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(54) Silver halide color photographic light-sensitive material, and method of processing the same.

(57) A silver halide color photographic light-sensitive material includes at least one of each of blue-, green-, and red-sensitive silver halide emulsion layers. At least one silver halide emulsion layer contains tabular silver halide grains, each having a thickness of less than 0.5 µm, a diameter of 0.3 µm or more, and a diameter/thickness ratio of 2 or more. The tabular silver halide grains occupy at least 50% of the total projected area of all silver halide grains contained in the silver halide emulsion layer. At least 50% in number of the tabular grains have 10 or more dislocations each. Further, at least one layer in the light-sensitive material contains a compound represented by the following formula (I) or (II):

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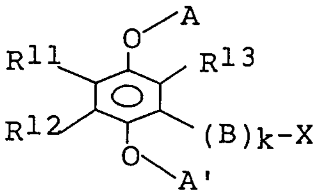
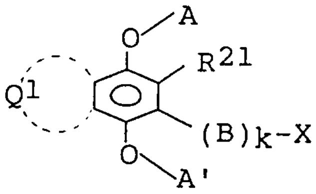
(3.10/3.5x/3.0.1)

Formula (I)



Formula (II)



The present invention relates to a silver halide photographic light-sensitive material and a method of processing the same, and more particularly to a silver halide photographic light-sensitive material which has high sensitivity and improved sharpness, and a method of processing the same.

As to tabular silver halide grains, methods of forming these grains, and methods of using these grains are disclosed in, for example, U.S. Patents 4,434,226, 4,439,520, 4,414,310, 4,433,048, 4,414,306 and 4,459,353, JP-A-59-99433, and JP-A-62-209445. ("JP-A" means Published Unexamined Japanese Patent Application.) It is known that tabular silver halide grains increase a sensitivity including an increase in color sensitizing efficiency by a sensitizing dye, improve the sensitivity-graininess relationship, and enhance sharpness and covering power because of the optical properties specific to the tabular grains.

Generally, a tabular silver halide grain emulsion is developed in the initial phase of a developing process at a higher rate than an emulsion of silver halide grains of any other shape, such as cubic grains, octahedral grains, tetradecahedral grains, or spherical grains. Due to the difference in rate of development, it is hard to use the tabular silver halide emulsion together with an emulsion of silver halide grains of any other shape.

In recent years, it has been increasingly demanded that silver halide emulsions for photographic use be improved further, in their photographic properties such as sensitivity and also in their toughness such as pressure resistance and storage stability. Use of the tabular silver halide grains known hitherto fail to meet this demand.

JP-A-63-220238 discloses the technique of introducing dislocations into tabular grains, and teaches that the use of tabular grains having dislocations serves to improve the sensitivity, pressure resistance, exposure illuminance and storage stability of a silver halide emulsion.

The emulsion of tabular grains having dislocations is developed at a higher rate than an emulsion of ordinary tabular grains. Thus, in particular, it is difficult for the emulsion of such tabular grains to be given inter-image effect and edge effect, resulting in small sharpness-increasing effect by inter-image effect and edge effect. Even if the tabular grains are used, thus reducing optical scattering thereby to improve the sharpness of any layer closer to a support than a layer containing the tabular grains, the layer containing the tabular grains fails to exhibit sufficient sharpness. In other words, good use cannot be made of the desirable characteristic of the tabular grains. Therefore it has been demanded that inter-image effect and edge effect be increased, even by using tabular grains containing dislocations.

Techniques of improving inter-image effect and edge effect have been known hitherto. One of these techniques used commonly is to use a DIR compound which imagewisely releases a development inhibitor.

Used commonly as a DIR compound is a DIR coupler which imagewisely releases an development inhibitor, and forms a coloring dye, upon coupling reaction with an oxidized form of a color developing agent. When a DIR coupler is used, however, there is the possibility that the dye obtained from the main coupler presents a turbid hue. Hence, a DIR coupler should not better be used, and a DIR compound which forms a colorless compound is requested for.

DIR compounds which form a colorless compound are classified into two types, i.e., coupling type and redox type, in accordance with the mode in which they react with an oxidized form of a color developing agent. Examples of DIR compounds of the coupling type are disclosed in, for example, JP-B-51-16141, JP-B-51-16142, U.S. Patent 4,226,943 and U.S. Patent 4,171,223. ("JP-B" means Published Examined Japanese Patent Application.) Examples of DIR compounds of the redox type are DIR hydroquinone compounds disclosed in, for example, U.S. Patents 3,379,529, U.S. Patent 3,639,417, JP-A-49-129536, JP-A-64-546, and JP-A-3-226744, and DIR hydrazide compounds disclosed in, for example, JP-A-61-213847, JP-A-64-88451, and U.S. Patent 4,684,604.

To process a color reversal material, first by black/white development (first development) and then by color development (second development), it is desirable that an inhibitor be released from a DIR compound in the first development. In the second development, all silver halide left undeveloped is developed, and the silver development speed is extremely high. Hence, if a development inhibition is to be applied imagewisely in the second development, the silver development speed must be decreased, inevitably making the color development unstable. Thus, it is desirable that a DIR compound be reacted in the first development. This DIR compound should be a redox type one which can also react with an oxidized form of a black/white developing agent, too.

Examples of a DIR compound which is very active and greatly serves to improve inter-image effect and edge effect are disclosed in, for example, JP-A-3-226744, JP-A-3-226745 and JP-A-3-226746. These references, however, make no mention of the problem inherent in tabular gains containing dislocations, generally describing only the improvement of inter-image effect and edge effect.

A DIR compound increases sharpness to one value when applied to tabular grains, and to another value when applied to grains of any other type. A DIR compound cannot sufficiently increase the sharpness of tabular grains in some cases, though it can greatly increases the sharpness of grains of any other type. Therefore, it has been demanded that a DIR compound be developed which is effective even if use is made of tabular grains containing dislocations.

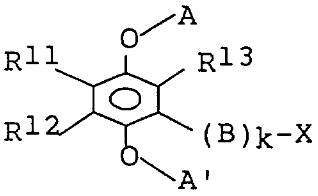
An object of the present invention is to provide a color photographic light-sensitive material which excels in sharpness.

Another object of the invention is to provide a method of processing the light-sensitive material.

These objects of the invention can be attained by (1) a photographic light-sensitive material described below, and by (2) a method of processing the photographic light-sensitive material, described below.

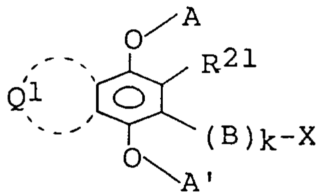
(1) A silver halide color photographic light-sensitive material comprising at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, on a support, at least one silver halide emulsion layer containing tabular silver halide grains, each having a thickness of less than 0.5 μm, a diameter of 0.3 μm or more, and a diameter/thickness ratio of 2 or more, said tabular silver halide grains occupying at least 50% of the total projected area of all silver halide grains contained in said at least one silver halide emulsion layer, at least 50% in number of said tabular grains having 10 or more dislocations each, and at least one layer in the light-sensitive material containing at least one compound represented by the following formula (I) or (II):

Formula (I)



In the formula (I), R^{11} is R^{14}-N(R^{16})CON(R^{15})-, R^{14}OCON(R^{15})-, $R^{14}SO_2N(R^{15})$-, R^{14}-N(R^{16})SO_2N-(R^{15})- or R^{17}CONH- wherein R^{14} is an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, R^{15} and R^{16} are hydrogen atoms, alkyl groups or aryl groups, and R^{17} is an alkyl group having 2 or more carbon atoms in which a heteroatom is not substituted on the carbon atom adjacent to the carbonyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. R^{12} and R^{13} are hydrogen atoms or substituent groups having a Hammett's substituent constant σ_p of 0.3 or less. B is a group releasing X after splitting off from an oxidized form of the hydroquinone nucleus. X is a development inhibitor. k is an integer, and A and A' are hydrogen atoms or groups which can be removed by alkali.

Formula (II)



In the formula (II), Q^1 is an atomic group containing at least one heteroatom, required to form, along with the carbon atoms, a 5- or more membered heterocyclic ring, R^{21} is a group which can be substituted on the hydroquinone nucleus, and B, X, k, A and A' are idential in meaning to those in the formula (I).

(2) A method of processing a silver halide color photographic light-sensitive material, comprising subjecting a light-sensitive material of claim 1 to an imagewise exposure and then processing the exposed material by a treating process including a balck-and-white developing step.

The present invention will now be described in detail.

The formula (I), set forth above, will now be explained in more detail.

R^{11} is R^{14}-N(R^{16})CON(R^{15})-, R^{14}OCON(R^{15})-, $R^{14}SO_2N(R^{15})$-, R^{14}-N(R^{16})$SO_2N(R^{15})$- or R^{17}CONH-. Here, R^{14} is a substituted or unsubstituted alkyl group (one having 1 to 30 carbon atoms, e.g., methyl, ethyl, isopropyl, decyl, hexadecyl, t-butyl, cyclohexyl, or benzyl), a substituted or unsubstituted alkenyl group (one having 2 to 30 carbon atoms, e.g., 1-butenyl or 1-octadecenyl), a substituted or unsubstituted alkynyl group (one having 2 to 30 carbon atoms, e.g., ethynyl or 1-octynyl), a substituted or unsubstituted aryl group (one having 6 to 30 carbon atoms, e.g., phenyl, naphthyl, 3-dodecanamidophenyl, 3-hexadecanesulfonamidophenyl, or 4-dococyloxyphenyl), or a heterocyclic group (a 5- to 20-membered one having at least one heteroatom selected from N, O, S and Se, e.g., 4-pyridyl, 2-furyl, pyrrolo, 2-thiazolyl, 2-oxazolyl, 2-imidazolyl, triazolyl, tetrazolyl, benzotriazolyl, or morpholinyl. Examples of the substituent groups which R^{14} has are an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a carboxylic acid amido group, a sulfonic acid amido group, an alkoxycarbonylamino group, a ureido group, a carbamoyl group, an alkoxycarbonyl group, a sulfamoyl group, a sulfonyl group, cyano, a halogen atom, an acyl group, hydroxyl group, a carboxyl group, a sulfo group, a nitro group, and a heterocyclic group.

R^{15} and R^{16} may be either identical or different, and can be hydrogen atoms or those exemplified as R^{14}. Preferable as R^{15} is a hydrogen atom.

R^{17} is a substituted or unsubstituted alkyl group having two or more carbon atoms, in which a hetero atom is not substituted on the carbon atom adjacent to the carbonyl group (preferably, one having 2 to 30 carbon atoms, e.g., ethyl, nonyl, pentadecyl, isopropyl, t-butyl, 1-hexylnonyl, 3-(2,5-di-t-pentylphenoxy)-propyl, cyclohexyl, or benzyl), a substituted or unsubstituted alkenyl group (one having 2 to 30 carbon atoms, e.g., vinyl, 1-octenyl, or 2-phenylvinyl), a substituted or unsubstituted alkynyl group (one having 2 to 30 carbon atoms, e.g., ethynyl or phenylethynyl), a substituted or unsubstituted aryl group (one having 6 to 30 carbon atoms, e.g., phenyl, naphthyl, 3,5-bis(octadecanamido)phenyl, 2-hexadecanesulfonamidophenyl, or 4-dodecyloxyphenyl), or a heterocyclic group (a 5- to 20-membered one having at least one heteroatom selected from N, O, S and Se, e.g., 3-pyridyl, 2-furyl, 3-thiazolyl, benzotriazolyl, or benzimidazolyl).

Examples of the substituent group which R^{17} has are those exemplified as the substitutent groups which R^{14} has.

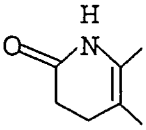
R^{12} and R^{13} shown in the formula (I) are hydrogen atoms or substituent groups having a Hammett's substituent constant σ_p of 0.3 or less. Examples of these substituent groups are: an alkyl group (one having 1 to 30 carbon atoms, e.g., methyl, ethyl, isopropyl, t-butyl, decyl, hexadecyl, cyclohexyl, benzyl, or t-octyl), an aryl group (one having 6 to 30 carbon atoms, e.g., phenyl or naphthyl), an alkoxy group (one having 1 to 30 carbon atoms, e.g., methoxy, hexyloxy, hexadecyloxy, 2-dodecyloxy, or benzyloxy), an aryloxy group (one having 6 to 30 carbon atoms, e.g., phenoxy or naphthoxy), an alkylthio group (one having 1 to 30 carbon atoms, e.g., methylthio, hexylthio, dodecylthio, or benzylthio), an arylthio group (one having 6 to 30 carbon atoms, e.g., phenylthio, naphthylthio, 2-butyloxy-6-t-octylphenyl), an amido group (one having 1 to 30 carbon atoms, e.g., acetamido, butanamido, hexadecanamido, or benzamido), a sulfonamido group (one having 1 to 30 carbon atoms, e.g., methanesulfonamido, octanesulfonamido, hexadecanesulfonamido, or benzenesulfonamido), a ureido group (one having 1 to 30 carbon atoms, e.g., 3-methylureido, 3-dodecylureido, or 3-phenylureido), an urethane group (one having 2 to 30 carbon atoms, e.g., methoxycarbonylamino, decyloxycabonylamino, or phenoxycarbonylamino), a sulfamoylamino group (one having 30 or less carbon atoms, e.g., 3-methylsulfamoylamino or 3-phenylsulfamoylamino), a halogen atom (e.g., chlorine, bromine, or fluorine), a hydroxy group, or $-(B)_k-X$.

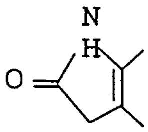
R^{12} and R^{13} may have a substituent group. Examples of this substituent group are those exemplified as substituent groups which R^{14} has.

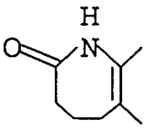
The formula (II), set forth above, will be explained in greater detail.

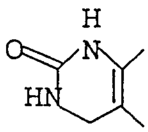
Q^1 in the formula (II) is a divalent group having at least one hetero atom. Examples of the divalent group are: an amide bond, a divalent amino group, an ether bond, a thioether bond, an imino bond, a sulfonyl group, a carbonyl group, an alkylene group, and an alkenylene group. The divalent group may be a combination of two or more of these. The examples of the divalent group, which are specified above, may have a substituent group. If Q^1 contains an ether bond, it does not form a 5-membered ring.

