthiourea), rhodanines, mercaptos, thioamides, thiohydantoin, 4-oxo-oxazolidin-2-thions, di- or polysulfides, polythionic acids, and elemental sulfur, and known sulfur-containing compounds described in U.S. Patent Nos. 3,857,711, 4,266,018, and 4,054,457, can be used. In many cases, sulfur sensitization is used in combination with noble metal sensitization.

A preferable amount of a sulfur sensitizing agent used for the silver halide grains is 1×10^{-7} to 1×10^{-3} mol, and more preferably 5×10^{-7} to 1×10^{-4} mol, per mol of the silver halide.

In the selenium sensitization, known unstable selenium compounds are used, such as those described, for example, in U.S. Patent Nos. 3,297,446 and 3,297,447, specific such selenium compounds are colloidal metal selenium, selenoureas (e.g. N,N-dimethylselenourea and tetramethylselenourea), selenoketones (e.g. selenoacetone), selenoamides (e.g. selenoacetamide), selenocarboxylic acids and esters, isoselenocyanates, selenides (e.g. diethylselenides and triphenylphosphine selenide), and selenophosphates (e.g. tri-p-tolylselenophosphate). In some cases, preferably the selenium sensitization is used in combination with one or both of sulfur sensitization and noble metal sensitization.

The amount of the selenium sensitizing agent to be used varies depending on the selenium compound, the type of the silver halide grains, the chemical ripening conditions, and the like that are used, and the amount is generally of the order of 10^{-8} to 10^{-4} mol, and preferably 10^{-7} to 10^{-5} mol, per mol of the silver halide.

As the tellurium sensitizing agent used in the present invention, compounds described, for example, in Canadian Patent No. 800,958, British Patent Nos. 1,295,462 and 1,396,696, and Japanese patent application Nos. 333819/1990 and 131598/1991 can be used.

In the noble metal sensitization, a salt of a noble metal, such as gold, platinum, palladium, and iridium, can be used, and specifically gold sensitization, palladium sensitization, and a combination thereof are particularly preferable. In the case of gold sensitization, a known compound, such as chloroauric acid, potassium chloroaurate, potassium aurothiocyanate, gold sulfide, and gold selenide, can be used. The palladium compound means salts of divalent or tetravalent palladium salt. A preferable palladium compound is represented by R_2PdX_6 or R_2PdX_4 , wherein R represents a hydrogen atom, an alkali metal atom, or an ammonium radical; and X represents a halogen atom, i.e. a chlorine atom, a bromine atom, or an iodine atom.

Specifically, K_2PdCl_4 , $(NH_4)_2PdCl_6$, Na_2PdCl_4 , $(NH_4)_2PdCl_4$, Li_2PdCl_4 , Na_2PdCl_6 , or K_2PdBr_4 is preferable. Preferably a gold compound and a palladium compound are used in combination with a thiocyanate or a selenocyanate.

Preferably the emulsion for use in the present invention is used in combination with gold sensitization. A preferable amount of the gold sensitizing agent is 1×10^{-7} to 1×10^{-3} mol, and more preferably 5×10^{-7} to 5×10^{-4} mol, per mol of the silver halide. A preferable amount of the palladium compound is in the range of 5×10^{-7} to 1×10^{-3} mol. A preferable amount of the thiocyan compound and the selenocyan compound is in the range of 1×10^{-6} to 5×10^{-2} mol.

Preferably that the silver halide emulsion is subjected to reduction sensitization during the formation of the grains, after the formation of the grains but before the chemical sensitization, or during or after the chemical sensitization.

Herein, the reduction sensitization can be selected from a method wherein a reduction sensitizer is added to a silver halide emulsion; a method called silver ripening, wherein the growth or ripening is made in an atmosphere having a pAg as low as 1 to 7; and a method called high-pH ripening, wherein the growth or ripening is made in an atmosphere having a pH as high as 8 to 11. Two or more methods can also be used in combination.

As the reduction sensitizer, known reduction sensitizers can be selected and used, such as stannous salts, ascorbic acid and its derivatives, amines and polyamines, hydrazine and its derivatives, formamidesulfonic acid, silane compounds, and boran compounds; and two or more compounds can be used in combination. As the reduction sensitizer, preferable compounds are stannous chloride, aminoiminomethanesulfonic acid (popularly called thiourea dioxide), dimethylamineboran, and ascorbic acid and its derivatives.

The chemical sensitization can be carried out in the presence of a so-called chemical sensitization auxiliary. As a useful chemical sensitization auxiliary, a compound is used that is known to suppress fogging and to increase the sensitivity in the process of chemical sensitization, such as azaindene, azapyridazine, and azapyrimidine. Examples of chemical sensitization auxiliary are described in U.S. Patent Nos. 2,131,038, 3,411,914, and 3,554,757, JP-A No. 126526/1983, and by G. F. Duffin in "Photographic Emulsion Chemistry" mentioned above, pages 138 to 143.

Preferably an oxidizing agent for silver is added during the process of the production of the emulsion. The oxidizing agent for silver refers to a compound that acts on metal silver to convert it to silver ions. Particularly useful is a compound that converts quite fine silver grains, which are concomitantly produced during the formation of silver halide grains and during the chemical sensitization, to silver ions. The thus produced silver ions may form a silver salt that is hardly soluble in water, such as a silver halide, silver sulfide, and silver selenide, or they may form a silver salt that is readily soluble in water, such as silver nitrate. The oxidizing agent for silver may be inorganic or organic compound. Example inorganic oxidizing agents include ozone, hydrogen peroxide and its adducts (e.g. $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, $2NaCO_3 \cdot 3H_2O_2$, $Na_4P_2O_7 \cdot 2H_2O_2$, and $2Na_2SO_4 \cdot H_2O_2 \cdot 2H_2O$); oxygen acid salts, such as peroxyacid salts (e.g. $K_2S_2O_8$, $K_2C_2O_6$, and $K_2P_2O_8$), peroxycomplex compounds (e.g. $K_2[Ti(O_2)C_2O_4] \cdot 3H_2O$, $4K_2SO_4 \cdot Ti(O_2)OH \cdot SO_4 \cdot 2H_2O$, and $Na_3[VO(O_2)(C_2H_4)_2] \cdot 6H_2O$), permanganates (e.g. $KMnO_4$), and chromates (e.g. $K_2Cr_2O_7$); halogen elements, such as iodine and bromine; perhalates (e.g. potassium periodate), salts of metals having higher valences (e.g. potassium hexacyanoferrate (III), and thiosulfonates.

Examples of the organic oxidizing agents include quinones, such as p-quinone; organic peroxides, such as peracetic acid and perbenzoic acid; and compounds that can release active halogen (e.g. N-bromosuccinimide, chloramine T, and chloramine B).

Use of a combination of the above reduction sensitization with the oxidizing agent for silver is a preferable mode.

In the photographic emulsion used in the present invention, various compounds can be incorporated for the purpose of preventing fogging during the process of the production of the light-sensitive material, during the storage of the light-sensitive material, or during the photographic processing, or for the purpose of stabilizing the photographic performance. That is, compounds known as antifoggants or stabilizers can be added, such as thiazoles including benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (such as 1-phenyl-5-mercaptotetrazole, and 1-(5-methylureidphenyl)-5-mercaptotetrazole), mercaptopyrimidines, mercaptotriazines; thioketo compounds, such as oxazolinthione; and azain-

denes, such as triazaindenes; tetraazaindenes (particularly 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene), and pentaazaindenes. For example, those described in U.S. Patent Nos. 3,954,474 and 3,982,947, and JP-B No. 28660/1987, can be used. A preferable compound is a compound described in JP-A No. 212932/1988. In accordance with the purpose, the antifoggant and the stabilizer can be added at various times, for example, before the formation of the grains, during the formation of the grains, after the formation of the grains, in the step of washing with water, at the time of dispersion after the washing with water, before the chemical sensitization, during the chemical sensitization, after the chemical sensitization, and before the application.

Preferably, the photographic emulsion to be used in the present invention is spectrally sensitized with methine dyes and the like. Dyes that can be used include a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonol dye. Particularly useful dyes are those belonging to a cyanine dye, a merocyanine dye, and a composite merocyanine dye. In these dyes, any of nuclei generally used in cyanine dyes as base heterocyclic nuclei can be applied. That is, a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, and a pyridine nucleus; and a nucleus formed by fusing a cycloaliphatic hydrocarbon ring or an aromatic hydrocarbon ring to these nuclei, that is, such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, a quinoline nucleus, can be applied. These nuclei may be substituted on the carbon atom.

In the merocyanine dye or the composite merocyanine dye, as a nucleus having a ketomethylene structure, a 5- to 6-membered heterocyclic nucleus, such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus, can be applied.

These sensitizing dyes can be used singly or in combination, and a combination of these sensitizing dyes is often used, particularly for the purpose of supersensitization. Typical examples thereof are described in U.S. Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patent Nos. 1,344,218 and 1,507,803, JP-B Nos. 4,936/1968 and 12,375/1978, and JP-A Nos. 110,618/1977 and 109,925/1977.

Together with the sensitizing dye, a dye having no spectral sensitizing action itself, or a compound that does not substantially absorb visible light and that exhibits supersensitization, may be included in the emulsion.

The timing when the sensitizing dye is added to the emulsion may be at any stage known to be useful in the preparation of emulsions. The addition is carried out most usually at a time after the completion of chemical sensitization and before coating, but it can be carried out at the same time as the addition of a chemical sensitizer, to carry out spectral sensitization and chemical sensitization simultaneously, as described in U.S. Patent Nos. 3,628,969 and 4,225,666; it can be carried out prior to chemical sensitization, as described in JP-A No. 113,928; or it can be carried out before the completion of the formation of the precipitate of silver halide grains to start spectral sensitization. Further, as taught in U.S. Patent No. 4,225,666, these foregoing compounds may be added in portions, i.e., part of these compounds is added prior to chemical sensitization, and the rest is added after the chemical sensitization, and also the addition may be carried out at any time during the formation of silver halide grains, as disclosed, for example, in U.S. Patent No. 4,183,756.