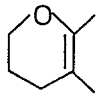
Examples of the heterocyclic ring which is completed with Q^1 are rings which are represented by the following formulas:

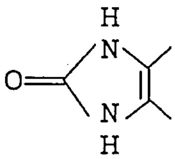


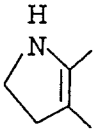


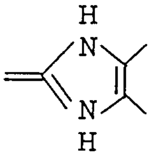


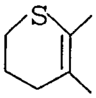


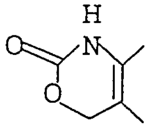


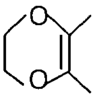


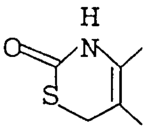












R^{21} in the formula (II) is a group which can be substituted on the hydroquinone nucleus. More specifically, examples of R^{21} are those specified above as examples of R^{13}. Other examples of R^{21} are a substituted or unsubstituted acyl group (preferably, one having 1 to 30 carbon atoms, e.g., acetyl, octanoyl, benzoyl, chloroacetyl, 3-carboxypropionyl, or actadecanoyl), a substituted or unsubstituted alkoxycarbonyl group (preferably, one having 2 to 30 carbon atoms, e.g., methoxycarbonyl, octyloxycarbonyl, phenoxycarbonyl, octadecyloxycarbonyl, or methoxyethoxycarbonyl), a substituted or unsubstituted carbamoyl group (preferably, one having 1 to 30 carbon atoms, e.g., carbamoyl, N-propylcarbamoyl, N-hexadecylcarbamoyl, N-(3-(2,4-di-tert-pentylphenoxy)propyl), N-phenylcarbamoyl, N-(3-dodecyloxybutyl), or pyrolidinocarbonyl), a substituted or unsubstituted sulfamoyl group (preferably, one having 0 to 30 carbon atoms, e.g., sulfamoyl or dibutylsulfamoyl), a substituted or unsubstituted sulfonyl group (preferably, one having 1 to 30 carbon atoms, e.g., methanesulfonyl, benzensulfonyl, or p-dodecylbenzenesulfonyl), and a heterocyclic group (a 5- to 20-membered one having at least one hetero atom selected from N, O, S and Se, e.g., 5-tetrazolyl, 2-benzoxazolyl, 2-thiazolyl, 2-imidazolyl, 2-pyridyl, or morpholino).

A, A', B, and X in the formulas (I) and (II) will be described in detial.

If A and A' in the formulas (I) and (II) are groups which can be removed by alkali (hereinafter called "precursor groups"), each of them is, preferably, a group which can be hydrolyzed, such as an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an imidoyl group, an oxalyl group, or a sulfonyl group; a precursor group of the type utilizing anti-Michael reaction, disclosed in U.S. Patent 4,009,029; a precursor group of the type using an anion generated after ring cleavage, as an intramolecular nucleophilic group, disclosed in U.S. Patent 4,310,612; a precursor group wherein an anion undergoes electron transfer along a conjugate system, causing cleavage reaction, which is disclosed in U.S. Patents 3,674,478; 3,932,480 and 3,993,661; a precursor group wherein an anion reacted after ring cleavage undergoes electron transfer, causing cleavage reaction, which is disclosed in U.S. Patent 4,335,200; or a precursor group utilizing an imidomethyl group, disclosed in U.S. Patents 4,363,865 and 4,410,618.

In the formulas (I) and (II), the group represented by B is a divalent group which can release $-(B)_k-X$ first and X then, after the hydroquinone nucleus has been oxidized into a quinone form by an oxdized form of a developing agent during development. It may have timing-adjusting function, or may be a group which becomes a coupler or a redox group releasing X upon reaction with another molecule of an oxidized form of a developing agent. If k is 0, X is bonded directly to the hydroquinone nucleus. If k is 2 or more, there are two or more groups B which are the same or different.

Examples of B, which is a group having timing-adjusting function, are disclosed in, for example, U.S. Patents 4,248,962 and 4,409,323, British Patent 2,096,783, U.S Patent 4,146,396, JP-A-51-146,828, and JP-A-57-56837. Two or groups, selected from these, may be used as Bs in combination.

Preferred examples of the timing-adjusting group are as follows:

(1) Group Utilizing Cleavage of Hemiacetal

Example of this group are disclosed in, for example, U.S. Patent 4,146,396, JP-A-60-249148, and JP-A-60-249149.

(2) Group Causing Cleavage by Using Intramolcular Nucleophilic Substitution

An example of this group is the timing group disclosed in U.S. Patent 4,248,292.

(3) Group Causing Cleavage by Using Electron Transfer along Conjugate System

Example of this group are disclosed in, for example, U.S. Patents 4,409,323 and 4,421,845.

(4) Group Utilizing Cleavage by Hydrolysis of Ester

An example of this group is the linking group disclosed in, for example, West German Laid-Open Patent Application 2,626,315.

(5) Group Utilizing Cleavage of Iminoketal

An example of this group is the linking group disclosed in U.S. Patent 4,546,073.

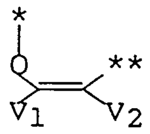
Examples of the group prepresented by B, which is a coupler or a redox group, are as follows:

An example of the coupler is a phenol type one which is bonded to the hydroquinone nucleus at the oxygen atom of the hydroxy group removed of the hydrogen atom thereof. Another example of the coupler is a 5-pyrazoline type coupler which is bonded to the hydroquinone nucleus at the oxygen atom of the hydroxy group of the tautomeried 5-hydroxypyrazole, removed of the hydrogen atom thereof.

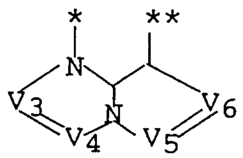
Only after these couplers have been released from hydroquinone nuclei, they act as couplers, reacting with an oxidized form of a developing agent to release X from the coupling position.

Preferable examples of B which is a coupler are those represented by the following formulas (C-1) to (C-4):

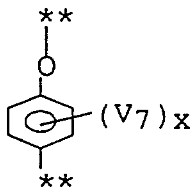
Formula (C-1)



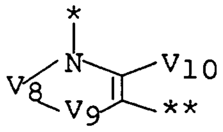
Formula (C-2)



Formula (C-3)



Formula (C-4)



In these formulas, V_1 and V_2 are substituent groups, and V_3, V_4, V_5, and V_6 are nitrogen atoms or substituted or unsubstituted methine groups. V_7 is a substituent group, and x is an integer ranging from 0 to 4. When x is 2 or more, plural groups V_7 may be the same or different. Two groups V_7 may combine together to form a ring structure. V_8 is -CO- group, $-SO_2$-group, an oxygen atom, or a substituted imino group, V_9 is a non-metallic atomic group required to form a 5- to 8-membered ring together with $-V_8$-N-C=C-, and V_{10} is a hydrogen atom or a substituent group. The mark * indicates a position where the coupler bonds to the hydroquinone nucleus, and the mark ** indicates a position where the coupler bonds to X.

If the group represented by B in the formulas (I) and (II) is a redox group, it is preferably represented by the following formula (R-1):

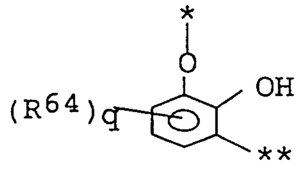
Formula (R-1)

$*\text{-P-}(X'=Y')_n\text{-Q-A}''$

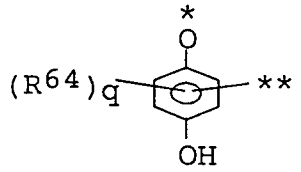
In the formula (R-1), P and Q are independently an oxygen atom or a substituted or unsubstituted imino group, at least one of n X's and n Y's is a methine group having -X as a substituent group, and the remaining X's and Y's are substituted or unsubstituted methine groups or nitrogen atoms, n is an integer ranging from 1 to 3 (n X's are identical or different, and n Y's are likewise identical or different), and A" is a hydrogen atom or a group which can be removed by an alkali, and is of the same meaning as A in the formula (I). Any two of substituent groups P, X', Y', Q, and A" may be a divalent groups, combining together to form a ring structure. For example, $(X'=Y')_n$ may form a benzene ring or a pyridine ring.

Of the groups which are represented by the formula (R-1), particularly preferable are those which are represented by the following formulas (R-2) and (R-3):

Formula (R-2)



Formula (R-3)



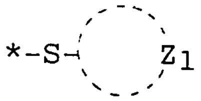
In the formulas (R-2) and (R-3), the mark * indicates the position where the group bonds to the hydroquinone nucleus, and the mark ** indicates the position where it bonds to X.

In these formulas, R^{64} is a substituent group, and q is 0, 1, 2 or 3. If q is 2 or 3, the groups R^{64} may be the same or different. If two substituent groups R^{64} are on adjacent carbon atoms, they may be divalent groups, bonding together to form a ring structure.

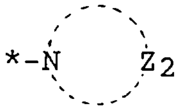
As an example of R^{64}, R^{21} in the formula (II) can be cited.

In the formulas (I) and (II), X represents a development inhibitor. Preferable examples of X are a compound having a mercapto group which bonds to the heterocyclic ring and represented by the following formula (X-1), and a heterocyclic compound which can form imino silver and represented by the following formula (X-2).

Formula (X-1)



Formula (X-2)



In the formulas (X-1) and (X-2), Z_1 is a non-metallic atomic group required to form a monocyclic or fused heterocyclic ring, Z_2 is a non-metallic atomic group required to form, together with N, a monocyclic or fused heterocyclic ring. The heterocyclic ring may have a substituent group. In the formulas (X-1) and (X-2), the mark * indicates the position where the inhibitor X bonds to B. Preferable as a heterocyclic ring formed by Z_1 or Z_2 are 5- to 8-membered heterocyclic rings, each having at least one heteroatom selected from a nitrogen atom, an oxygen atom, a sulfur atom and a selenium atom. Of these, the most preferred is a 5- or 6-membered heterocyclic ring.

Examples of the heterocyclic ring represented by Z_1 are: azoles (tetrazole, 1,2,4-triazole, 1,2,3-triazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole, 1,3-thiazole, 1,3-oxazole, imidazole, benzothiazole, benzoxazole, benzimidazole, pyrrole, pyrazole, and indazole), azaindenes (tetraazaindene, pentaazaindene, and triazaindene), and azines (pyrimidine, triazine, pyrazine, and pyridazine).

Examples of the heterocyclic ring represented by Z_2 are: triazoles (1,2,4-triazole, benzotriazole, and 1,2,3-triazole), indazole, benzimidazole, azaindenes (tetraazaindene and pentaazaindene), and tetrazole.

Preferable as the substituent group which the development inhibitors of the formula (X-1) and (X-2) have are as follows:

R_{77} group, R_{78}O- group, R_{77}S- group, R_{77}OCO-group, $R_{77}OSO_2$- group, a halogen atom, a cyano group, a nitro group, $R_{77}SO_2$- group, R_{78}CO- group, R_{77}COO-group, $R_{77}SO_2N(R_{78})$- group, $R_{78}N(R_{79})SO_2$- group, $R_{78}N(R_{79})$CO- group, $R_{77}C(R_{78})=N$- group, $R_{77}N(R_{78})$- group, $R_{78}CON(R_{79})$- group, R_{77}OCON-(R_{78})-group, $R_{78}N(R_{79})CON(R_{80})$- group, or $R_{77}SO_2O$- group.

Here, R_{77} is an aliphatic group, an aromatic group, or a heterocyclic group. R_{78}, R_{79}, and R_{80} are each an aliphatic group, an aromatic group, a heterocyclic group, or a hydrogen atom. If there are two or more R_{77} groups, two or more R_{78} groups, and two or more R_{80} groups, these may bond together, forming a ring (e.g., a benzene ring).

Examples of the compound represented by the formula (X-1) are: substituted or unsubstituted mercaptoazoles (e.g., 1-phenyl-5-mercaptotetrazole, 1-propyl-5-mercaptotetrazole, 1-butyl-5-mercaptotetrazole, 2-methylthio-5-mercapto-1,3,4-thiadiazole, 3-methyl-4-phenyl-5-mercapto-1,3,4-triazole, 1-(4-ethylcarbamoylphenyl)-2-mercaptoimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-phenyl-5-mercapto-1,3,4-oxadiazole, 1-{3-(3-methylureido)phenyl}-5-mercaptotetrazole, 1-(4-nitrophenyl)-5-mercaptotetrazole, and 5-(2-ethylhexanoylamino)-2-mercaptobenzimidazole), substituted or unsubstituted mercaptoazaindenes (e.g., 6-methyl-4-mercapto-1,3,3a,7-tetraazaindene and 4,6-dimethyl-2-mercapto-1,3,3a,7-tetraazaindene), and substituted or unsubstituted mercaptopyrimidines (e.g., 2-mercaptopyrimidine and 2-mercapto-4-methyl-6-hydroxypyrimidine).

Examples of the heterocyclic compound which can form imino silver are: substituted or unsubstituted triazoles (e.g., 1,2,4-triazole, benzotriazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-bromobenzotriazole, 5-n-butylbenzotriazole, and 5,6-dimethylbenzotriazole), substituted or unsubstituted indazoles (e.g., indazole, 5-nitroindazole, 3-nitroindazole, and 3-chloro-5-nitroindazole), and substituted or unsubstituted benzimidazoles (e.g., 5-nitrobenzimidazole and 5,6-dichlorobenzimidazole).

In the formulas (I) and (II), X may be a compound becoming a development-inhibiting compound upon releasing from B, which in turn undergoes a certain reaction with a developer component, turning into to a compound which substantially does not have a development-inhibiting property or of which development-inhibiting property is remarkably reduced. A functional group which undergo such chemical reaction is, for example, an ester group, a carbonyl group, an imino group, an immonium group, a Mickael-addition receptor group, or imido group.

Examples of such a deactivating type development inhibitor are the development-inhibiting residual groups described in, for example, U.S. Patents 4,477,563, JP-A-60-218644, JP-A-60-221750, JP-A-60-233650, and JP-A-61-11743.

Of these compounds, those having an ester group are particularly preferred. Examples of such a compound are: 1-(3-phenoxycarbonylphenyl)-5-mercaptotetrazole, 1-(4-phenoxycarbonylphenyl)-5-mercaptotetrazole, 1-(3-maleinimidophenyl)-5-mercaptotetrazole, 5-phenoxycarbonylbenzotriazole, 5-(4-cyanophenoxycarbonyl)benzotriazole, 2-phenoxycarbonylmethylthio-5-mercapto-1,3, 4-thiadiol, 5-nitro-3-phenoxycarbonylimidazole, 5-(2,3-dichloropropyloxycarbonyl)benzotriazole, 1-(4-benzoyloxyphenyl)-5-mercaptotetrazole, 5-(2-methanesulfonylethoxycarbonyl)-2-mercaptobenzothiazole, 5-cinnamoylaminobenzotriazole, 1-(3-vinylcarbonylphenyl)-5-mercaptotetrazole, 5-succinimidomethylbenzotriazole, 2-(4-succinimidophenyl)-5-mercapto-1,3,4-oxadiazole, 6-phenoxy carbonyl-2-mercatobenzoxazole, 2-(1-methoxycarbonylethylthio)-5-mercapto-1,3,4-thiaidazole, 2-butoxycarbonylmethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole, 2-(N-hexylcarbamoylmethoxycarbonylmethyl-thio)-5-mercapto-1,3,4-thiadiazole, and 5-butoxycarbonylmethoxycarbonylbenzotriazole.