Generally the amount of the sensitizing dye to be added is of the order of 4×10^{-6} to 8×10^{-3} mol per mol of the silver halide, but when the silver halide grain size is 0.2 to 1.2 μm , which is more preferable, the amount of the sensitizing dye to be added is more effectively about 5×10^{-5} to 2×10^{-3} mol per mol of the silver halide.

To the light-sensitive material related to the present technique, may be added the above-mentioned various additives, and also other various additives in accordance with the purpose.

These additives are described in more detail in Research Disclosure, Item 17643 (December 1978); Research Disclosure, Item 18716 (November 1979); and Research Disclosure, Item 307105 (November 1989), and the particular parts are given below in a Table.

Additive	RD 17643	RD 18716	RD 307105
1 Chemical sensitizers	p.23	p.648 (right column)	p.996
2 Sensitivity-enhancing agents	-	p.648 (right column)	-
3 Spectral sensitizers and Supersensitizers	pp.23-24	pp.648 (right column) -649 (right column)	pp.996 (right column) -998 (right column)
4 Brightening agents	p.24	-	p.998 (right column)
5 Antifogging agents and Stabilizers	pp.24-25	p.649 (right column)	pp.998 (right column) -1000 (right column)
6 Light absorbers, Filter dyes, and UV Absorbers	pp.25-26	pp.649 (right column) -650 (left column)	p.1003 (left to right column)
7 Stain-preventing agents	p.25 (right column)	p.650 (left to right column)	-
8 Image dye stabilizers	p.25	-	-
9 Hardeners	p.26	p.651 (left column)	pp.1004 (right column) -1005 (left column)
10 Binders	p.26	p.651 (left column)	pp.1003 (right column) -1004 (right column)
11 Plasticizers and Lubricants	p.27	p.650 (right column)	p.1006 (left to right column)
12 Coating aids and Surface-active agents	pp.26-27	p.650 (right column)	pp.1005 (left column) -1006 (left column)
13 Antistatic agents	p.27	p.650 (right column)	pp.1006 (right column) -1007 (left column)

As the total coated amount of silver of the light-sensitive material of the present invention, preferably 0.003 to 12 g per m² in terms of silver is used. In the case of a transparent material, such as color negative film, the total coated amount of silver is preferably 1 to 12 g, and more preferably 3 to 10 g. In the case of a reflective material, such as color printing paper, the total coated amount of silver is preferably 0.003 to 1 g, in view of rapid processing or low rate replenishment, and in that case, the added amount in each layer is preferably 0.001 to 0.4 g per light-sensitive layer. In particular, when the light-sensitive material of the present invention is intensified, the amount is preferably 0.003 to 0.3 g, more preferably 0.01 to 0.1 g, and particularly preferably 0.015 to 0.05 g. In this case, the amount per light-sensitive layer is preferably 0.001 to 0.1 g, and more preferably 0.003 to 0.03 g.

In the present invention, if the coated amount of silver of each light-sensitive layer is too small, the dissolution of the silver salt proceeds, and therefore a satisfactory color density cannot be obtained. On the other hand, when intensification is carried out, if the coated amount of silver of each light-sensitive layer is too large, an increase in Dmin or formation of bubbles occurs, to make the appreciation of the resultant product difficult.

The total amount of gelatin of the light-sensitive material of the present invention is generally 1.0 to 30 g, and preferably 2.0 to 20 g, per m². In swelling the light-sensitive material of the present invention in an alkali solution having a pH of 12, the time for the swollen film thickness to reach 1/2 of the saturated swollen film thickness (90% of the maximum swollen film thickness) is preferably 15 sec or less, and more preferably 10 sec or less. The swell ratio ($[(\text{maximum swollen film thickness} - \text{film thickness})/\text{film thickness}] \times 100$) is preferably 50 to 300%, and particularly preferably 100 to 200%.

Processing materials and processing methods used in the present invention will now be described in detail.

In the present invention, the light-sensitive material is developed (silver development/cross oxidation of the built-in reducing agent), desilvered, and washed with water or stabilized. In some cases, after the washing with water or the stabilizing processing, a treatment of alkalization for color formation intensification is carried out.

When the light-sensitive material of the present invention is developed with a developing solution, preferably the developing solution may contain a compound that serves as a developing agent of silver halides and/or allows the developing agent oxidation product resulting from the silver development to cross-oxidize the color-forming reducing

agent built in the light-sensitive material. Preferably, pyrazolidones, dihydroxybenzenes, reductones, and aminophenols are used, and particularly preferably pyrazolidones are used.

Among pyrazolidones, 1-phenyl-3-pyrazolidones are preferable, and they include 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-phenyl-5-phenyl-3-pyrazolidone, 1-p-tolyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-p-chlorophenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-phenyl-2-hydroxymethyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-2-acetyl-3-pyrazolidone, and 1-phenyl-2-hydroxymethyl-5-phenyl-3-pyrazolidone.

Dihydroxybenzenes include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dichlorohydroquinone, 2,5-dimethylhydroquinone, and potassium hydroquinonemonosulfonate.

As reductones, ascorbic acid and its derivatives are preferable, and compounds described in JP-A No. 148822/1994, pages 3 to 10, can be used. In particular, sodium L-ascorbate and sodium erythorbate are preferable.

p-Aminophenols include N-methyl-p-aminophenol, N-(β -hydroxyethyl)-p-aminophenol, N-(4-hydroxyphenyl)glycine, and 2-methyl-p-aminophenol.

Although these compounds are generally used singly, use of two or more of them in combination is also preferable, to enhance the development and cross oxidation activity.

The amount of these compounds to be used in the developing solution is generally 2.5×10^{-4} to 0.2 mol/liter, preferably 0.0025 to 0.1 mol/liter, and more preferably 0.001 to 0.05 mol/liter.

Example preservatives for use in the developing solution include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite, formaldehyde/sodium bisulfite adduct, and hydroxylamine $\cdot$ sulfate, which can be used in an amount in the range of generally 0.1 mol/liter or below, and preferably 0.001 to 0.02 mol/liter. If a high-silver-chloride emulsion is used in the light-sensitive material, the above compound is used in an amount of generally 0.001 mol/liter or below, and preferably it is not used at all.

In the present invention, instead of the above hydroxylamine or sulfite ions, organic preservatives such as diethylhydroxylamine, dialkylhydroxylamines described in JP-A No. 97355/1992, can be preferably used.

The developing solution may contain halide ions, such as chloride ions, bromide ions, and iodide ions.

Herein the halide ions may be added directly to the developing solution, or they may be dissolved out from the light-sensitive material into the developing solution during the development processing.

The developing solution used in the present invention preferably has a pH of 8 to 13, and more preferably 9 to 12.

To maintain the above pH, it is preferable to use various buffers. Preferably, carbonates, phosphates, tetraborates, and hydroxybenzoates are used.

The amount of the buffers to be added to the developing solution is preferably 0.05 mol/liter or over, and particularly preferably 0.1 to 0.4 mol/liter.

In addition, in the developing solution, as a sediment-preventive agent against calcium and magnesium, or as an agent for stabilizing the developing solution, various chelating agents can be used.

With respect to the amount of these chelating agents to be added, preferably the amount is enough to sequester the metal ions in the developing solution, and, for example, these chelating agents are generally used in an amount in the order of 0.1 to 10 g per liter.

In the present invention, if required, an arbitrary antifoggant can be added. As the antifoggant, nitrogen-containing heterocyclic compounds, and alkali metal halide, such as sodium chloride, potassium bromide, and potassium iodide, can be used.

The amount of the nitrogen-containing heterocyclic compounds to be added is generally 1×10^{-5} to 1×10^{-2} mol/liter, and preferably 2.5×10^{-5} to 1×10^{-3} mol/liter.

In the developing solution, if necessary, an arbitrary development accelerator can be added.

Preferably the developing solution contains a fluorescent whitening agent. In particular, it is preferable to use 4,4'-diamino-2,2'-disulfostilbene-series compounds.

The processing temperature of the developing solution to be applied to the present invention is generally 20 to 50 °C, and preferably 30 to 45 °C. The processing time is generally 5 sec to 2 min, and preferably 10 sec to 1 min. With respect to the replenishing rate, although a small amount is preferable, the replenishing rate is generally 15 to 600 ml, preferably 25 to 200 ml, and more preferably 35 to 100 ml, per m² of the light-sensitive material.

After the development, a desilvering process can be carried out. The desilvering process comprises a fixing process, or both bleaching process and a fixing process. When both bleaching and fixing are carried out, the bleaching process and the fixing process may be carried out separately or simultaneously (bleach-fixing process). Also, according to the purpose, the processing may be carried out in a bleach-fixing bath having two successive tanks; or the fixing process may be carried out before the bleach-fixing process; or the bleaching process may be carried out after the bleach-fixing process.

In some cases, it is preferable to carry out the stabilizing process, to stabilize silver salts and dye images, without carrying out the desilvering process after the development.