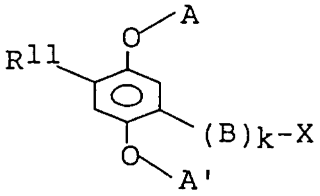
Preferable examples of X are mercaptoazoles and benzotriazoles. Of mercaptoazoles, mercaptotetrazoles, 5-mercapto-1,3,4-thiadiazoles, and 5-mercapto-1,3,4-oxadiazoles are particularly preferred.

The most preferable as X are 5-mercapto-1,3,4-thiadiazoles.

In the formulas (I) and (II), k is preferably 0, 1 or 2.

Of the compounds represented by the formula (I), preferable are those which are represented by the following formula (IA):

Formula (IA)



In the formula (IA), R^{11}, B, X, A, A', and k are identical in meaning to those in the formula (I).

In the formula (IA), preferable as R^{11} are: R^{14}-N(R^{16})CON(R^{15})- and R^{14}OCON(R^{15})-. R^{14}, R^{15}, and R^{16} are of the meanings which have been explained. In the formula (IA), k is preferably 0 or 1.

In the formulas (I) and (II), A and A' are prefer ably hydrogen atoms.

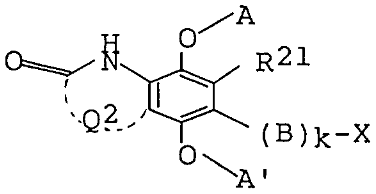
In the formula (II), Q^1 is preferably -N(R^{28})-CO-Q^2-, where Q^2 is, for example, a divalent amino group, an ether bond, a thioether bond, an alkylene group, an ethylene bond, an imino bond, a sulfonyl group, a carbonyl group, an arylene group, or a divalent heterocyclic group, or a group consisting of two or more of these.

R^{28} is a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group, and may have a substituent group. Preferable as R^{28} is a hydrogen atom.

R^{21} is preferably a hydrogen atom or or a substituent group having a Hammett substituent group constant σ_p of 0 or more.

The heterocyclic ring containing Q^1 is preferably 5- to 7-membered. Of the compounds represented by the formula (II), the compound represented by the following formula (IIA) is preferable.

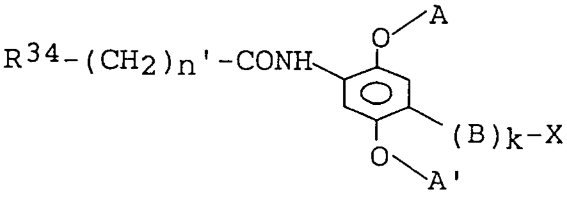
Formula (IIA)



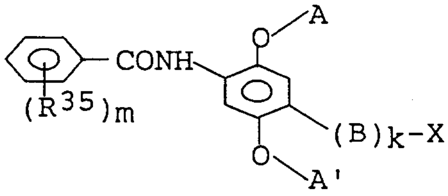
In the formula (IIA), Q^2 is of the same meaning as has been explained in conjunction with Q^1. R^{21}, A, A', B, X, and k are identical in meaning to those in the formula (II).

If R^{11} in the formula (IA) is R^{17}CONH-, the compounds represented by the following formulas (IB) and (IC) are preferable:

Formula (IB)



Formula (IC)



In the formulas (IB) and (IC), R^{34} and R^{35} are substituent groups, n' is an integer of 2 or more, and m is an integer ranging from 1 to 5. If m is 2 or more, groups R^{35} may be identical or different. A, A', B, X, and k are identical in meaning to those in the formula (I).

Examples of R^{34} and R^{35} are those exemplified above as substituent groups which R^{14} has. These substituent groups may further be substituted. In the formula (IB), R^{34} is preferably a substituent group having 5 to 30 carbon atoms, and n' is preferably 2 to 5. In the formula (IC), R^{35} has preferably 5 to 30 carbon atoms.

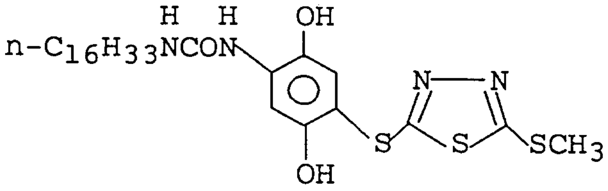
The compound represented by the formulas (I) and (II) can be synthesized by the methods disclosed in, for example, JP-A-49-129536, JP-A-52-57828, JP-A-60-21044, JP-A-60-233642, JP-A-60-233648, JP-A-61-18946, JP-A-61-156043, JP-A-61-213847, JP-A-61-230135, JP-A-61-236549, JP-A-62-62352, JP-A-62-103639, and U.S. Patents 3,379,529; 3,620,746; 4,332,828; 4,377,634 and 4,684,604.

If the compounds of the formulas (I) and (II) according to the invention are used in a multilayered color photographic light-sensitive material, they are contained in a silver halide emulsion layer or at least one of the layers adjacent to the silver halide emulsion layer, such as a yellow filter layer, an antihalation layer, an interlayer and a protective layer. It is desirable that the compounds be contained in a silver halide emulsion or the interlayer located adjacent thereto.

The amounts in which to use the compounds of the formula (I) and (II) in any layer of the silver halide photographic light-sensitive material depends on the features of the material, the application of the material, and the method of developing the material. Generally, the compound is used in an amount of 1 to 10^{-7} mol, preferably 3×10^{-2} to 3×10^{-5} mol, per mol of silver halide contained in the same layer or in an adjacent layer.

To describe the present invention more specifically, specific examples of the compounds represented by the formulas (I) and (II) will be described below. However, the compounds which can be used in the invention are not limited to these.

I-(1)



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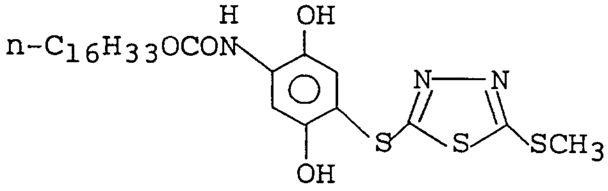

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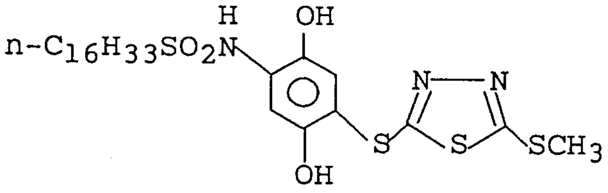

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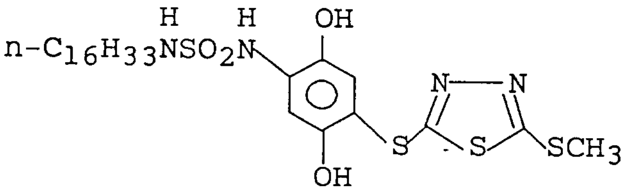

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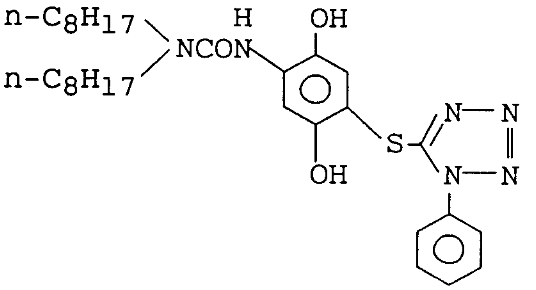

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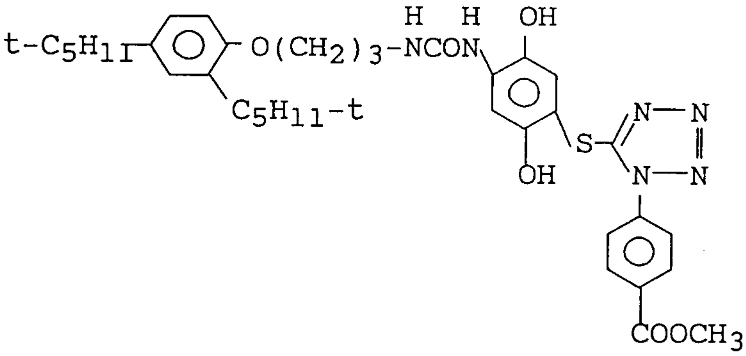

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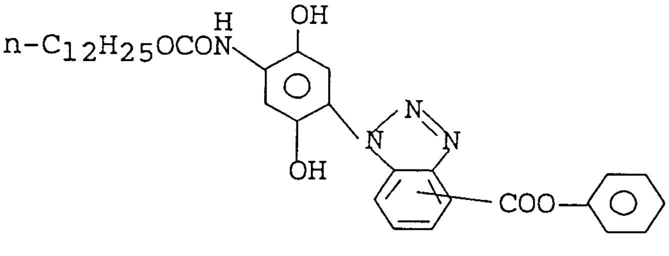

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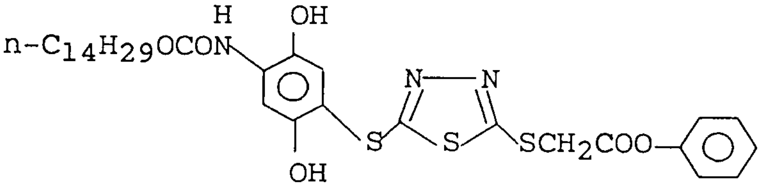

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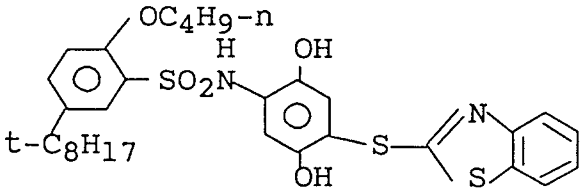

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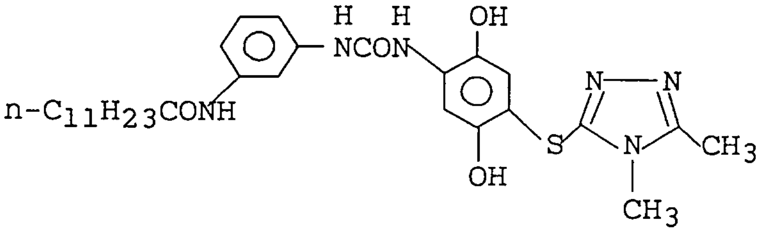

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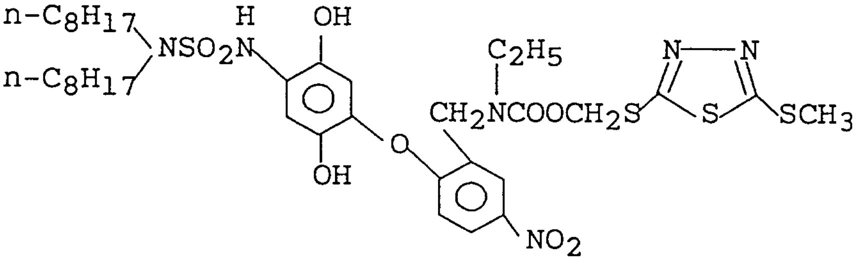

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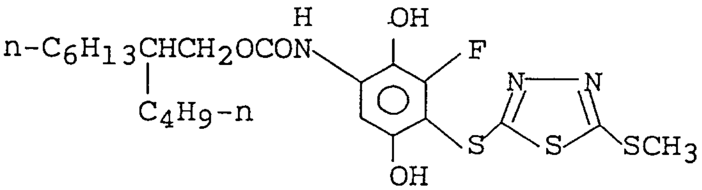

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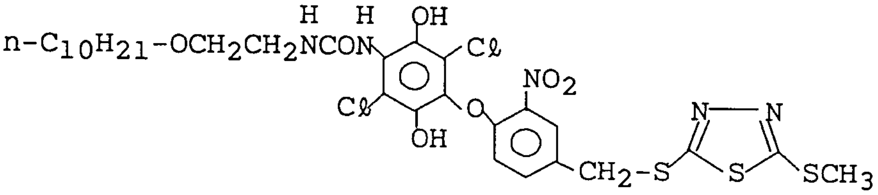

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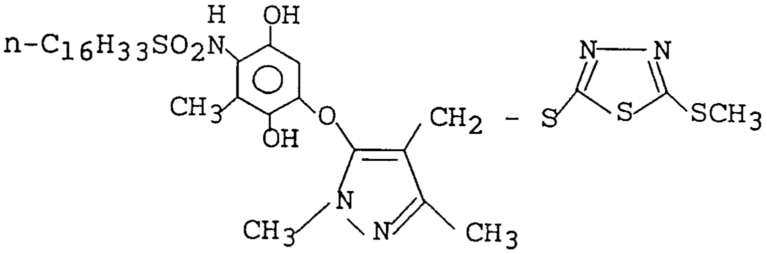

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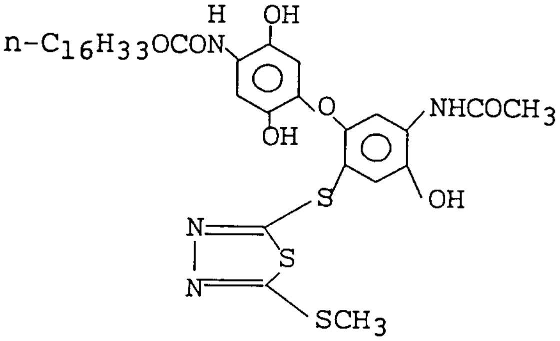

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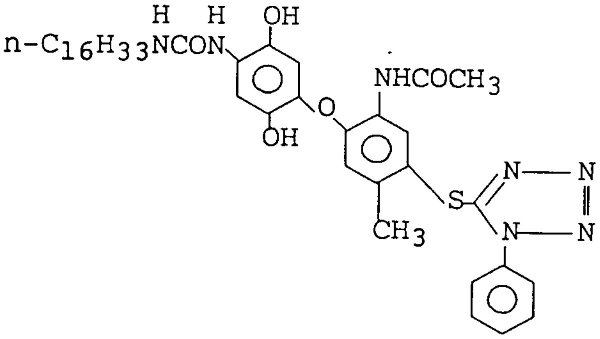

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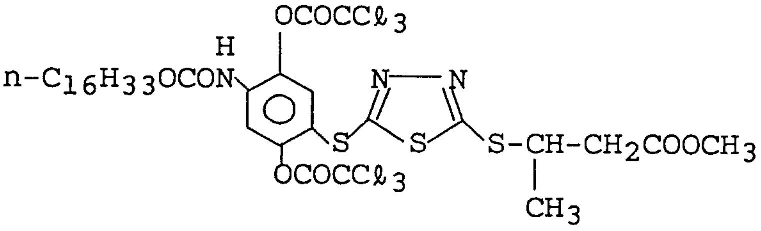
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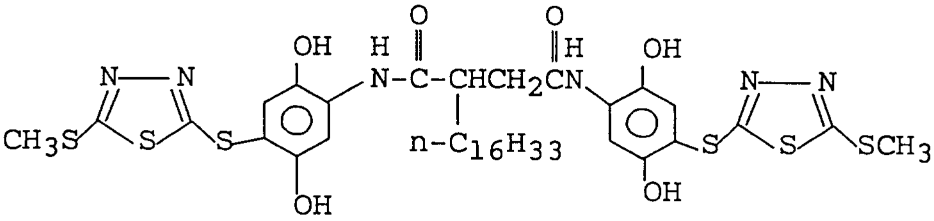
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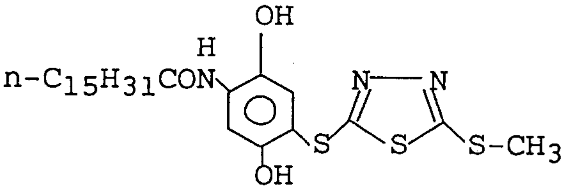
I-(19)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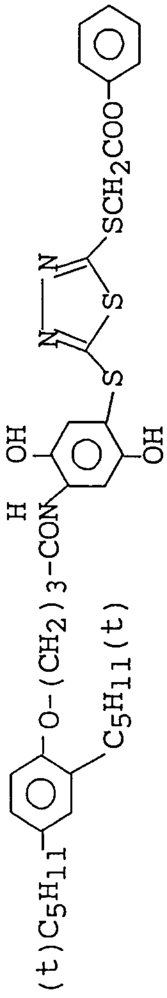
I-(20)



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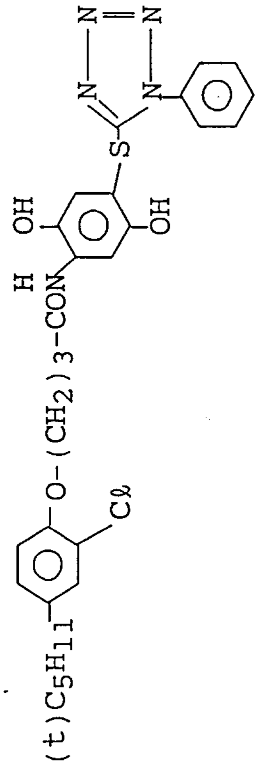

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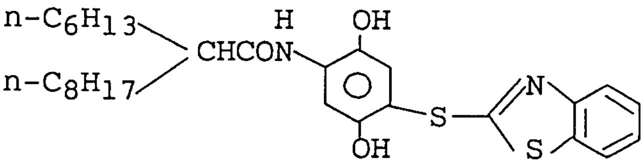

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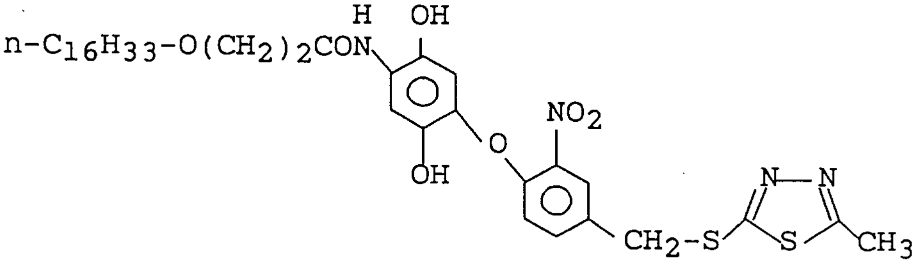

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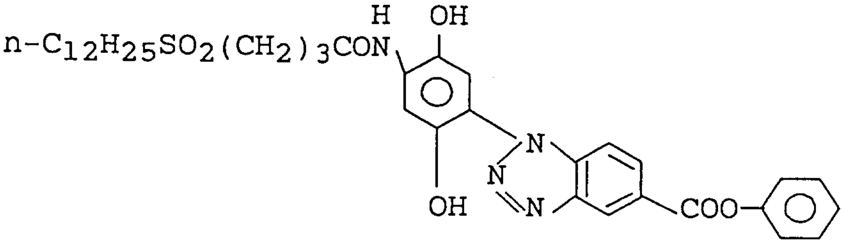

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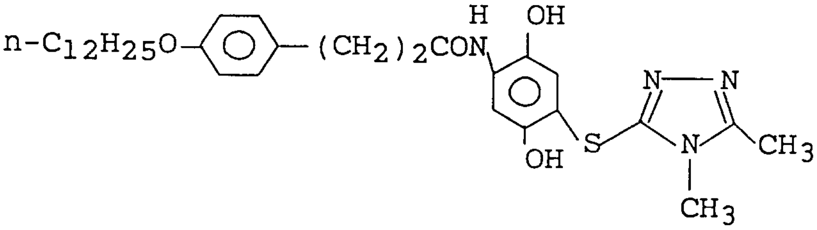

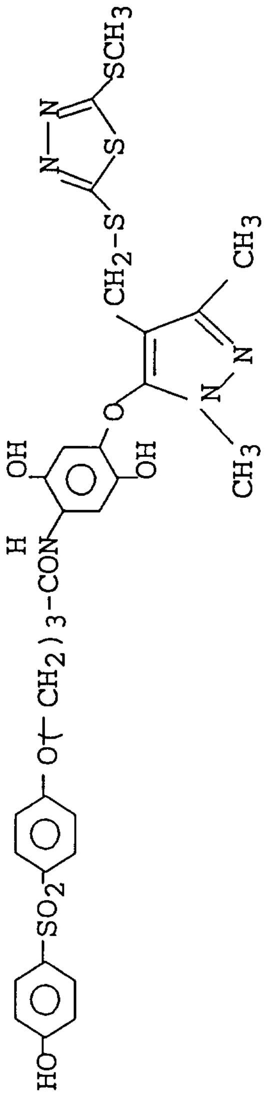

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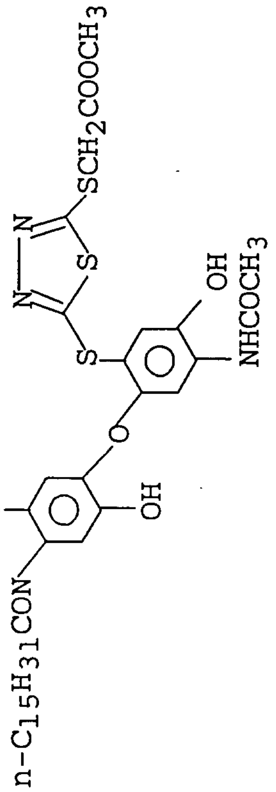

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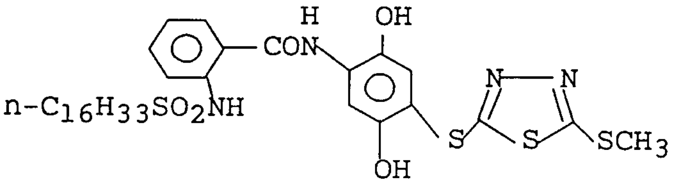
I-(28)



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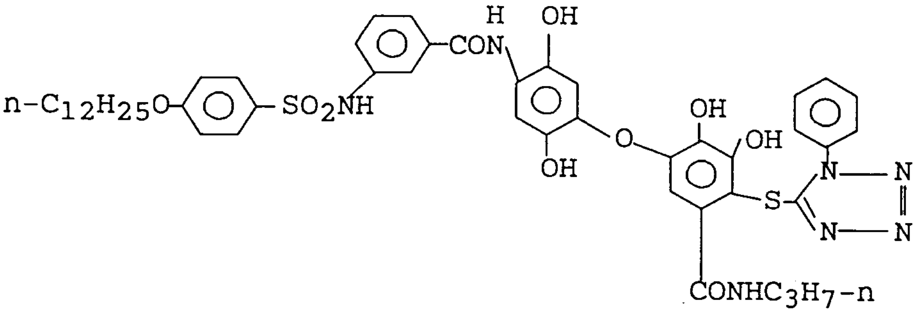

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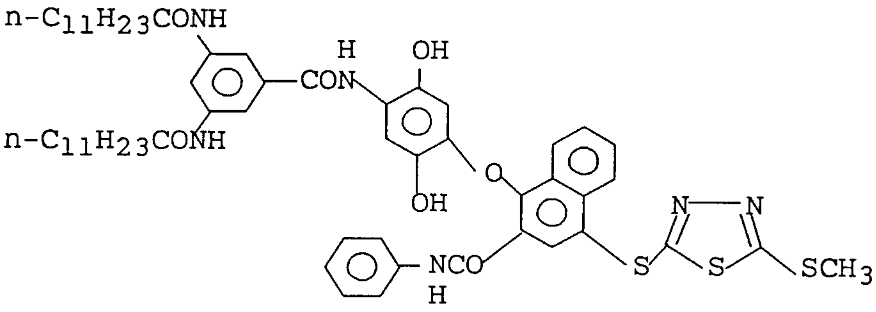

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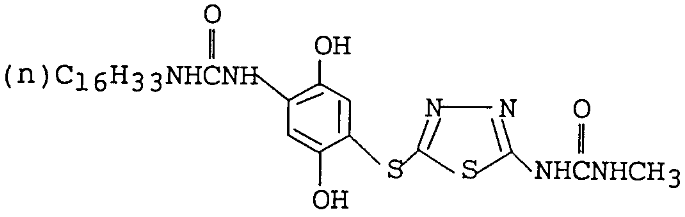

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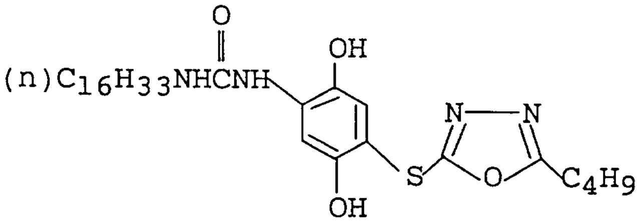

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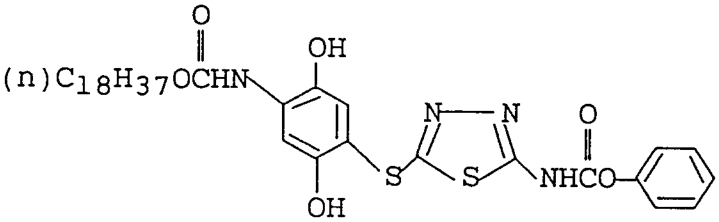

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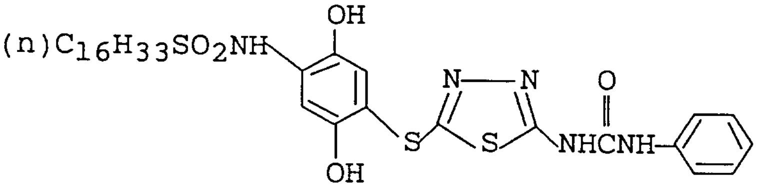

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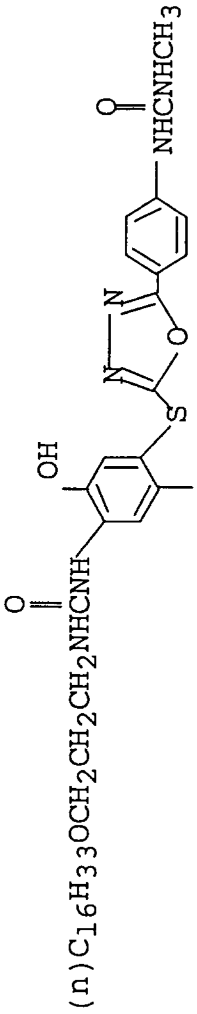

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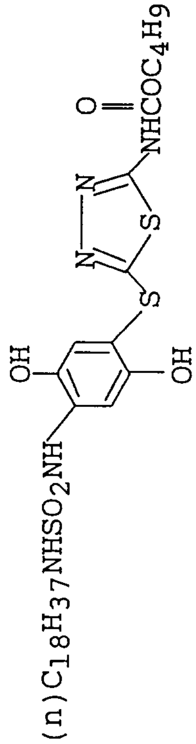

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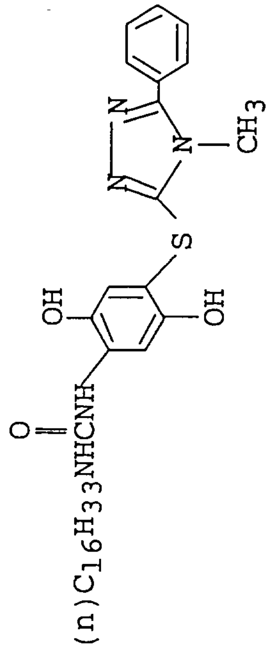

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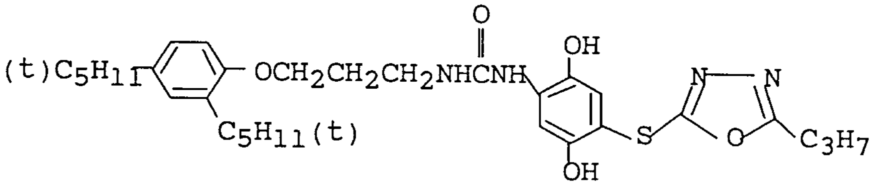

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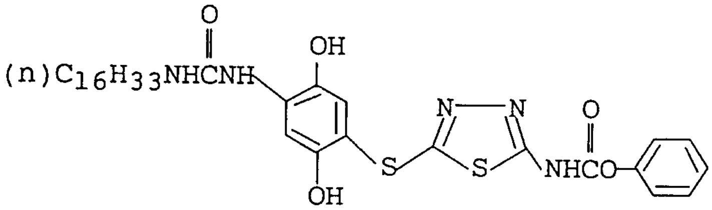

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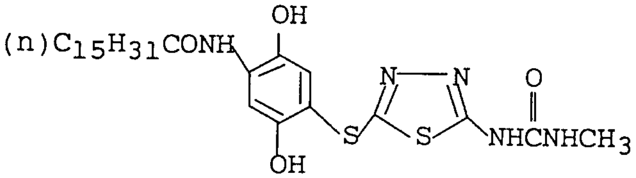

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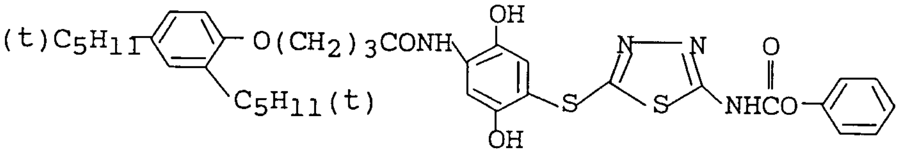

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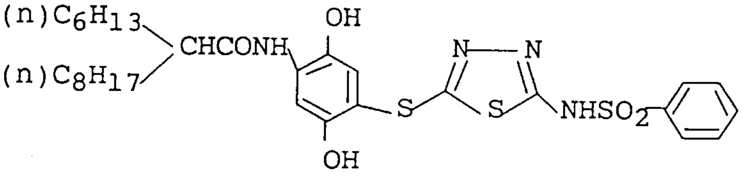