After the development, image-intensifying process (intensification) can be performed using peroxides, halorous

acids, iodoso compounds, and cobalt(III) complex compounds described, for example, in West Germany Patent (OLS) Nos. 1,813,920, 2,044,993, and 2,735,262, and JP-A Nos. 9728/1973, 84240/1974, 102314/1974, 53826/1976, 13336/1977, and 73731/1977. To further intensify the image, an oxidizing agent for intensifying the image can be added to the above developer, so that the development and the intensification may be carried out at the same time in one bath. In particular, hydrogen peroxide is preferable, because the amplification rate is high. These intensification methods are preferable processing methods in view of environmental conservation. This is because the amount of silver in the light-sensitive material can be reduced considerably, and therefore, for example, a bleaching process is not required and silver (or silver salts) will not be released, for example, by a stabilizing process or the like.

Example bleaching agents for use in the bleaching solution or the bleach-fix solution include, for example, compounds of polyvalent metals, such as iron (III), cobalt (III), chromium (IV), and copper (II); peracids; quinones; and nitro compounds. Among them, aminopolycarboxylic acid iron (III) complex salts, such as ethylenediaminetetraacetic acid iron (III) complex salt and 1,3-diaminopropanetetraacetic acid iron (III) complex salt; hydrogen peroxide, persulfates, and the like are preferred, in view of rapid processing and the prevention of environmental pollution.

The bleaching solution and bleach-fix solution that use these aminopolycarboxylic acid iron (III) complex salts can be used at a pH of generally 3 to 8, and preferably 5 to 7. The bleaching solution that uses persulfates or hydrogen peroxide can be used at a pH of generally 4 to 11, and preferably 5 to 10.

In the bleaching solution, the bleach-fix solution, and the bath preceding them, if required, a bleach-accelerating agent can be used.

In the bleaching solution, the bleach-fix solution, and the fixing solution, use can be made of known additives, such as a rehalogenating agent, a pH buffering agent, and a metal corrosion-preventive agent. In particular, it is preferable to contain an organic acid, to prevent bleach stain. The organic acid is preferably a compound having an acid dissociation constant (pKa) of 2 to 7.

Example fixing agents for use in the fixing solution and the bleach-fix solution include thiosulfates, thiocyanates, thioureas, a large amount of iodide salts, and thioether compounds, metho-ionic compounds, and nitrogen-containing heterocyclic compounds, having a sulfide group, as described in JP-A No. 365037/1992, pages 11 to 21, and JP-A No. 66540/1993, pages 1088 to 1092.

Preferable preservatives for the fixing solution and the bleach-fix solution are sulfites, bisulfites, carbonylbisulfite adducts, and sulfinic acid compounds described in European Patent No. 294769A.

In the fixing solution and the bleach-fix solution, further, for example, any of various fluorescent whitening agents, antifoaming agents, surface-active agents, polyvinylpyrrolidones, and methanol can be contained.

The processing temperature of the desilvering step is generally 20 to 50 °C, and preferably 30 to 45 °C. The processing time is generally 5 sec to 2 min, and preferably 10 sec to 1 min. Although a small replenishing rate is preferable, the replenishing rate is generally 15 to 600 ml, preferably 25 to 200 ml, and more preferably 35 to 100 ml, per m² of the light-sensitive material. The processing is also preferably carried out without replenishment in such a way that the evaporated amount is supplemented with water.

The light-sensitive material of the present invention is generally passed through a washing step after the desilvering process. If a stabilizing process is carried out, the washing step can be omitted. In such a stabilizing process, processes described in JP-A Nos. 8543/1982, 14834/1983, and 220345/1985, and all known processes described in JP-A Nos. 127926/1983, 137837/1983, and 140741/1983, can be used. A washing-stabilizing process, in which a stabilizing bath containing a dye stabilizer and a surface-active agent typically used for the processing of color light-sensitive materials for photographing is used as a final bath, can be carried out.

In the washing solution (washing water) and stabilizing solution, use can be made of a water softener, such as sulfites, inorganic phosphoric acids, polyaminocarboxylic acids, and organic aminophosphonic acids; a metal salt, such as Mg salts, Al salts, and Bi salts; a surface-active agent, a hardener, a pH buffer, a fluorescent whitening agent, and a silver-salt-forming agent, such as nitrogen-containing heterocyclic compounds.

Example dye-stabilizing agents of the stabilizing solution include, for example, aldehydes, such as formalin and glutaraldehyde; N-methylol compounds, hexamethylenetetramine, or aldehyde sulfite adducts.

The pH of the washing water and the stabilizing solution is generally 4 to 9, and preferably 5 to 8. The processing temperature is generally 15 to 45 °C, and preferably 25 to 40 °C. The processing time is generally 5 sec to 2 min, and preferably 10 sec to 40 sec.

The overflow solution associated with the replenishment of the above washing water and/or the stabilizing solution, can be reused in other processes, such as the desilvering process.

The amount of the washing water and/or the stabilizing solution can be set in a wide range depending on various conditions, and the replenishing rate is preferably 15 to 360 ml, and more preferably 25 to 120 ml, per m² of the light-sensitive material. To reduce the replenishing rate, it is preferable to use multiple tanks and a multi-stage countercurrent system.

In the present invention, in order to save water, water can be used that has been obtained by treating the overflow solution or the in-tank liquid using a reverse osmosis membrane. For example, the treatment by reverse osmosis is preferably carried out for water from the second tank, or the more latter tank of the multi-stage countercurrent washing process.

ess and/or the stabilizing process.

In the present invention, preferably the stirring is intensified as much as possible. To intensify the stirring, specifically a method wherein a jet stream of a processing solution is caused to impinge on the emulsion surface of a light-sensitive material, as described in JP-A Nos. 183460/1987 and 183461/1987; a method wherein a rotating means is used to increase the stirring effect, as described in JP-A No. 183461/1987; a method wherein a light-sensitive material is moved, with the emulsion surface of the material being in contact with a wiper blade provided in a solution, so that a turbulent flow may occur near the emulsion surface, to improve the stirring effect; and a method wherein the total amount of a processing solution to be circulated is increased, can be mentioned. These means of improving the stirring are useful in any of the developing solution, the bleaching solution, the fixing solution, the bleach-fix solution, the stabilizing solution, and the washing water. These methods are effective in that the effective constituents in the solution are supplied to the light-sensitive material and the diffusion of unnecessary components in the light-sensitive material is promoted.

In the present invention, any state of the solution opening rate [contact area of air (cm^2)/solution volume (cm^3)] of any of the baths can exhibit excellent performance, but in view of the stability of the solution components, preferably the solution opening rate is 0 to 0.1 cm^{-1} . In the continuous processing, from a practical point of view, the solution opening rate is preferably 0.001 to 0.05 cm^{-1} , and more preferably 0.002 to 0.03 cm^{-1} .

The automatic developing machine used for the light-sensitive material of the present invention is preferably provided with a means of transporting a light-sensitive material, as described in JP-A No. 191257/1985, 191258/1985, and 191259/1985. Such a transporting means can reduce remarkably the carry-in of the processing solution from a preceding bath to a succeeding bath. Therefore it is high in the effect of preventing the performance of a processing solution from being deteriorated. Such an effect is particularly effective in shortening the processing time of each process and in reducing the process replenishing rate. To shorten the processing time, it is preferable to shorten the crossover time (the aerial time), and a method wherein a light-sensitive material is transported between processes through a blade having a screening effect, as described, for example, in JP-A No. 86659/1992, Fig. 4, 5, or 6, and JP-A No. 66540/1993, Fig. 4 or 5, is preferable.

Further, if each of the processing solutions in the continuous process is concentrated due to evaporation, preferably water is added to compensate for the evaporation.

The processing time in each process according to the present invention means the time required from the start of the processing of the light-sensitive material at any process, to the start of the processing in the next process. The actual processing time in an automatic developing machine is determined generally by the linear speed and the volume of the processing bath, and in the present invention, as the linear speed, 500 to 4,000 mm/min can be mentioned as a guide. Particularly in the case of a small-sized developing machine, 500 to 2,500 mm/min is preferable.

The processing time in the whole processing steps, that is, the processing time from the developing process to the drying process, is preferably 360 sec or below, more preferably 120 sec or below, and particularly preferably 90 to 30 sec. Herein the processing time means the time from the dipping of the light-sensitive material into the developing solution, till the emergence from the drying part of the processor.

In the processing that may be applied in the present invention, various additives can be used, and more details are described in Research Disclosure Item 36544 (September 1994), whose related section is summarized below.

Processing agent	Page
Developing agents	536
Preservatives of developing agents	537, left column
Antifoggants	537
Chelating agents	537, right column
Buffers	537, right column
Surface-active agents	538, left column, and 539, left column
Bleaching agents	538,
Bleach-accelerating agents	538, right column to 539, left column
Chelating agents for bleaching	539, left column
Rehaloganating agents	539, left column
Fixing agents	539, right column
Preservatives for fixing agents	539, right column
Chelating agents for fixing	540, left column
Surface-active agents for stabilization	540, left
Scum-preventing agents for stabilization	540, right
Chelating agents for stabilization	540, right
Antifungus/mildew-proofing agents	540, right
Image dye stabilizers	540, right

As for water-saving techniques that may applied in the present invention, details are described in Research Disclosure Item 36544 (September, 1994), page 540, right column, to page 541, left column.

By processing the light-sensitive material containing the color-forming reducing agent, the coupler, and the sulfinic acid compound according to the present invention with an alkaline solution, an image having low minimum density and high color density can be obtained. Further, an image high in clarity (color definition) can be obtained that, when stored for a long period of time, produces less stain, for example, due to color formation with the lapse of time.

EXAMPLES

Now, the present invention will be described specifically with reference to examples. However, the present invention is not restricted to these examples.

Example 1

(Preparation of Light-Sensitive Material)

A paper base whose both surfaces had been laminated with a polyethylene, was subjected to surface corona discharge treatment; it was then provided with a gelatin undercoat layer containing sodium dodecylbenzenesulfonate, and it was coated with various photographic constitutional layers, to prepare a multi-layer color printing paper having the layer constitution shown below, which was named Sample (100).