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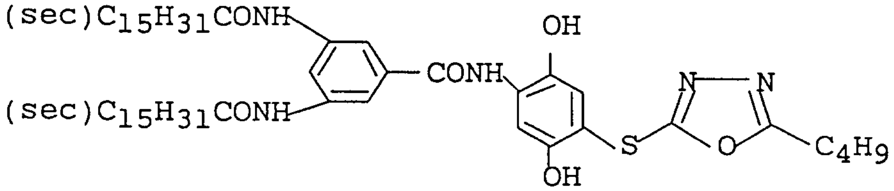

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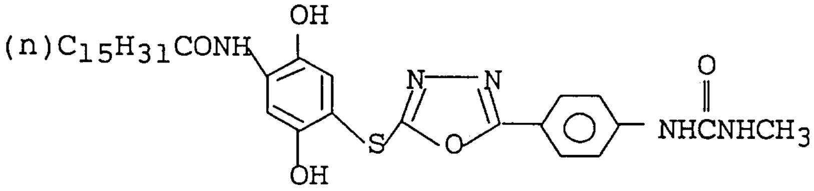

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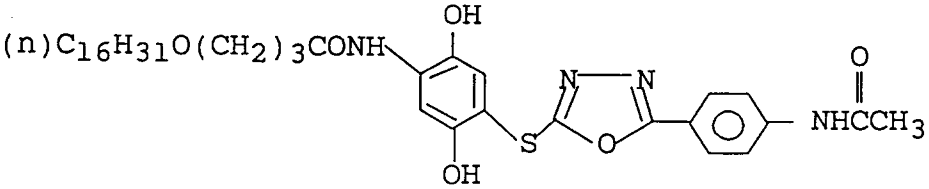

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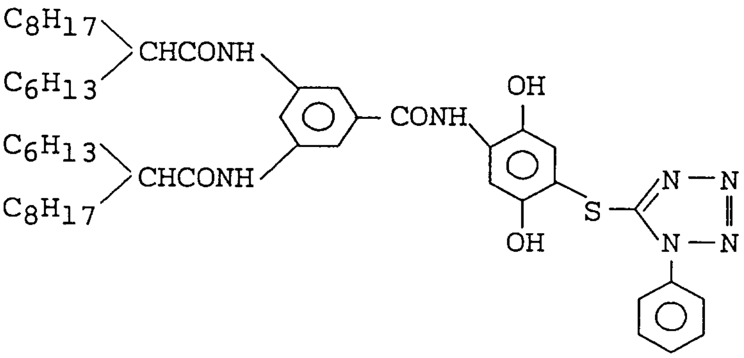

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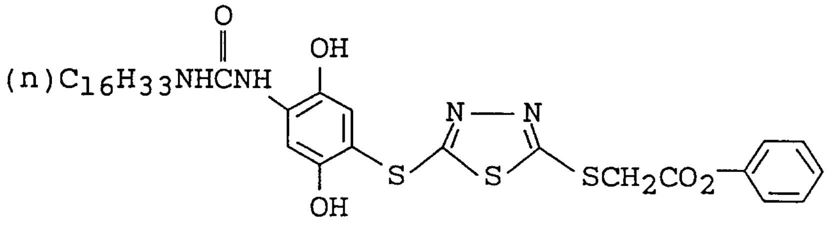

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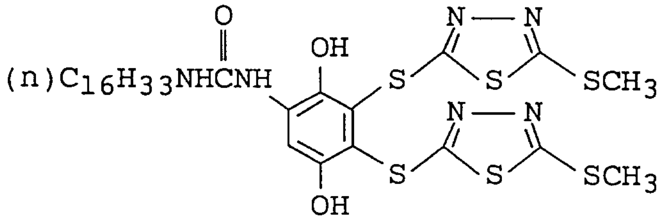

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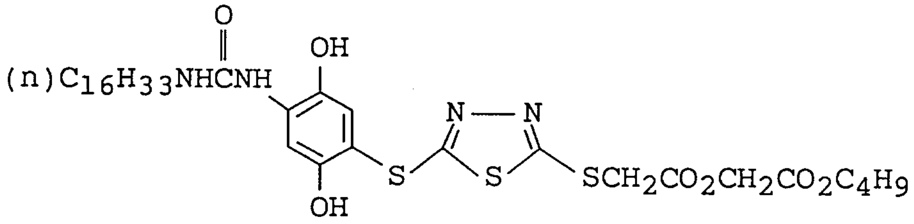

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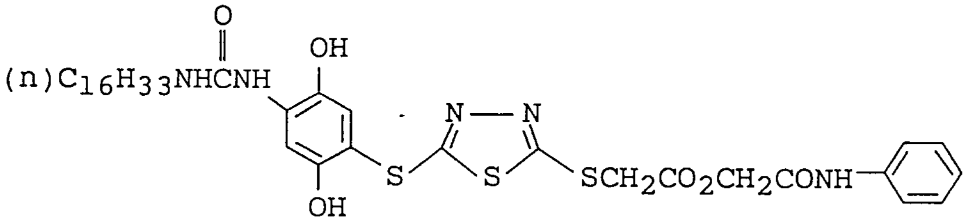

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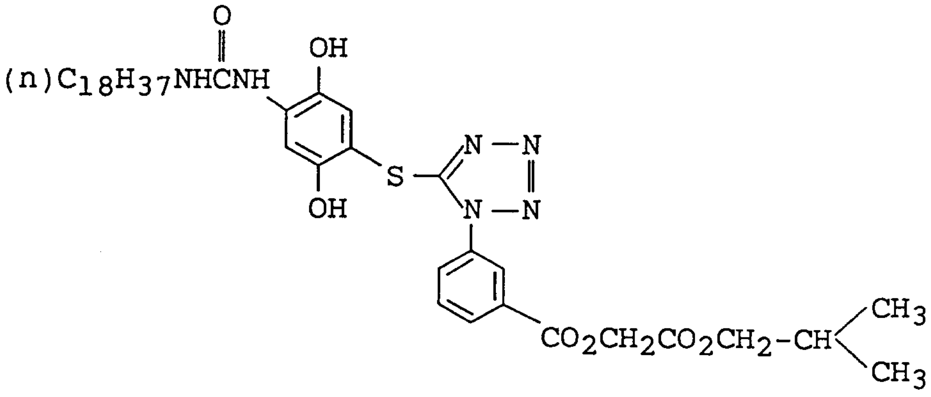
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CH3
CH3

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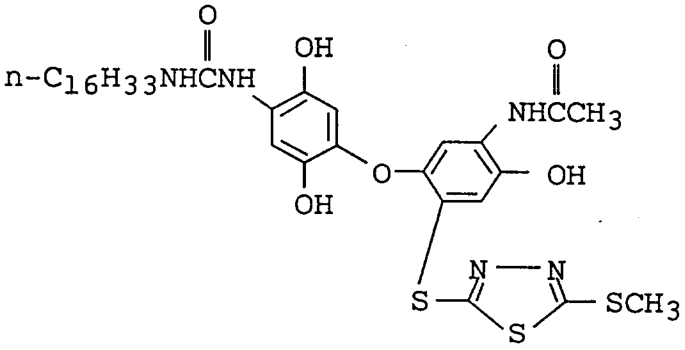
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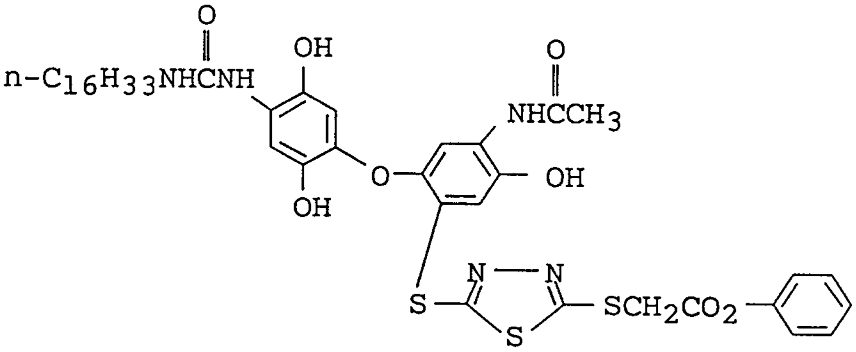
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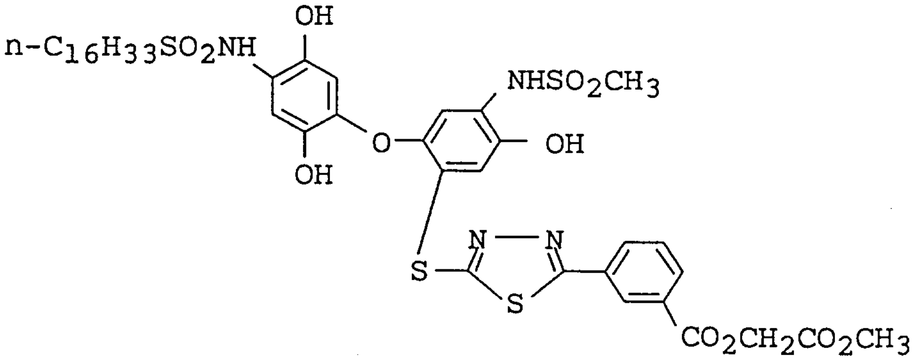

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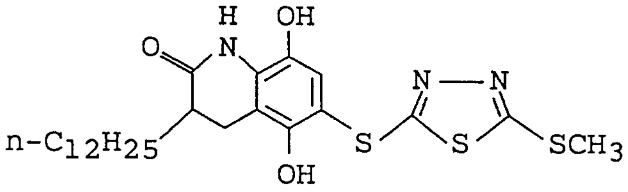

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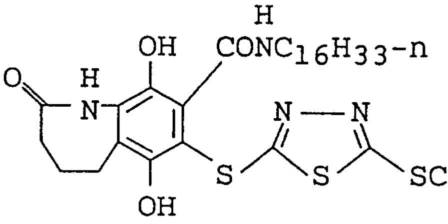

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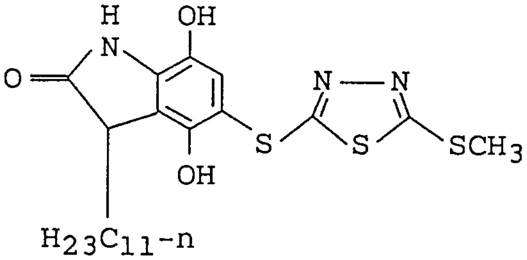

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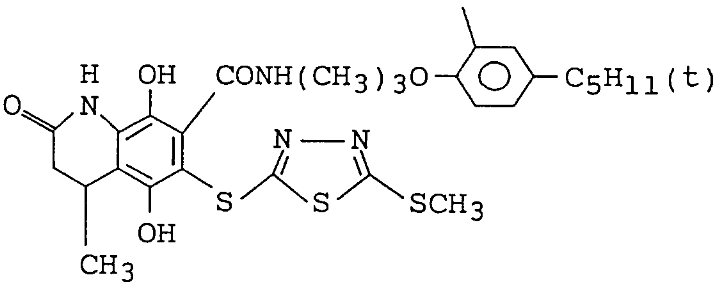

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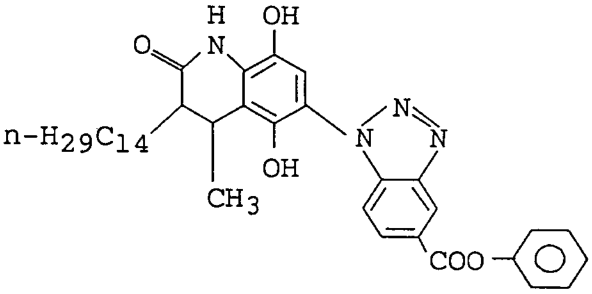

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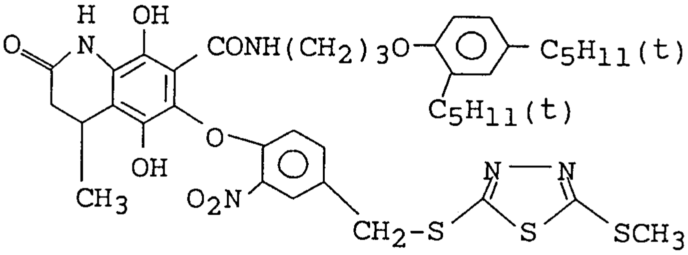

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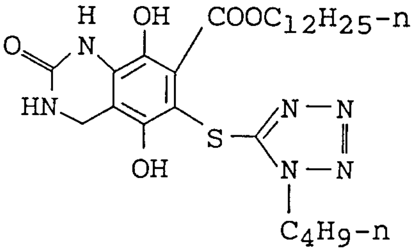

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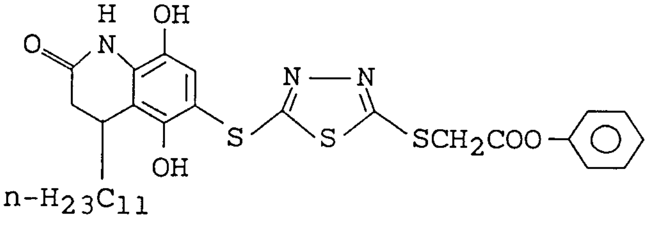

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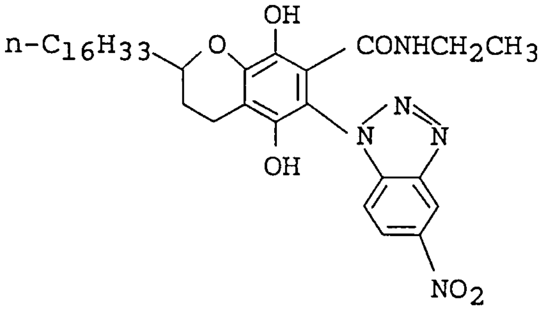

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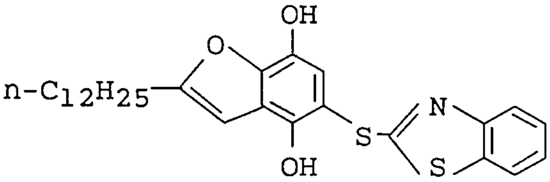

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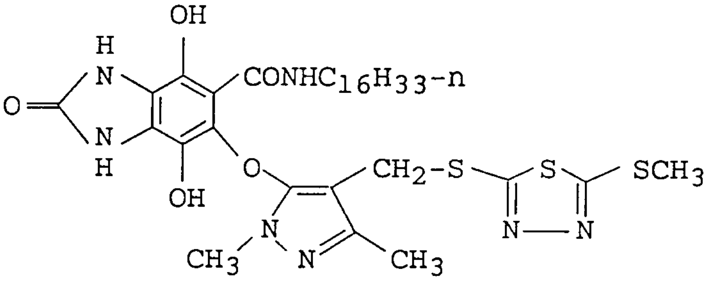

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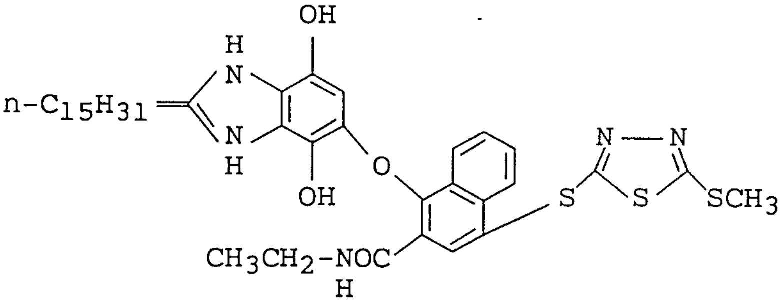

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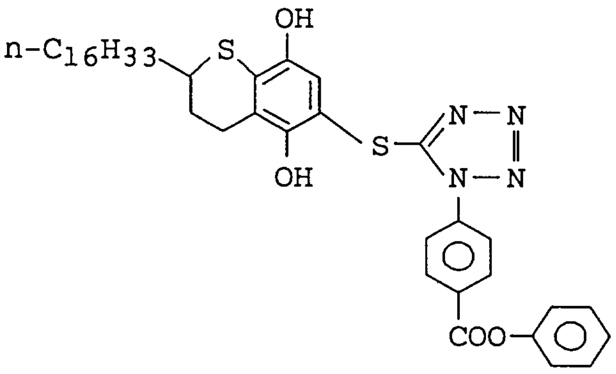

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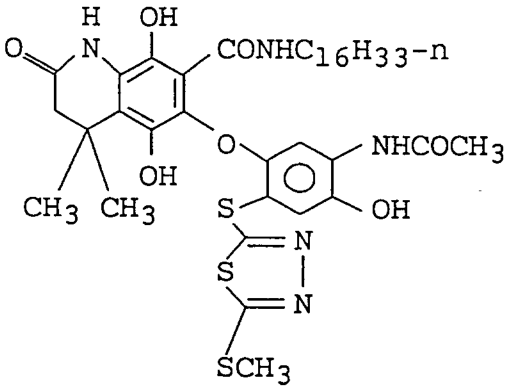

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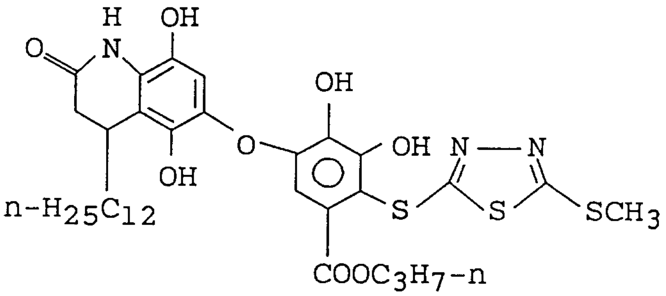

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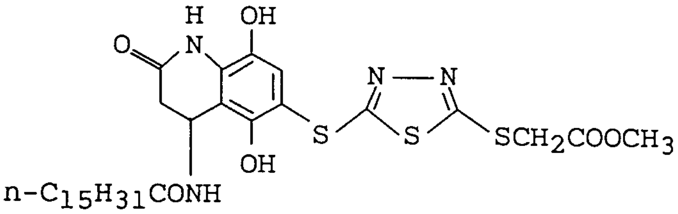

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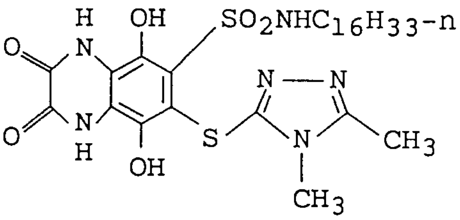

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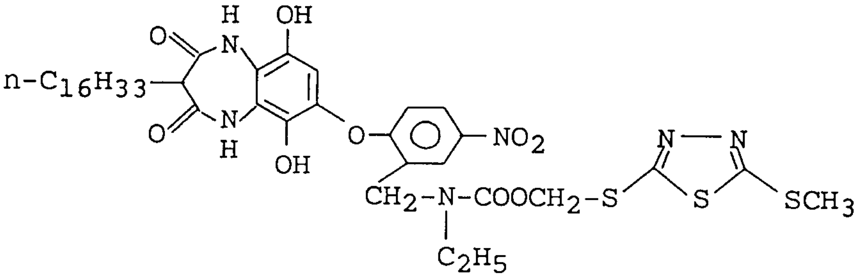

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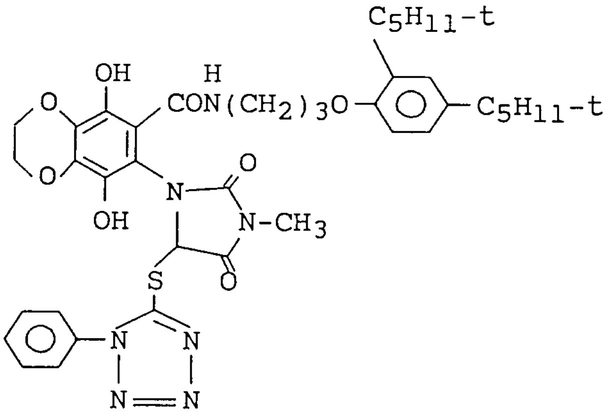

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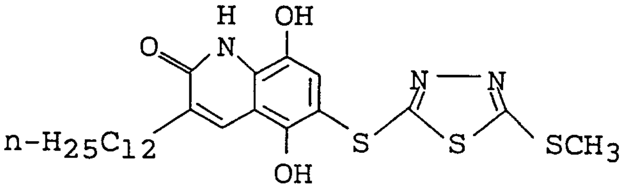

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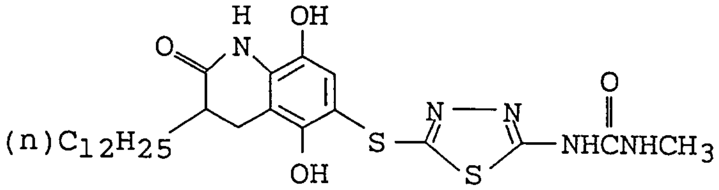

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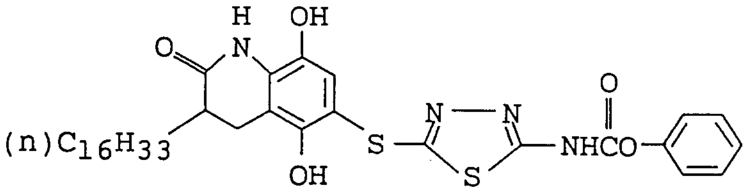

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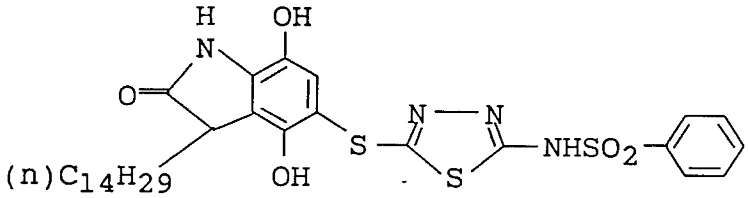

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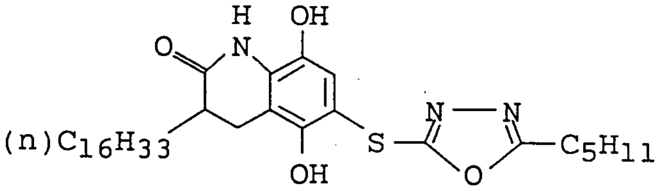

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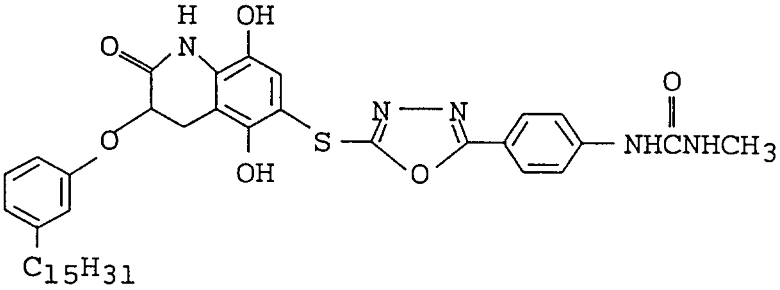

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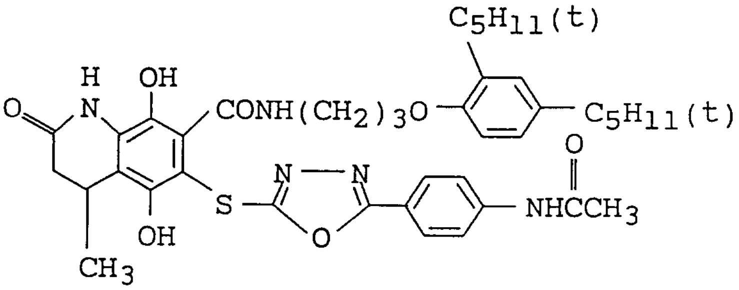

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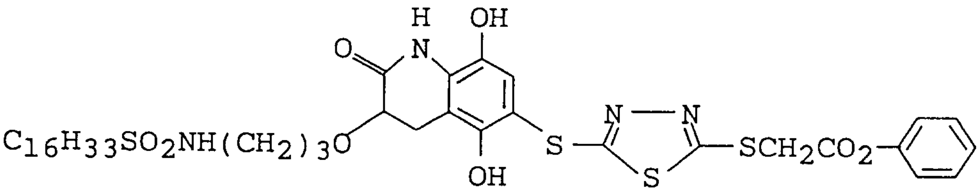

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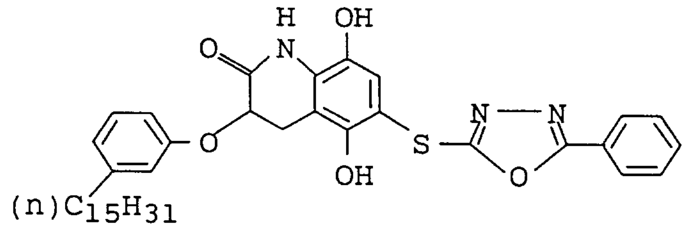

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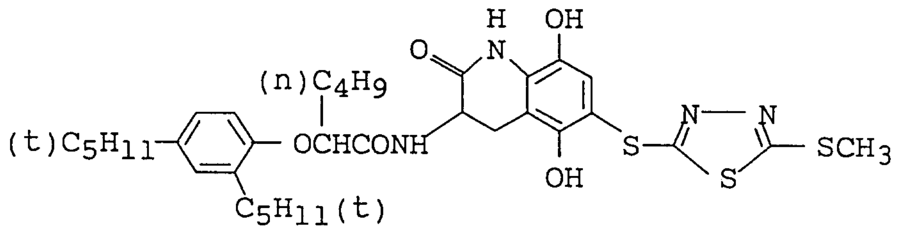


Tabular silver halide grains used in the present invention will now be described.

The tabular silver halide grain (hereinafter called "tabular grain") in the present invention is a grain having two opposed major surfaces parallel to each other, each having an equivalent-circle diameter (a diameter of a circle having the same area as the projected area of the major surface) which is two or more times greater than the distance between the major surfaces (i.e., the thickness of the grain).

In the present invention, it is desirable that the tabular grains have an average diameter/thickness ratio of 2 to 12, preferably 2 to 8.

The diameter/thickness ratio can be obtained by dividing the sum of the diameter/thickness ratios of the individual tabular grains by the number of the individual grains. It can, nonetheless, be determined by a more simple method, that is, by dividing the average diameter of the tabular grains by the average thickness thereof.

The tabular grains of the invention have a (equivalent-circle) diameter of 0.3 μm or more, usually 0.3 to 0.5 μm, preferably 0.3 to 4.0 μm, and more preferably 0.3 to 3.0 μm. They have a thickness of less than 0.5 μm, preferably 0.05 to less than 0.5 μm, more preferably 0.08 to 0.3 μm.

In the present invention, the diameter and thickness of a grain can be determined from an electron micrograph, as is described in U.S. Patent 4,434,226. The halogen composition of the tabular grains is preferably silver bromoiodide or silver bromochloroiodide. In particular, silver bromoiodide containing 0.1 to 20 mol% of silver iodide is preferred. More preferable is silver bromoiodide containing 1 to 10 mol% of silver iodide. Still more preferable is silver bromoiodide containing 1 to 5 mol% of silver iodide.

As tabular grains, those may be used which have each (111) planes, (100) planes, or both of (111) and (100) planes.

The dislocations in tabular silver halide grains can be observed by a direct method disclosed in J.F. Hamilton, Phot. Sci. Eng., 11, 57 (1967) and T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213 (1972), in which use is made of a transmission electron microscope at low temperatures. More specifically, silver halide grains are extracted from the emulsion, not applying so high a pressure as to cause dislocation in the grains, are placed on a mesh designed for use in electron microscope observation, and are observed by a transmission method while being cooled not to have damages (e.g., printouts) due to electron beams. The thicker the grains, the more hard it is for electron beams to pass through the grains. Hence, a high-voltage (200 KV or more for grains having a thickness of 0.25 μm) electron microscope should better be employed to obtain clear photos of the grains. In the photos thus taken, the dislocations in each grain, as viewed in the direction perpendicular to the major surface, can be counted and located.

Each of the dislocations in each tabular grain of the invention can be described as extending, to an edge of the grains, from a position (start position of the dislocation) which is away from the center of the long axis of the grain by a distance corresponding to x% of the length from the center to the edge. The value for x is preferably $10 \leqq x < 100$, more preferably $30 \leqq x < 98$, still more preferably $50 \leqq x < 95$. The closed line figure formed by connecting the start positions of the dislocation is substantially similar to the shape of the grain, but may not be perfectly similar. The line of dislocation substantially linearly extends from the start position to the edge, but often meanders.

Preferably, 50% (in number) or more of the tabular grains contained in the silver halide emulsion of the invention have 10 or more dislocation lines each. More preferably, 80% or more of the tabular grains have 10 or more dislocation lines each. Still more preferably, 80% or more of the tabular grains have 20 or more dislocation lines each.

Also, it is desirable that the tabular grains used in this invention have as small a relative standard deviation of halogen composition of an individual grain as is possible. The relative standard deviation is preferably 30% or less, more preferably 20% or less.

The halogen composition of individual emulsion grains can be measured by analyzing the composition of each gain by means of, for example, an X-ray micro-analyzer. The term "relative standard deviation of halogen composition of an individual grain" means the value obtained by measuring the contents of a specified halogen in at least 100 grains by the X-ray micro-analyzer, calculating the average content of the specified halogen in these grains, and obtaining the quotient of the standard deviation of the contents of the specified halogen divided by the average content, and then multiplying the quotient by 100. A method of measuring the halogen composition of each grain is described in, for example, in European Patent 147,848A.