The coating solutions were prepared as follows.

Preparation of First-Layer Coating Solution

22.5 g of a cyan color-forming coupler (ExC-1) and 27.8 g of a color-forming reducing agent (I-16) were dissolved in 52 g of a solvent (Solv-4) and 73 ml of ethyl acetate, and the resultant solution was emulsified and dispersed in 420 ml of a 12% aqueous gelatin solution containing 10% sodium dodecylbenzenesulfonate and citric acid, to prepare an

emulsion A.

On the other hand, a silver bromochloride emulsion A (cubes; average grain size: 0.18 μm ; silver bromide: 25 mol %) was prepared. To this emulsion, had been added red-sensitive sensitizing dyes A-1 and A-2. The chemical ripening of this emulsion was carried out optimally with a sulfur sensitizer and a gold sensitizer being added.

The above emulsified dispersion A and this silver bromochloride emulsion A were mixed and dissolved, and a first-layer coating solution was prepared so that it would have the composition shown below.

Preparation of Second- to Seventh-Layer Coating Solutions

The second-layer to seventh-layer coating solutions were prepared in the similar manner as that for the first-layer coating solution.

The above coating solutions for each layer were applied onto the base, to prepare Sample (100) of a light-sensitive material having the below-shown layer constitution.

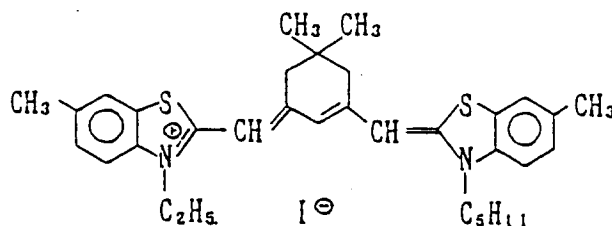
As the gelatin hardener for each layer, 1-oxy-3,5-dichloro-s-triazine sodium salt was used.

Further, Cpd-4 and Cpd-5 were added to each layer so that the total amount would be 25.0 mg/m^2 and 50 mg/m^2 , respectively.

In the silver chlorobromide emulsion of each light-sensitive emulsion layer, the following spectrally sensitizing dyes were used, respectively.

Red-sensitive emulsion layer

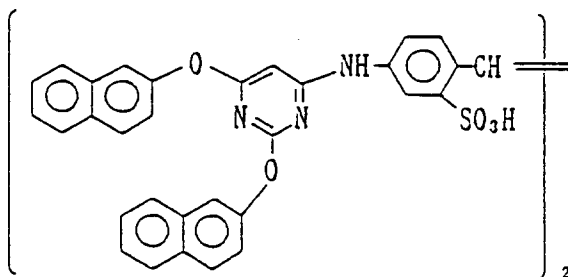
Sensitizing dye A-1



(2.5×10^{-4} mol per mol of the silver halide)

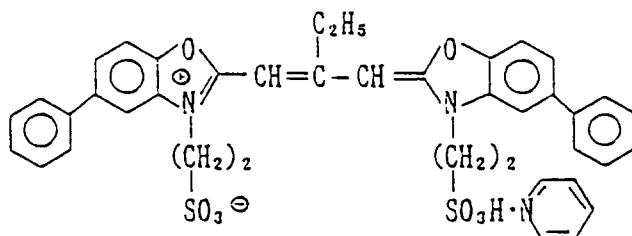
Further, the following compound was added in an amount of 5×10^{-3} mol per mol of the silver halide.

A-2



Green-sensitive emulsion layer

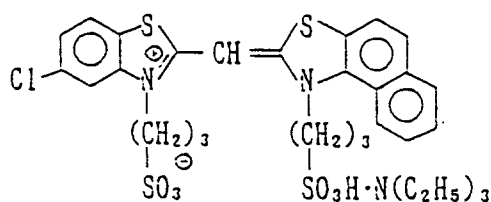
Sensitizing dye B



(9.5×10^{-4} mol per mol of the silver halide)

Blue-sensitive emulsion layer

Sensitizing dye C



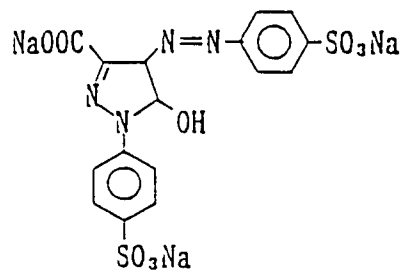
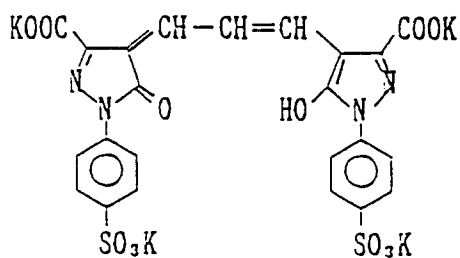
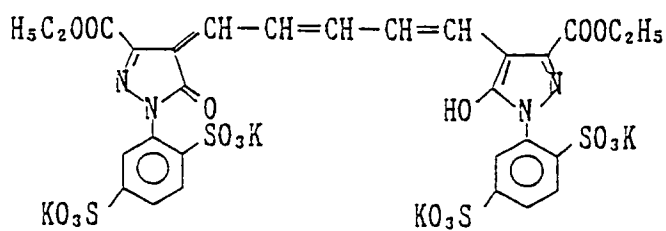
(3.0×10^{-4} mol per mol of the silver halide)

Further, to the red-sensitive emulsion layer, the green-sensitive emulsion layer, and the blue-sensitive emulsion layer, was added 1-(5-methylureidophenyl)-5-mercaptotetrazole in amounts of 3.0×10^{-4} mol, 2.0×10^{-4} mol, and 8.0×10^{-4} mol, respectively, per mol of the silver halide.

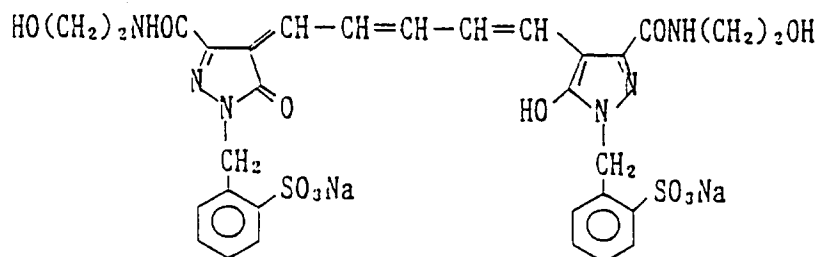
To the blue-sensitive emulsion layer and the green-sensitive emulsion layer, was added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in amounts of 1×10^{-4} mol and 2×10^{-4} mol, respectively, per mol of the silver halide.

Further, to prevent irradiation, the following dye (the figure in the parentheses shows the coated amount) was added to the emulsion layers:

Irradiation neutralizing dye

(10mg/m²)(10mg/m²)(40mg/m²)

and

(20mg/m²)

(Layer Constitution)

The composition of each layer is shown below. The figures indicate coated amounts (g/m²). As for the silver halide emulsions, the amounts are given in terms of silver.

Base

Polyethylene-laminated paper

[The polyethylene on the first layer side contained a white pigment (TiO₂, 15 wt%) and a bluish dye (ultramarine)]

First layer (red-sensitive emulsion layer)	
The above silver chlorobromide emulsion A	0.20
Gelatin	1.18
Cyan coupler (ExC-1)	0.19
Color-forming reducing agent (I-16)	0.20
Solvent (Solve-4)	0.78

Second layer (color-mixing inhibition layer)	
Gelatin	1.00
Color-mixing inhibitor (Cpd-1)	0.08
Solvent (Solv-1)	0.25
Solvent (Solv-2)	0.15
Solvent (Solv-3)	0.13

Third layer (green-sensitive emulsion layer)	
Silver chlorobromide emulsion (cubes; average grain size: 0.12 μm; silver bromide: 25 mol %)	0.20
Gelatin	1.25
Magenta coupler (ExM-1)	0.26
Color-forming reducing agent (I-16)	0.22
Solvent (Solv-4)	0.78

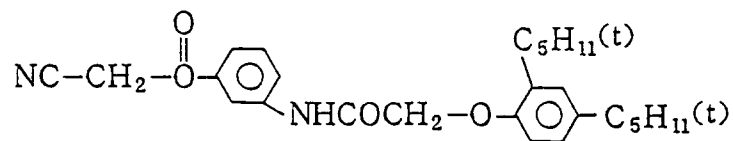
Fourth layer (color-mixing inhibition layer)	
Gelatin	1.00
Color-mixing inhibitor (Cpd-1)	0.08
Solvent (Solv-1)	0.25
Solvent (Solv-2)	0.15
Solvent (Solv-3)	0.13

Fifth layer (blue-sensitive emulsion layer)		
5	Silver chlorobromide emulsion (cubes; average grain size: 0.41 μm ; silver bromide: 0.3 mol %)	0.015
	Gelatin	1.26
	Yellow coupler (ExY-1)	0.29
10	Color-forming reducing agent (I-16)	0.24
	Solvent (Solv-4)	0.78

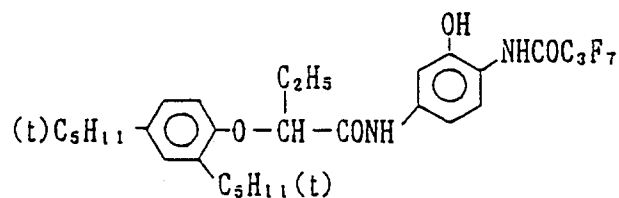
Sixth layer (ultraviolet absorbing layer)		
20	Gelatin	0.60
	Ultraviolet absorber (UV-1)	0.57
	Dye image stabilizer (Cpd-2)	0.06
	Solvent (Solv-1)	0.05