A structure as to the halogen composition of the tabular grains can be determined by using various methods in combination. Among these methods are: X-ray diffraction; EPMA method (also known as "XMA method; ESCA analysis (also known as "EPS method"). In the EPMA method, silver halide grains are scanned with electron beams, thereby to detect the composition of the grains. In the ESCA method, X rays are applied onto grains, and the photoelectrons emanating from the grains are analyzed by a spectroscope.

In the present invention, the words "surface of a grain" means the surface region of the grain which is about 50 angstroms deep from the surface. The halogen composition of this region can be determined by means of the ESCA method. The words "inner portion of a grain" means the region of the grain other than the "surface" thereof.

It will now be described how to form the tabular grains.

The methods known in the art can be employed in combination to form the tabular grains.

The tabular grains can be obtained by, for example, forming seed crystals, 40% or more by weight of which are tabular grains, in a relatively high-pAg atmosphere having a pBr value of 1.3, and then growing the seed crystals while adding a silver solution and a halogen solution while maintaining the pBr value at a similar value or a greater value.

It is desirable that the silver and the halogen solutions be added during the growth of grains by the addition of the silver and halogen, so that no new crystal seeds are formed.

The size of the tabular grains can be adjusted by, for example, changing the temperature, selecting the type and amount of the solvent, and the type of a silver salt, and controlling the speed of adding the halide.

The emulsion of the present invention can be principally prepared by the method disclosed in JP-A-63-220238. Preferably, the silver halide emulsion of the present invention has a narrow grain-size distribution and a narrow diameter and/or thickness distribution. It can be manufactured, preferably by the method described in JP-A-63-151618, in which the grains are formed through unclei formation, Ostwald ripening and grain growth.

To introduce dislocations into each grain under control, as in the emulsion of this invention, the sizes and shapes of the Ostwald-ripened grains should be as uniform as possible. Further, a silver nitrate aqueous solution and an alkali halide aqueous solution should better be added by double jet method, while maintaining the pAg value constant at 6.0 to 10.0, during growth stage. In particular, to perform a uniform growth, it is desirable that the solutions being added should have as much over-saturated as is possible. For example, the method disclosed in U.S. Patent 4,242,445 can be employed, in which the solutions are added which are so over-saturated that grains grow at 30 to 100% of the critical crystal-growing speed.

The dislocations in the tabular grains of the invention can be introduced under control by forming a phase within each grain, which phase has a largely different halogen composition. To introduce the dislocations at a high density, the dislocations can be introduced preferably by forming an iodine-rich phase within the grain. More specifically, substrate grains are first prepared, then, an inner iodine-rich phase is formed, covering each substrate grain, and finally a phase containing less iodine than the iodine-rich phase is formed, covering the iodine-rich phase. In this case, it is important to suitably select conditions for forming the iodine-rich phase.

The term "inner iodine-rich phase" means a silver halide solid-solution containing iodine. Preferable as silver halide for the iodine-rich phase is silver iodide, silver bromoiodide, or silver bromochloroiodide. Of these, more preferable are silver iodide and silver bromoiodide (iodine content: 10 to 40 mol%). The most preferable is silver iodide.

The inner iodine-rich phase may be either one uniformly precipitated on the- substrate grain, or one locally present on a major surface, a side, a ridge, or an apex of the substrate grain. Alternatively, the inner iodine-rich phase can be epitaxially orientated at such a position.

To so localize the inner iodine-rich phase, so-called conversion method wherein an iodide salt is singly added, or epitaxial junction method of the type disclosed in, for example, JP-A-59-133540, JP-A-58-108526 and JP-A-59-162540 can be employed. In order to perform the localization, it is preferred that the following conditions are used to effectively introduce the dislocations: a pAg value before the addition of the iodide salt is preferably 8.5 to 10.5, more preferably 9.0 to 10.5; the temperature is maintained preferably at 30 ° C to 60 ° C; and the iodide salt is preferably added in an amount of 1 mol% or less of the total silver, over 30 second to 5 minutes, while the solution is being sufficiently stirred.

The outer phase covering the iodine-rich phase has a lower iodine content than the iodine-rich phase. Its iodine content is preferably 0 to 12 mol%, more preferably 0 to 10 mol%, and most preferably 0 to 3 mol%.

It is desirable that the iodine-rich phase exists within an annular region with its center coinciding with the center of the long axis of the grains, in which region 5 mol% to 80 mol%, preferably 10 mol% to 70 mol%, more preferably 20 mol% to 70 mol% of the total silver content of the grain are present, measured along the long-axis direction of the grain.

The term "long-axis direction" means the diameter direction of each tabular grain, in contrast to the short-axis direction which is the direction of the thickness of the gain.

The iodine content of the inner iodine-rich phase is higher than the average iodine content of the silver bromide, silver bromoiodide or silver bromochloroiodide existing in the surface of the grain; it is preferably 5 or more times higher, more preferably 20 times or more higher.

In forming the tabular grains for use in this invention, a method is preferably employed in which a silver salt solution (e.g., $AgNO_3$ aqueous solution) and a silver halide solution (e.g., KBr aqueous solution) are added at a relatively high speed, in a comparatively great amount, and in a relatively high concentration, in order to increase the speed of growing the grains.

Various methods similar to this are described in, for example, British Patent 1,335,925, U.S. Patents 3,672,900; 3,650,757 and 4,242,445, JP-A-55-142329, and JP-A-55-158124.

Solvents for silver halide are useful in accelerating ripening. For example, it is known that halogen ions is introduced in an excessive amount into the reaction vessel, in order to accelerate ripening. Thus, it is obvious that ripening can be accelerated merely by introducing an excessive amount of a halide solution into the reaction vessel. Other ripening agents can be used. A ripening agent can be contained, in its entirety, in the dispersion medium placed in the reaction vessel, before silver and halide salts are added. It can also be introduced in the reaction vessel together with the addition of one or more halide salts, silver salts, or deflocculants. Alternatively, a ripening agent can be independently introduced at the stage of adding halide salt and silver salt.

As ripening agents other than halogen ions, ammonia, amine compound, and thiocyanate, such as alkali metal thiocyanate, particularly sodium thiocyanate, potassium thiocyanate or ammonium thiocyanate, can be used. Use of thiocyanate as a ripening agent is taught in U.S. Patents 2,222,264; 2,448,534 and 3,320,069. Also, thioether, ordinarly used, such as as those disclosed in U.S. Patents 3,271,157, 3,574,628 and 3,737,313 can be used as ripening agents. Alternatively, thion compounds of the type disclosed in JP-A-53-82408 and JP-A-53-144319 can be used.

The nature of silver halide grains can be controlled in the presence of various compounds during the precipitation of silver halide. These compounds may be introduced into the reaction vessel from the beginning. Alternatively, they may be added, together with one or more salts, by the ordinary method. The nature of silver halide can be controlled during the precipitation of silver halide, in the presence of a compound of copper, iridium, lead, bismuth, cadmium or zinc, a chalcogen compound such as a compound of sulfur, selenium or tellurium, or a compound of gold or a Group VIII noble metal, as is described in U.S. Patents 2,448,060; 2,628,167; 3,737,313 and 3,772,031, and Research Disclosure Vol. 134, No. 13452, June 1975. As is described in JP-B-58-1410 and Moisar et al., Journal of Photographic Science, Vol. 25, 1977, pp. 19-27, the inner parts of the grains can be reduction-sensitized during the precipitation of silver halide.

In the tabular grains for use in the invention, silver halides having different compositions may be joined by an epitaxial junction, or compounds other than silver halide, such as silver rhodanide or lead oxide, may be joined. These emulsion grains are disclosed in, for example, U.S. Patents 4,094,684; 4,142,900 and

4,459,353, British Patent 2,038,792, U.S. Patents 4,349,622; 4,395,478; 4,433,501; 4,463,087; 3,656,962 and 3,852,067, and JP-A-59-162540.

The tabular grains for use in the present invention are, usually, chemically sensitized.

Chemical sensitization can be carried out by using active gelatin as is described in T.H. James, "The Theory of the Photographic Process, 4th Ed.," Macmillan, 1977, pp. 67-76. Alternatively, chemical sensitization can be effected by using a sulfur sensitizer, a selenium sensitizer, a tellurium sensitizer, a gold sensitizer, a platinum sensitizer, an iridium sensitizer, or a combination of two or more of these sensitizers, at a pAg of 5 to 10 and a pH of 5 to 8 and at a temperature of 30 to 80°C, as is described in Research Disclosure No. 12008, Vol. 120, April 1974, Research Disclosure No. 13452, Vol. 34, June 1975, U.S. Patents 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 1,315,755. Chemical sensitization is optimally carried out in the presence of a gold compound and a thiocyanate compound. Also, chemical sensitization can be carried out in the presence of a sulfur-containing compound of the type disclosed in U.S. Patents 3,857,711; 4,266,018 and 4,054,457 or a sulfur-containing compound such as a hypo, a thiourea-based compound or rhodanine-based compound. Further, chemical sensitization can be performed in the presence of a chemical sensitization aid. Used as chemical sensitization aid is a compound known to suppress fog and increase sensitivity during the chemical sensitization, such as azaindene, azapyridadine or azapyrimidine. Various instances of a modifier of chemical sensitization aid are described in U.S. Patents 2,131,038, 3,411,914 and 3,554,757, JP-A-58-126526, and G.F. Duffin, "Photographic Emulsion Chemistry," Focal Press, 1966, pp. 138-143. In addition to, or in place of, the chemical sensitization, reduction sensitization using, for example, hydrogen, can be carried out, as is described in U.S. Patents 3,891,446 and 3,984,249. Further, reduction sensitization can be performed using a reducing agent such as stannous chloride, thiourea dioxide or polyamine, or can be effected by means of low-pAg process (pAg value of, for example, less than 5) and/or high-pH process (pH value of, for example, greater than 8), as is disclosed in U.S. Patents 2,518,698, 2,743,182 and 2,743,183. Also, the grains can be subjected to the chemical sensitization disclosed in U.S. Patents 3,917,485 and 3,966,476 to have their spectral sensitizability enhanced.

The sensitization described in JP-A-61-3134 or JP-A-61-3136, wherein an oxidizing agent is used, can be applied to the present invention.

In the tabular grain emulsion of the present invention, the tabular grains of the invention occupy preferably 50% or more of the projected area of all silver halide grains contained in the emulsion, more preferably 70% or more thereof, and most preferably 90% or more thereof.

The tabular grain emulsion of this invention can be used in the same silver halide emulsion layer, together with an emulsion of ordinary, chemically sensitized silver halide grains (hereinafter referred to as "non-tabular grains".) Particularly, in the case of a color photographic light-sensitive material, the tabular grain emulsion and the non-tabular grain emulsion can be used in the same emulsion layer and/or different emulsion layers. Examples of the non-tabular grains are: regular grains having regular crystal shapes, such as cubic grains, octahedral grains and tetradecahedral grains, and irregular grains having irregular crystal shapes, such as spherical grains and potato-shaped grains. These non-tabular grains may be made of any silver halide such as silver bromide, silver bromoiodide, silver bromochloroiodide, silver bromochloride, or silver chloride. Of these silver halides, preferable are silver bromoiodide and silver bromochloroiodide, each containing 30 mol% or less of silver iodide, and particularly preferable is silver bromoiodide containing 2 mol% to 25 mol% of silver iodide.

The non-tabular grains may be fine grains having a grain size of 0.1 µm or less, or large grains having a projected area diameter of up to 10 µm, and the emulsion may be a monodisperse emulsion having a narrow distribution, or a polydisperse emulsion having a broad distribution.

The non-tabular grains used in the present invention can be formed by the methods described in, for example, P. Glafkides, "Chemie et Phisi que Photographique", Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964. In other words, the grains can be formed by acid method, neutral method, or ammonia method. As a sheme for reacting a soluble silver salt and a soluble halogen salt, a single-ject method, or a double-ject method, or a combination thereof may be employed. Alternatively, the so-called reverse mixing method can be used, in which grains are formed in the presence of an excessive amount of silver ions. One type of the double-jet method is so-called "controlled double jet method" in which the liquid phase in which silver halide is formed is maintained at a constant pAg value. By this method there can be prepared a silver halide emulsion of grains having a regular crystal shape and an almost uniform grain size.

Two or more silver halide emulsions, prepared independently, may be used in the form of a mixture.

A silver halide emulsion comprising the regular grains described above can be prepared by controlling the pAg value and the pH value during the forming of the grains. This is detailed in, for example, Photographic Science and Engineering, Vol. 6, pp. 159-165 (1962), Journal of Photographic Science, Vol. 12, pp. 242-251 (1964), U.S. Patent 3,655,394, and British Patent 1,413,748.

Monodispers emulsions are described in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635, JP-A-58-49938, JP-B-47-11386, U.S. Patent 3,655,394, and British Patent 1,413,748.

The crystal structure of the non-tabular grain may be uniform, may have different halogen compositions in the inner and outer portions thereof, or may be a layered structure. Emulsion grains of such types are disclosed in, for example, British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877, and JP-A-60-143331.

In the present invention, an emulsion of non-light-sensitive fine grains having a grain size of 0.6 μm or less, preferably 0.2 μm or less, may be added to a silver halide emulsion layer, an interlayer, or a protective layer, for the purpose of, for example, accelerating development, improving storage stability, and making good use of reflected light.

As has been described above, the tabular grain emulsions and the non-tabular grain emulsions, all for use in the present invention, are usually those which have been subjected to physical ripening, chemical ripening and spectral sensitization. The additives used in these processes are described in Research Disclosure No. 17643 and Research Disclosure No. 18716, as will be specified in the following Table A.

Known additives for use in photographic materials, which can be used in this invention, are disclosed in the two Research Disclosures, too, as will be specified in the Table A.

Table A

Additives	RD17643 Dec. 1978	RD18716 Nov., 1979
1. Chemical sensitizers	page 23	page 648, right column
2. Sensitivity increasing agents		ditto
3. Spectral sensitizers, super sensitizers	pages 23 - 24	page 648, right column to page 649, right column
4. Brighteners	page 24	
5. Antifoggants and stabilizers	pages 24 - 25	page 649, right column
6. Light absorbents, filter dyes, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column
7. Stain preventing agents	page 25, right column	page 650, left to right columns
8. Dye image stabilizers	page 25	

(Continued)

Additives	RD17643 Dec. 1978	RD18716 Nov., 1979
9. Hardening agents	page 26	page 651, left column
10. Binders	page 26	ditto
11. Plasticizers, lubricants	page 27	page 650, right column
12. Coating aids, surface active agents	pages 26 - 27	ditto
13. Antistatic agents	page 27	ditto

Various color couplers can be used in the present invention, and specific examples of these couplers are described in patents described in above-mentioned Research Disclosure (RD), No. 17643, VII-C to VII-G. Important as dye-forming couplers are those which present, by color development, the three primary colors of subtractive color process (i.e., yellow, magenta, and cyan). The examples of non-diffusing, 4-equivalent or 2-equivalent couplers, specified below, can preferably used in this invention, in addition to the couplers described in RD No. 17643, VII-C and VII-D.