Seventh layer (protective layer)		
30	Gelatin	1.00
	Acryl-modified copolymer of polyvinyl alcohol (degree of modification: 17 %)	0.05
35	Liquid paraffin	0.02
	Surface-active agent (Cpd-3)	0.01

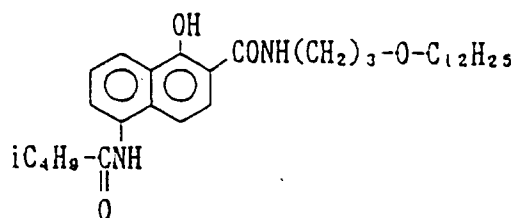
(ExY-1) Yellow coupler



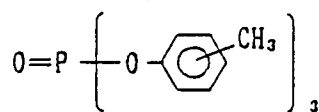
(ExM-1) Magenta coupler



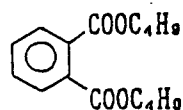
(ExC-1) Cyan coupler



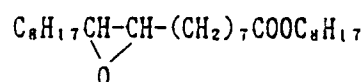
(Solv-1) Solvent



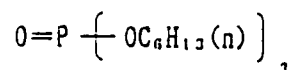
(Solv-2) Solvent



(Solv-3) Solvent

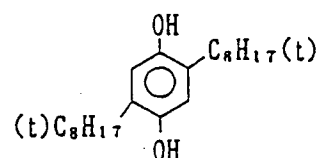
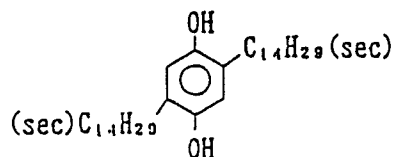
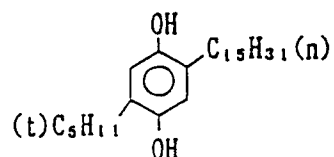


(Solv-4) Solvent

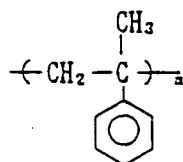


(Cpd-1) Color-mixing inhibitor

a mixture in 1:1:1 in weight ratio of



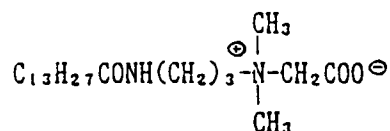
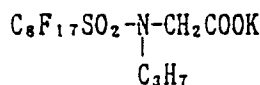
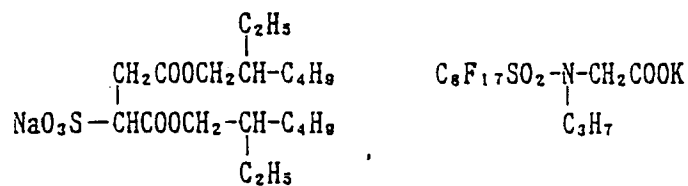
(Cpd-2) Dye image stabilizer



number average molecular weight 600

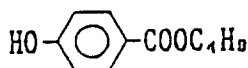
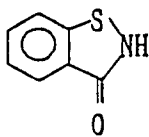
(Cpd-3) Surface-active agent

a mixture in 2:1:1 in weight ratio of



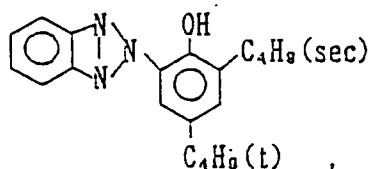
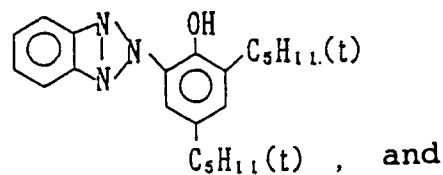
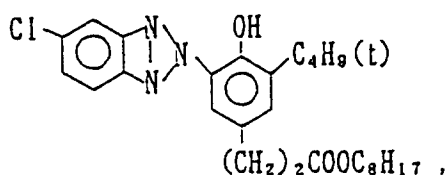
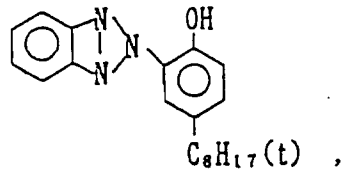
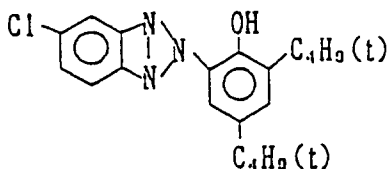
(Cpd-4) Antiseptic

(Cpd-5) Antiseptic



(UV-1) Ultraviolet Absorber

a mixture in 1:2:2:3:1 in weight ratio of



Sample (101) was prepared in the same manner as Sample (100), except that, to the second and fourth layers, i.e. the intermediate layers, was added an auxiliary developing agent (ETA-6) in the state of a fine particle solid dispersion in an amount of 1.4×10^{-4} mol per m^2 , respectively.

Further, Samples (102) to (109) were prepared in the same manner as Sample (100) or (101), except that a sulfinic acid compound (S-3) was added to the blue-sensitive emulsion, the green-sensitive emulsion, and the red-sensitive emulsion, respectively, in multiple amounts, shown in Table 1, based on the added amount (in terms of mol) of the color-forming reducing agent.

The thus prepared samples were cut; then they were given gradation exposure to light through a three-color separation filters for sensitometry by using a sensitometer (manufactured by Fuji Photo Film Co., Ltd.; FW type; color temperature of the light source: 3,200 °K), respectively.

The exposed samples were processed in the following processing steps using the following processing solution compositions.

Processing step	Temperature	Replenishment rate	Time	Tank volume (liter)
Development	40 °C	30 ml	20 sec	1.0
Bleach-fix	40 °C	30 ml	15 sec	1.0
Rinse (1)	30 °C	-	3 sec	0.3
Rinse (2)	30 °C	-	3 sec	0.3
Rinse (3)	30 °C	-	3 sec	0.3
Rinse (4)	30 °C	-	3 sec	0.3
Rinse (5)	30 °C	60 ml	5 sec	0.3
(the replenishment rate was the amount per m ² of the light-sensitive material) (the rinse was conducted in a 5-tank counter-current system of Rinse (5) to Rinse (1))				

In the above processing, the water of Rinse (4) was pumped to a reverse osmosis membrane, and the passed water was supplied to Rinse (5), while the concentrated water not passed through the reverse osmosis membrane was returned to Rinse (4). To shorten the crossover time between the rinses, a blade was placed between the tanks, and the sample was passed between them.

Samples (100) and (102) to (105) were developed with Developer-1, and Samples (101) and (106) to (109) were developed with Developer-2 (alkali activation solution).

Developer-1	Tank solution	Replenishing solution
Water	800 ml	800 ml
Tripotassium phosphate	30 g	39 g
5-Nitrobenzotriazole	0.1 g	0.25 g
Disodium-N,N-bis sulfonatoethyl)hydroxylamine	3.3 g	6.6 g
Potassium chloride	10 g	-
Hydroxyethylidene-1,1-diphosphonic acid (30% solution)	4 ml	4 ml
ETA-6	0.2 g	-
Water to make 1 liter pH: 12.0		

Developer-2 (alkali activation solution)

A solution prepared by excluding the auxiliary developing agent (ETA-6) from the above developer was used.

Blix solution	Tank solution	Replenishing solution
Water	600 ml	150 ml
Ammonium thiosulfate (700 g/liter)	100 ml	250 ml
Ammonium sulfite monohydrate	40 g	40 g
Ethylenediaminetetraacetic acid iron(III) ammonium	77 g	154 g
Ethylenediaminetetraacetic acid	5 g	10 g
Ammonium bromide	10 g	20 g
Acetic acid (50 %)	70 ml	140 ml
Water to make	1000 ml	1000 ml
Rinse solution		
Tap water		

After the samples were processed under respective conditions, the yellow, magenta, and cyan image densities were measured through B, G, and R filters corresponding to the dyes, to measure the minimum density ($D_{\min}$) and the maximum density ($D_{\max}$).

Then, after the thus prepared and processed samples were stored for 1 week in a thermo-hydrostat in which the set conditions were 80 °C and 70% humidity, the measurement was carried out similarly to the above. The values of $\Delta D_{\min}$ and $\Delta D_{\max}$, obtained by subtracting the density (D^{f}) before the storage from the density (D^{s}) after the storage, are given in Table 1.

$$\Delta D_{\min} = D^{\text{s}}_{\min} - D^{\text{f}}_{\min}$$

$$\Delta D_{\max} = D^{\text{s}}_{\max} - D^{\text{f}}_{\max}$$

Table 1

Sample No.	ETA-6	Added amount of S-3	Yellow		Magenta		Cyan		Remarks
			ΔD_{min}	ΔD_{max}	ΔD_{min}	ΔD_{max}	ΔD_{min}	ΔD_{max}	
(100)	none	none	0.21	-0.30	0.13	-0.25	0.15	-0.20	Comparative example
(102)	"	0. 0 2	0.08	-0.30	0.06	-0.25	0.07	-0.20	This invention
(103)	"	0. 2 0	0.04	-0.28	0.02	-0.24	0.03	-0.19	"
(104)	"	0. 5 0	0.03	-0.28	0.02	-0.24	0.01	-0.19	"
(105)	"	1. 0 0	0.02	-0.27	0.00	-0.23	0.00	-0.18	"
(101)	present	none	0.21	-0.30	0.13	-0.25	0.15	-0.20	Comparative example
(106)	"	0. 0 2	0.08	-0.30	0.06	-0.25	0.07	-0.20	This invention
(107)	"	0. 2 0	0.03	-0.28	0.02	-0.24	0.03	-0.19	"
(108)	"	0. 5 0	0.02	-0.28	0.02	-0.24	0.01	-0.19	"
(109)	"	1. 0 0	0.00	-0.27	0.00	-0.23	0.00	-0.18	"

As is apparent from the results shown in Table 1, after the storage of the images, both in Samples (100) and (101), color was formed in the white background (as shown in ΔD_{min}). On the other hand, it can be understood that, when the sulfinic acid compound (S-3) according to the present invention was used, the above color formation was suppressed remarkably and the maximum density was maintained after the storage, to keep a good image state.

Example 2

Samples (201), (202), (203), (204), (205), (206), and (207) were prepared in the same manner as Sample (107) in the above Example 1, except that, in place of the sulfinic acid compound (S-3) in the Sample (107), a sulfinic acid compound (S-2), (S-6), (S-7), (S-9), (S-16), (S-18), or (S-23) was used, respectively, each in the same molar amount.

For the thus prepared Samples, the processing was carried out in the same manner in Example 1 using the alkali activation solution (Developer 2) of Example 1, and the evaluation was carried out in the same manner in Example 1. The results are shown in Table 2, along with that in Sample (101) in Example 1 as a comparison.

Table 2

Sample No.	S	Yellow		Magenta		Cyan		Remarks
		$\Delta D_{\min}$	$\Delta D_{\max}$	$\Delta D_{\min}$	$\Delta D_{\max}$	$\Delta D_{\min}$	$\Delta D_{\max}$	
(101)	none	0.21	-0.30	0.13	-0.25	0.15	-0.20	Comparative example
(201)	S - 2	0.03	-0.28	0.02	-0.24	0.03	-0.19	This invention
(202)	S - 6	0.02	-0.28	0.01	-0.24	0.02	-0.19	This invention
(203)	S - 7	0.01	-0.28	0.01	-0.24	0.01	-0.19	This invention
(204)	S - 9	0.02	-0.26	0.02	-0.23	0.02	-0.19	This invention
(205)	S - 16	0.03	-0.25	0.02	-0.22	0.02	-0.17	This invention
(206)	S - 18	0.04	-0.26	0.03	-0.23	0.04	-0.18	This invention
(207)	S - 23	0.05	-0.26	0.03	-0.23	0.05	-0.18	This invention

As is apparent from the results shown in Table 2, similarly to the cases in which the sulfinic acid compound was used in Example 1, even after storage of the images, stain due to color formation in the white background was remarkably suppressed, and images high in maximum density could be obtained.

Example 3

Samples (301), (302), (303), (304), (305), and (306) were prepared in the same manner as Sample (107) in the above Example 1, except that, in place of the color-forming reducing agent in RL (red-sensitive layer) in the Sample (107), a color-forming reducing agent (I-1), (I-17), (I-23), (I-24), (I-61), or (I-72) was used, respectively, each in the same molar amount. Samples wherein Compound (S-3) was removed from these samples were also prepared.

For the thus-prepared Samples, the processing was carried out in the same manner in Example 1 using the alkali activation solution (Developer 2) of Example 1, and the evaluation was carried out in the same manner in Example 1. The results are shown in Table 3.

Table 3

Sample No.	S - 3	I	Cyan		
			ΔD_{min}	ΔD_{max}	
(301)	present	I - 1	0.10	-0.07	This invention
	none	I - 1	0.35	-0.09	Comparative example
(302)	present	I - 17	0.03	-0.19	This invention
	none	I - 17	0.16	-0.20	Comparative example
(303)	present	I - 23	0.05	-0.19	This invention
	none	I - 23	0.19	-0.21	Comparative example
(304)	present	I - 24	0.02	-0.17	This invention
	none	I - 24	0.14	-0.19	Comparative example
(305)	present	I - 61	0.13	-0.19	This invention
	none	I - 61	0.20	-0.20	Comparative example
(306)	present	I - 72	0.11	-0.16	This invention
	none	I - 72	0.16	-0.16	Comparative example

As is apparent from the results shown in Table 3, similarly to the cases wherein the color-forming reducing agent was used in Example 1, when the sulfinic acid compound according to the present invention was additionally used, even after the storage of the images, stain due to color formation in the white background could be similarly suppressed, and images high in maximum density could be obtained. In particular, when carbamoylhydrazine compounds were used as a color-forming reducing agent, images having less stain due to color formation in the white background after the storage of the images, could be obtained.

Example 4

(Preparation of Light-Sensitive Material)

On the same base used in Example 1, layers having the below-described constitution were formed, to prepare a multi-layer color printing paper. This was named Sample (400).

The coating solutions were prepared as follows.

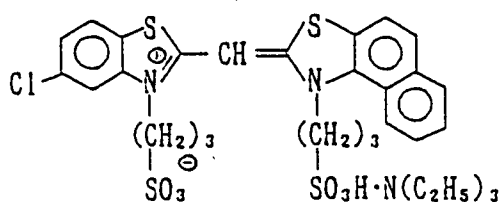
Preparation of First-Layer Coating Solution

27.8 g of a yellow color-forming coupler (ExY-2) and 20.5 g of a color-forming reducing agent (I-32) were dissolved in 52 g of a solvent (Solv-4) and 73 ml of ethyl acetate, and the resulting solution was emulsified and dispersed in 420 ml of a 12% aqueous gelatin solution containing 10% sodium dodecylbenzenesulfonate and citric acid, to prepare an emulsion D.

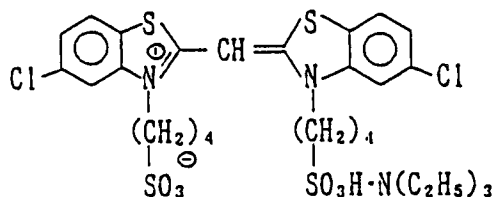
On the other hand, a silver chlorobromide emulsion D (cubes; a mixture of a large-size emulsion having an average grain size of 0.88 μm , and a small-size emulsion having an average grain size of 0.70 μm (3 : 7 in terms of mol of silver), the deviation coefficients of the grain size distributions being 0.08 and 0.10, respectively, and each emulsion having 0.3 mol% of silver bromide locally contained in part of the grain surface whose substrate was made up of silver chloride) was prepared. To the large-size emulsion of this emulsion, had been added 1.4×10^{-4} mol, per mol of silver, of each of blue-sensitive sensitizing dyes-1, -2, and -3 shown below, and to the small-size emulsion of this emulsion, had been added 1.7×10^{-4} mol, per mol of silver, of each of blue-sensitive sensitizing dyes-1, -2, and -3 shown below. The chemical ripening of this emulsion was carried out optimally with a sulfur sensitizer and a gold sensitizer being added. The above emulsified dispersion D and this silver chlorobromide emulsion D were mixed and dissolved, to prepare a first-layer coating solution.

Blue-sensitive sensitizing dye

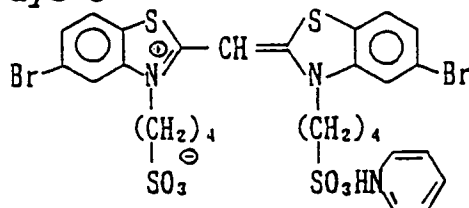
Sensitizing dye 1



Sensitizing dye 2



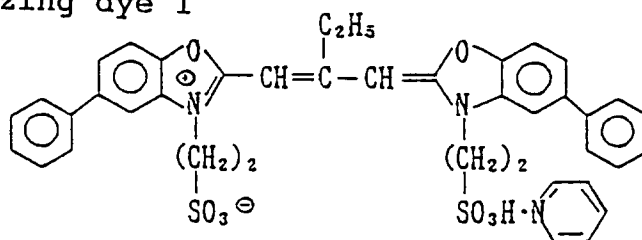
Sensitizing dye 3



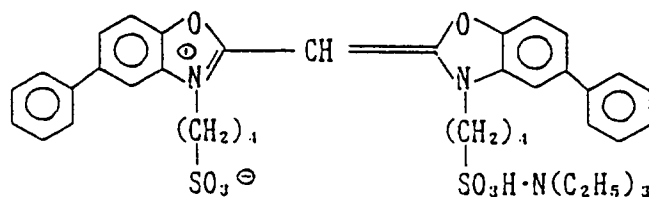
Similarly to the first-layer coating solution, coating solutions for the third layer and the fifth layer were prepared in the following manner. A silver chlorobromide emulsion E (cubes; a mixture of a large-size emulsion having an average grain size of 0.50 μm , and a small-size emulsion having an average grain size of 0.41 μm (1 : 4 in terms of mol of silver), the deviation coefficients of the grain size distributions being 0.09 and 0.11, respectively, and each emulsion having 0.8 mol% of silver bromide locally contained in part of the grain surface whose substrate was made up of silver chloride) for the third layer was prepared. To the large-size emulsion of this emulsion, had been added 3.0×10^{-4} mol, per mol of silver, of a green-sensitive sensitizing dye-1 shown below, and to the small-size emulsion of this emulsion, had been added 3.6×10^{-4} mol, per mol of silver, of the green-sensitive sensitizing dye-1 shown below; and to the large-size emulsion of this emulsion, had been added 4.0×10^{-5} mol, per mole of silver, of a green-sensitive sensitizing Dye-2 shown below, and to the small-size emulsion of this emulsion, had been added 7.0×10^{-5} mol, per mol of silver, of the green-sensitive sensitizing dye-2 shown below; and to the large-size emulsion of this emulsion, had been added 2.0×10^{-4} mol, per mol of silver, of a green-sensitive sensitizing dye-3 shown below, and to the small-size emulsion of this emulsion, had been added 2.8×10^{-4} mol, per mol of silver, of the green-sensitive sensitizing dye-3 shown below. This silver chlorobromide emulsion E, and an emulsion E containing a magenta color-forming coupler (ExM-2), which was prepared in the same manner as for the above emulsion D, were mixed and dissolved, to prepare the third-layer coating solution.

Green-sensitive sensitizing dye

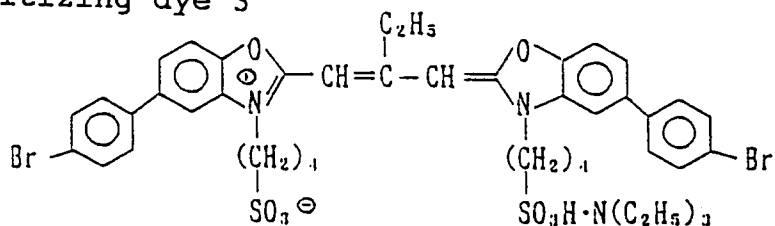
Sensitizing dye 1



Sensitizing dye 2



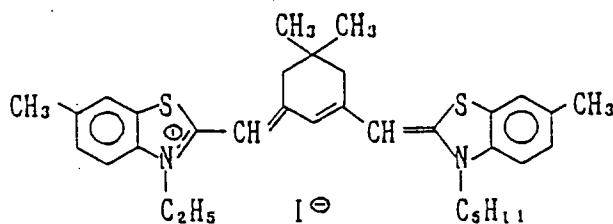
Sensitizing dye 3



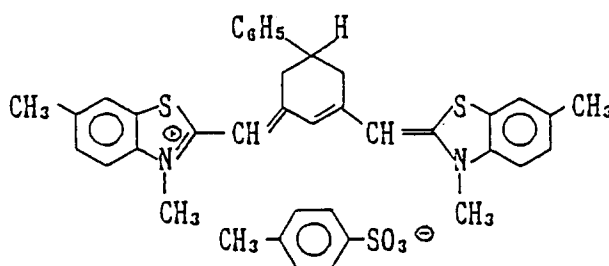
A silver chlorobromide emulsion F (cubes; a mixture of a large-size emulsion having an average grain size of 0.50 μm , and a small-size emulsion having an average grain size of 0.41 μm (1 : 4 in terms of mol of silver), the deviation coefficients of the grain size distributions being 0.09 and 0.11, respectively, and each emulsion having 0.8 mol% of silver bromide locally contained in part of the grain surface whose substrate was made up of silver chloride) for the fifth layer was prepared. To the large-size emulsion of this emulsion, had been added 5.0×10^{-5} mol, per mol of silver, of each of red-sensitive sensitizing dyes-1 and -2 shown below; and to the small-size emulsion of this emulsion, had been added 6.0×10^{-5} mol, per mol of silver, of each of red-sensitive sensitizing dye-1 and 2 shown below.

Red-sensitive sensitizing dye

Red-sensitive sensitizing dye-1



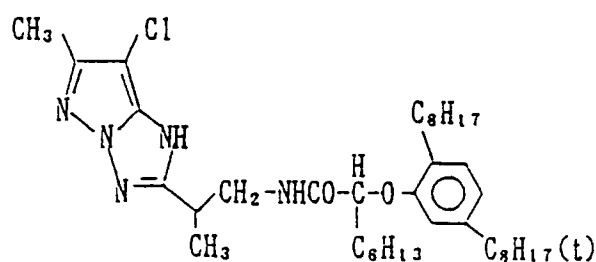
Red-sensitive sensitizing dye-2



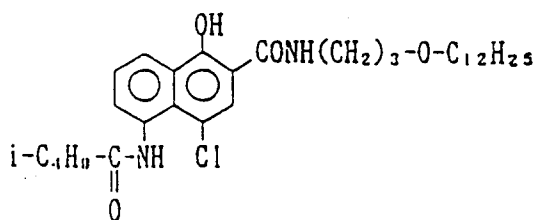
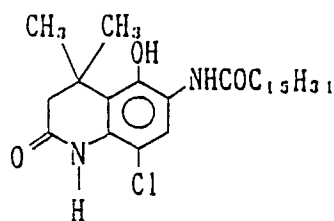
Further, the same A-2 compound as used in Example 1 was added to the fifth layer in an amount of 2.6×10^{-3} mol per mol of silver.

This silver chlorobromide emulsion F, and an emulsion F containing a cyan color-forming coupler (ExC-2), which was prepared in the same manner as for the above emulsion D, were mixed and dissolved, to prepare the fifth-layer coating solution.

(ExY-2) Yellow coupler



(ExM-2) Magenta coupler (ExC-2) Cyan coupler



The second, sixth and seventh layers were prepared such that they would have the compositions shown below.

To each of the second and fourth layers, i.e. the intermediate layers, was added an auxiliary developing agent (ETA-6) in the state of a fine particle solid dispersion in an amount of 1.4×10^{-4} mol.

With respect to solvents, image dye stabilizers, ultraviolet absorbers, color mixing inhibitors, surface-active agents, and the like, the same compounds as used in Example 1 were used.

As the gelatin hardener of each layer, 1-oxy-3,5-dichloro-s-triazine sodium salt was used.

Further, Cpd-4 and Cpd-5 were added to each layer so that the total amount would be 25 mg/m² and 50 mg/m², respectively.

To the blue-sensitive emulsion layer, the green-sensitive emulsion layer, and the red-sensitive emulsion layer, was added 1-(5-mthylureidophenyl)-5-mercaptotetrazole in amounts of 8.5×10^{-5} mol, 9.0×10^{-4} mol, and 2.5×10^{-4} mol, respectively, per mol of the silver halide. Further, to the blue-sensitive emulsion layer and the green-sensitive emulsion layer, was added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in amounts of 1×10^{-4} mol and 2×10^{-4} mol, respectively, per mol of the silver halide.

Further, to prevent irradiation, the same dye as used in Sample (100) of Example 1 was added to the emulsion layers in the same amount.

(Layer Constitution)

The composition of each layer is shown below. Each figure indicates the coated amount (g/m²). For the silver halide emulsions, the amounts are given in terms of silver.

Base

Polyethylene-laminated paper

[The polyethylene on the first layer side contained a white pigment (TiO₂) and a bluish dye (ultramarine)]

First layer (blue-sensitive emulsion layer)	
The above Silver Chlorobromide Emulsion D	0.20
Gelatin	1.54
Yellow coupler (ExY-2)	0.35
Color-forming reducing agent (I-32)	0.26
Solvent (Solve-4)	0.78

Second layer (color-mixing inhibition layer)	
Gelatin	1.00
Color-mixing inhibitor (Cpd-1)	0.08
Solvent (Solv-1)	0.25
Solvent (Solv-2)	0.15
Solvent (Solv-3)	0.13

Third layer (green-sensitive emulsion layer)	
Silver Chlorobromide Emulsion E	0.20
Gelatin	1.55
Magenta coupler (ExM-2)	0.34
Color-forming reducing agent (I-32)	0.26
Solvent (Solv-4)	0.78

Fourth layer (color-mixing inhibition layer)	
Gelatin	1.00
Color-mixing inhibitor (Cpd-1)	0.08
Solvent (Solv-1)	0.25
Solvent (Solv-2)	0.15
Solvent (Solv-3)	0.13

Fifth layer (blue-sensitive emulsion layer)	
Silver Chlorobromide Emulsion F	0.20
Gelatin	1.50
Cyan coupler (ExC-2)	0.29
Color-forming reducing agent (I-16)	0.26
Solvent (Solv-4)	0.78

Sixth layer (ultraviolet absorbing layer)	
Gelatin	0.60
Ultraviolet absorber (UV-1)	0.57
Dye image stabilizer (Cpd-2)	0.06
Solvent (Solv-1)	0.05

Seventh layer (protective layer)	
Gelatin	1.00
Acryl-modified copolymer of polyvinyl alcohol (degree of modification: 17%)	0.05
Liquid paraffin	0.02
Surface-active agent (Cpd-3)	0.01

Sample (401) was prepared in the same manner as Sample (400), except that a sulfinic acid compound (S-1) was added to the blue-sensitive emulsion, the green-sensitive emulsion, and the red-sensitive emulsion, respectively, in an amount of 0.2 times, in terms of mol, the added amount of the color-forming reducing agent.

The thus prepared samples were cut; then they were given gradation exposure to light through a three-color separation filters for sensitometry by using a sensitometer (manufactured by Fuji Photo Film Co., Ltd.; FW type; color temperature of the light source: 3,200 °K), respectively.

The exposed samples were processed in the following processing steps using the following processing solution compositions.

Processing step	Temperature	Time
Development	40 °C	30 sec
Blix	40 °C	15 sec
Stabilization	30 °C	10 sec
Drying	80 °C	10 sec

Developer-3 (alkali activation bath)	Tank solution
Water	800 ml
Sodium 5-sulfosalicylate	29 g
Potassium chloride	10 g
Hydroxyethylidene-1,1-diphosphonic acid (30% solution)	4 ml
Water to make 1 liter pH: 12.0	

As for the blix solution, the same tank solution as used in Example 1 was used.

Stabilizing solution	
Water	900 ml
Citric acid	4.2 g
Hydroxyethylidene-1,1-diphosphonic acid (30% solution)	1.0 ml
5-chloro-2-methyl-4-isothiazolin-3-one	0.02 g
Water to make 1 liter pH: 6.0	

The same evaluation as in Example 1 was carried out. The results are shown in Table 4.

Table 4

Sample No.	S-1	Yellow		Magenta		Cyan		
		$\Delta D_{\min}$	$\Delta D_{\max}$	$\Delta D_{\min}$	$\Delta D_{\max}$	$\Delta D_{\min}$	$\Delta D_{\max}$	
(400)	none	0.15	-0.14	0.10	-0.12	0.15	-0.20	Comparative example
(401)	present	0.01	-0.12	0.00	-0.11	0.03	-0.19	This invention

As is apparent from the results shown in Table 4, it can be understood that when Compound (S-1) was used additionally, stain due to color formation after long-term storage of the image was suppressed remarkably and that high quality images could be maintained even after the storage.

Example 5

Samples (501), (502), (503), (504), (505), and (506) were prepared in the same manner as Sample (401) in the above Example 4, except that the color-forming reducing agent in BL (blue-sensitive layer) in the Sample (401) was replaced with a color-forming reducing agent (I-27), (I-29), (I-31), (I-39), (I-40), or (I-67), respectively, each in the same molar amount. Samples wherein Compound (S-1) was not used in these samples were also prepared.

For the thus-prepared Samples, the same processing and evaluation as in Example 4 were carried out. The results are shown in Table 5.

Table 5

Sample No.	S - 1	I	Yellow		
			$\Delta D_{\min}$	$\Delta D_{\max}$	
(501)	present	I - 27	0.00	-0.13	This invention
	none	I - 27	0.11	-0.15	Comparative example
(502)	present	I - 29	0.01	-0.12	This invention
	none	I - 29	0.13	-0.14	Comparative example
(503)	present	I - 31	0.01	-0.12	This invention
	none	I - 31	0.15	-0.14	Comparative example
(504)	present	I - 39	0.02	-0.14	This invention
	none	I - 39	0.17	-0.15	Comparative example
(505)	present	I - 40	0.02	-0.12	This invention
	none	I - 40	0.18	-0.14	Comparative example
(506)	present	I - 67	0.09	-0.12	This invention
	none	I - 67	0.15	-0.12	Comparative example

As is apparent from the results shown in Table 5, similarly to the cases wherein the color-forming reducing agent was used in Example 4, when the sulfinic acid compound according to the present invention was additionally used, distinct images (images high in clarity) having less color formation in the white background even after storage of the images, could be obtained.

Example 6

Sample (601) was prepared in the same manner as Sample (107) in the above Example 1, except that the coating

amounts of silver in the first, third, and fifth layers were 0.01 g, 0.01 g, and 0.015 g, respectively, per m².

This sample was exposed to light in the same manner as in Example 1, and then it was processed with an intensifier of a 0.3% aqueous hydrogen peroxide solution having a pH of 12.0, which was prepared by adding hydrogen peroxide to Developer-2. The result showed that, even when the light-sensitive material considerably reduced in silver was used, an image having high maximum density, similar to in Example 1, was obtained. A distinct image having good storage preservability with less stain after the storage was obtained.

It has been found that the light-sensitive material of the present invention is also preferable for the formation of an image by a light-sensitive material with a low silver content amplified with an intensifying processing.

Example 7

Sample (401) of Example 4 was processed and evaluated in the same manner as in Example 4, with the following alteration of exposure to light.

(Exposure to light)

473 nm, which was taken out from a YAG solid laser (emitting wavelength: 946 nm) using a semiconductor laser GaAlAs (emitting wavelength: 808.5 nm) as an excitation light source, with the wavelength conversion effected with an SHG crystal of KNbO₃; 532 nm, which was taken out from a YVO₄ solid laser (emitting wavelength: 1064 nm) using a semiconductor laser GaAlAs (emitting wavelength: 808.7 nm) as an excitation light source, with the wavelength conversion effected with an SHG crystal of KTP; and AlGaInP (emitting wavelength: about 670 nm; Type No. TOLD 9211, manufactured by Toshiba Co.), were used as light sources. The apparatus was such that the laser beams could be scanned, by respective rotating polyhedrons, successively over a color printing paper moved perpendicularly to the scanning direction. Using this apparatus, the amount of light was varied, to find the relationship (D - log E) between the density (D) of the light-sensitive material and the amount of light (E). At that time the amounts of lights of the laser beams having three wavelengths were modulated using an external modulator, to control the exposure amount. In this scanning exposure, 400 dpi was used, and the average exposure time per picture element was about 5×10^{-8} sec. As for the semiconductor laser, to suppress fluctuation in the amount of light due to temperature, a Peltier element was used to keep the temperature constant.

As a result, even in an image that was formed with digital exposure of high intensity, an image having high maximum density could be obtained, and the stain of the image was less even after the storage.

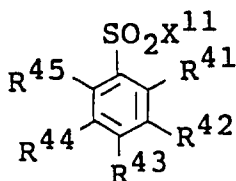
Claims

1. A silver halide color photographic light-sensitive material having at least one light-sensitive silver halide emulsion layer on a base, wherein at least one photographic constitutional layer contains at least one dye-forming coupler, and at least one color-forming reducing agent represented by formula (I):



wherein R¹¹ represents an aryl group or a heterocyclic group; R¹² represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group; and X represents a group selected from the group consisting of -SO₂-, -CO-, -COCO-, -CO-O-, -CO-N(R¹³)-, -COCO-O-, -COCO-N(R¹³)-, and -SO₂-N(R¹³)-, in which R¹³ represents a hydrogen atom or a group represented by R¹²; and at least one photographic constitutional layer contains a compound represented by formula (S):

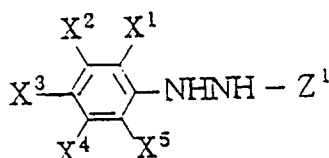
formula (S)



wherein X^{11} represents a hydrogen atom, some other atom, or a group of atoms, which atom or atoms form an inorganic or organic salt; and R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} , which are the same or different, each represent a hydrogen atom or a substituent, or the groups of R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} in the ortho-positions may bond together to form a 5- to 6-membered ring, provided that the sum total of the carbon atoms of R^{41} , R^{42} , R^{43} , R^{44} , and R^{45} is 10 or more.

2. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein the compound represented by formula (I) is represented by formula (II) or (III):

formula (II)



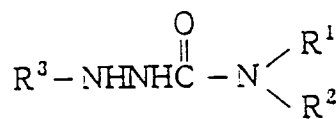
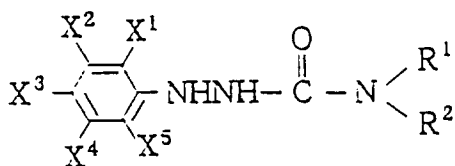
formula (III)

wherein Z^1 represents an acyl group, a carbamoyl group, an alkoxy carbonyl group, or an aryloxy carbonyl group; Z^2 represents a carbamoyl group, an alkoxy carbonyl group, or an aryloxy carbonyl group; X^1 , X^2 , X^3 , X^4 , and X^5 each represent a hydrogen atom or a substituent, provided that the sum of the Hammett substituent constant σ_p values of X^1 , X^3 , and X^5 , and the Hammett substituent constant σ_m values of X^2 and X^4 , is 0.80 or more but 3.80 or less; and R^3 represents a heterocyclic group.

3. The silver halide color photographic light-sensitive material as claimed in claim 2, wherein the compound represented by formula (II) or (III) is represented by formula (IV) or (V), respectively:

formula (IV)

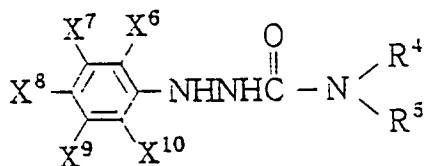
formula (V)



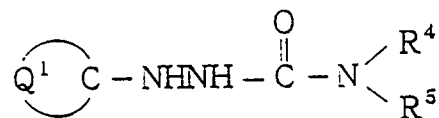
wherein R^1 and R^2 each represent a hydrogen atom or a substituent; X^1 , X^2 , X^3 , X^4 , and X^5 each represent a hydrogen atom or a substituent, provided that the sum of the Hammett substituent constant σ_p values of X^1 , X^3 , and X^5 , and the Hammett substituent constant σ_m values of X^2 and X^4 , is 0.80 or more but 3.80 or less; and R^3 represents a heterocyclic group.

4. The silver halide color photographic light-sensitive material as claimed in claim 3, wherein the compound represented by formula (IV) or (V) is represented by formula (VI) or (VII), respectively:

formula (VI)



formula (VII)



wherein R^4 and R^5 each represent a hydrogen atom or a substituent; X^6 , X^7 , X^8 , X^9 , and X^{10} each represent a hydrogen atom, a cyano group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyl group, a trifluoromethyl group, a halogen atom, an acyloxy group, an acylthio group, or a heterocyclic group, provided that the sum of the Hammett substituent constant σ_p values of X^6 , X^8 , and X^{10} , and the Hammett substituent constant σ_m values of X^7 and X^9 , is 1.20 or more but 3.80 or less; and Q^1 represents a group of non-metal atoms required to form, together with the C, a 5- to 8-membered nitrogen-containing heterocyclic group.

5. The silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, or 4, comprising an auxiliary developing agent and/or its precursor.
6. The silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, 4, or 5, comprising a silver halide such that the total applied silver amount of all the applied layers is 0.003 to 0.3 g/m² in terms of silver.
7. The silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, 4, 5, or 6, wherein the said silver halide color photographic light-sensitive material is exposed to light by scanning exposure, with the exposure time per picture element being 10⁻⁸ to 10⁻⁴ sec.
8. The silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, 4, 5, 6, or 7, wherein the dye-forming coupler has a substituent at the coupling reactive position.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 9208

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 463 639 A (FUJI PHOTO FILM CO LTD) 2 January 1992 ---		G03C7/392
D,A	EP 0 545 491 A (KODAK LTD ;EASTMAN KODAK CO (US)) 9 June 1993 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 February 1997	Examiner Philosoph, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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