A typical examples of a yellow coupler which can be used in the light-sensitive material according to the present invention is the hydrophobic acylacetamide-based coupler having ballast groups. Specific examples of the yellow coupler are disclosed in, for example, U.S. Patents 2,407,210, 2,875,057, and 3,265,506. In the present invention, a two-equialent yellow coupler is preferably used. Typical examples of the two-equivalent yellow coupler are: oxygen-releasing yellow couplers disclosed in, for example, U.S. Patents 3,408,194; 3,447,928; 3,933,501 and 4,022,620, and nitrogen-releasing yellow couplers disclosed in, for example, JP-B-58-10739, U.S. Patents 4,401,752 and 4,326,024, RD No. 18035 (April 1979), British Patent 1,425,020, and West German Laid-Open Applications 2,219,917, 2,261,361, 2,329,587 and 2,433,812. An α-pivaloylacetanilide-based coupler excels in fastness, particularly light fastness, of the formed dye, and an α-benzoylacetoanilide-based coupler can present high color-forming density.

Examples of a magenta coupler which can be used in the light-sensitive material according to this invention are an indazolone-based coupler or a cyanoacetyl-based coupler, each being hydrophobic and having ballast groups. The magenta coupler is preferably 5-pyrazolone-based or pyrazoloazole-based coupler. Of 5-pyrazolone-based couplers, one wherein 3-position is substituted with an arylamino group or an acylamino group is preferable in view of the formed dye hue and color-forming density. Typical examples of such a 5-pyrazolone-based coupler are described in, for example, U.S. Patents 2,311,082;

2,343,703; 2,600,788; 2,908,573; 3,062,653; 3,152,896 and 3,936,015. Particularly preferable as the leaving group of the two-equivalent 5-pyrazolone-based coupler are the nitrogen atom-releasing group disclosed in U.S. Patent 4,310,619 and the arylthio group disclosed in U.S. Patent 4,351,897. The 5-pyrazolone-based coupler described in European Patent 73,636, which has ballast groups, can achieve high color-forming density. Examples of pyrazoloazole-based couplers are pyrazolobenzimidazoles described in U.S. Patent 3,061,432. Preferable examples of pyrazoloazole-based couplers are pyrazolone[5,1-c] [1,2,4]triazoles disclosed in U.S. Patent 3,715,067, pyrazolotetrazoles disclosed in Research Disclosure 24220 (June 1984) and JP-A-60-33552, and pyrazolopyrazoles disclosed in Research Disclosure 24230 (June 1984) and JP-A-60-43659. Imidazo[1,2-b]pyrazoles disclosed in U.S. Patent 4,500,630 are desirable because of its excellence in light fastness and smallness in auxiliary yellow absorption, of the formed dye. Pyrazolo[1,5-b]-[1,2,4]triazoles disclosed in U.S. Patent 4,540,654 are particularly preferred.

Examples of a cyan coupler which can be used in the light-sensitive material according to the present invention are hydrophobic and non-diffusing naphthol-based and phenol-based couplers. Typical examples of a naphthol-based coupler are the naphthol-based coupler disclosed in U.S. Patent 2,474,293 and, preferably the two-equivalent naphthol-based couplers releasing an oxygen atom, which are disclosed in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Specific examples of a phenol-based coupler are described in, for example, U.S. Patents 2,369,929; 2,801,171; 2,772,162 and 2,895,826.

A coupler which can form a cyan dye resistant to temperature and humidity is preferably used in the present invention. Typical examples of this coupler are: the phenol-based cyan coupler disclosed in U.S. Patent 3,772,002, which has ethyl or a higer alkyl group at the metha position of the phenol nucleus; the 2,5-diacylamino-substituted phenol-based coupler disclosed in, for example, U.S. Patents 2,772,162, 3,758,308; 4,126,396; 4,334,011 and 4,327,173, West German Laid-Open Application 3,329,729, and European Patent 121,365; and the phenol-based coupler having a phenylureido group and an acylamino group at 2-position and 5-position, respectively, disclosed in, for example, U.S. Patents 3,446,622; 4,333,999; 4,451,559 and 4,427,767. Also, the cyan coupler in which a sulfonamido group or an amido group is substituted at 5-position of naththol, disclosed in European Patent 161,626A, can be preferably used in the present invention since it excels in color-image fastness.

It is desirable that masking be carried out, by using a colored coupler, together with other couplers, in a color light-sensitive material for photographic use, in order to correct undesirable absorption of the formed dye. Typical examples of this colored coupler are: the yellow-colored magenta couplers disclosed in, for example, U.S. Patent 4,163,670 and JP-B-57-39413; and the magenta-colored cyan couplers disclosed in, for example, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368. Other colored couplers are described in RD No. 17643, VII-G, mentioned above.

A coupler capable of forming colored dyes having proper diffusibility can be used, along with other couplers, in order to improve graininess. Examples of such a coupler are the magenta couplers described in U.S. Patent 4,366,237 and British Patent 2,125,570, and the yellow, magenta and cyan couplers described in European Patent 96,570 and West German Laid-Open Application 3,234,533.

The dye-forming coupler and the special coupler, both described above, may form a dimer or a higher polymer. Typical examples of a polymerized dye-forming coupler are described in, for example, U.S. Patents 3,451,820 and 4,080,221. Specific examples of a polymerized magenta coupler are disclosed in British Patent 2,102,173 and U.S. Patent 4,367,282.

A coupler releasing a photographically useful residue upon coupling can also preferably be used in the present invention. Useful as DIR couplers, i.e., couplers releasing a development inhibitor, are those described in the patents cited in the above-described RD No. 17643, VII-F.

DIR couplers, which are preferable for use in combination with the DIR couplers of the present invention are: a developer-deactivating type one, typical examples of which are disclosed in JP-A-57-151944; a timing type one, typical examples of which are disclosed in U.S. Patent 4,248,963 and JP-A-57-154234; and a reaction type one, typical examples of which are disclosed in JP-A-60-184248. Particularly preferable are the developer-deactivating type DIR couplers described in, for example, JP-A-57-151944, JP-A-58-217932, JP-A-60-218645, JP-A-60-225156, JP-A-59-82214, and JP-A-60-233650, and the reaction type DIR coupler disclosed in, for example, JP-A-60-184248.

In the light-sensitive material of this invention, use can be made of a coupler which imagewise releases a nucleating agent, a development accelerator, or a precursor of either. Specific examples of this compound are described in British Patents 2,097,140 and 2,131,188. Particularly preferable as such is, for example, a coupler which releases a nucleating agent capable of absorbing to silver halide. Typical example of this coupler is described in, for example, JP-A-59-157638, and JP-A-59-170840.

The couplers for use in this invention can be introduced into the light-sensitive material by various known dispersion methods.

Examples of a high-boiling organic solvent to be used in the oil-in-water dispersion method are described in, for example, U.S. Patent 2,322,027.

Steps and effects of a latex dispersion method and examples of a loading latex are described in, for example, U.S. Patent 4,199,363 and German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

A support which can be suitably used in the present invention is described in, for example, RD. No. 17643, page 28, and RD. No. 18716, from the right column, page 647 to the left column, page 648.

The color photographic light-sensitive material according to the present invention can be developed by the conventional methods described in RD. No. 17643, pp. 28 and 29, RD. No. 18716, the left to right columns, page 651, and RD. No. 307105, pp. 880 and 881.

A color developer used in development of the light-sensitive material of the present invention is an aqueous alkaline solution containing as a main component, preferably, an aromatic primary amine-based color developing agent. As the color developing agent, although an aminophenol-based compound is effective, a p-phenylenediamine-based compound is preferably used. Typical examples of the p-phenylenediamine-based compound are: 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, and sulfates, hydrochlorides and p-toluene sulfonates thereof. Of these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline or a sulfate thereof is particularly preferable. These compounds can be used in a combination of two or more thereof in accordance with the application.

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or an antifoggant such as a chloride salt, a bromide salt, an iodide salt, a benzimidazole, a benzothiazole or a mercapto compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diethylhydroxylamine, a sulfite, a hydrazine such as N,N-biscarboxymethylhydrazine, a phenylsemicarbazide, triethanolamine, or a catechol sulfonic acid; an organic solvent such as ethyleneglycol or diethyleneglycol; a development accelerator such as benzylalcohol, polyethyleneglycol, a quaternary ammonium salt or an amine; a dye-forming coupler; a competing coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity-imparting agent; and a chelating agent such as aminopolycarboxylic acid, an aminopolyphosphonic acid, an alkylphosphonic acid, or a phosphonocarboxylic acid. Typical examples of the chelating agent are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof.

In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, well-known black-and-white developing agents, e.g., a dihydroxybenzene such as hydroquinone, a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof. The pH of the color and black-and-white developers is generally 9 to 12. Although a replenishment amount of the developer depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m^2 of the light-sensitive material. The replenishment amount can be decreased to be 500 mℓ or less by decreasing a bromide ion concentration in a replenishing solution. In order to decrease the replenishment amount, a contact area of a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air.

The contact area of the solution with air in a processing tank can be represented by an aperture defined below:

Aperture = [contact area (cm^2) of processing solution with air]/[volume (cm^3) of the solution]

The above aperture is preferably 0.1 or less, and more preferably, 0.001 to 0.05. In order to reduce the aperture, a shielding member such as a floating cover may be provided on the surface of the photographic processing solution in the processing tank. In addition, a method of using a movable cover described in JP-A-1-82033 or a slit developing method descried in JP-A-63-216050 may be used. The aperture is preferably reduced not only in color and black-and-white development steps but also in all subsequent steps, e.g., bleaching, bleach-fixing, fixing, washing, and stabilizing steps. In addition, the quantity of replenisher can be reduced by using a means of suppressing accumulation of bromide ions in the developing solution.

A color development time is normally 2 to 5 minutes. The processing time, however, can be shortened by setting a high temperature and a high pH and using the color developing agent at a high concentration.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with the application. Examples of the bleaching agent are a compound of a multivalent metal, e.g., iron (III); peroxides; quinones; and a nitro compound. Typical examples of the bleaching agent are: an organic complex salt of iron (III), e.g., a complex salt thereof with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiamine tetraacetic acid, and a complex salt thereof with an organic acid such as citric acid, tartaric acid, or malic acid. Of these compounds, iron (III) complex salts of aminopolycarboxylic acid, such as an iron (III) complex salt of ethylenediamine tetraacetic acid and a iron (III) complex salt of 2,3-diaminopropanetetraacetic acid, are preferred because they can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of aminopolycarboxylic acid is particularly useful in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution using the iron (III) complex salt of aminopolycarboxylic acid is normally 4.0 to 8. In order to increase the processing speed, however, processing can be performed at a lower pH.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution, and their prebath, if necessary. Useful examples of the bleaching accelerator are: compounds having a mercapto group or a disulfide group described in, for example, U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, and JP-A-53-141623, and JP-A-53-28426, and Research Disclosure No. 17129 (July, 1978); a thiazolidine derivative described in JP-A-50-140129; thiourea derivatives disclosed in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,706,561; iodide salts described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds descried in West German Patents 977,410 and 2,748,730; a polyamine compound described in JP-B-45-8836; compounds descried in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and a bromide ion. Of these compounds, a compound having a mercapto group or a disulfide group is preferable since the compound has a large accelerating effect. In particular, compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferred. A compound described in U.S. Patent 4,552,834 is also preferable. These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are useful especially in bleach-fixing of a photographic color light-sensitive material.

It is desirable that an organic acid be contained in the bleaching solution or the bleach-fixing solution for the purpose of preventing bleach stain. Particularly preferred as such an organic acid is a compound having an acid-dissociation constant (pKa) of 2 to 5. Specific examples of this organic acid are acetic acid, propionic acid, and hydroxyacetic acid.

Examples of the fixing agent used in the fixing solution or the bleach-fixing solution are a thiosulfate, a thiocyanate, a thioether-based compound, a thiourea and a large amount of an iodide. Usually, a thiosulfate is used. Especially, ammonium thiosulfate can be used in the widest range of applications. Further, a thiosulfate and, for example, a thiocyanate, a thioether-based compound, or a thiourea can preferably be used in combination. Preferable as preservative of the bleach-fixing solution are: a sulfite, a bisulfite, a carbonyl bisulfite adduct, or the sulfinic acid compound disclosed in European Patent 294,769A. It is desirable that various aminopolycarbonic acids or organic sulfonic acids be added to the fixing solution or the bleach-fixing solution for the purpose of stabilizing the solution.

In the present invention, a compound having a pKa of 6.0 to 9.0 should better be added to the fixing solution or the bleach-fixing solution, in an amount of 0.1 to 10 mol per liter. Preferable as this compound are imidazoles, especially imidazole, 1-methylimidazole, 1-ethylimidazole, and 2-methylimidazole.

The total desilverization time should better be as short as possible, as long as desilvering defect does not occur. The time is preferably 1 to 3 minutes, more preferably 1 to 2 minutes. The desilverization temperature is 5° C to 50° C, preferably 35° C to 45° C. Within the preferable desilverization temperature, the desilverization proceeds at high speed, and stain formation after the processing is effectively prevented.

In the desilvering step, stirring is preferably as strong as possible. Examples of a method of intensifying the stirring are a method of colliding a jet stream of the processing solution against the emulsion surface of the light-sensitive material described in JP-A-62-183460, a method of increasing the stirring effect using rotating means described in JP-A-62-183461, a method of moving the light-sensitive material while the emulsion surface is brought into contact with a wiper blade provided in the solution to cause disturbance on the emulsion surface, thereby improving the stirring effect, and a method of increasing the circulating flow amount in the overall processing solution. Such a stirring improving means is effective in any of the bleaching solution, the bleach-fixing solution, and the fixing solution. It is assumed that the improvement in stirring increases the speed of supply of the bleaching agent and the fixing agent into the emulsion film to lead to an increase in desilvering speed. The above stirring improving means is more effective when the bleaching accelerator is used, i.e., significantly increases the accelerating speed or eliminates fixing interference caused by the bleaching accelerator.

An automatic developing machine for processing the light-sensitive material of the present invention preferably has a light-sensitive material conveyer means described in JP-A-60-191257, JP-A-60-191258, or JP-A-60-191259. As described in JP-A-60-191257, this conveyer means can significantly reduce carry-over of a processing solution from a pre-bath to a post-bath, thereby effectively preventing degradation in performance of the processing solution. This effect significantly shortens especially a processing time in each processing step and reduces the quantity of replenisher of a processing solution.

The silver halide color photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties (e.g., a property determined by used material such as a coupler) of the light-sensitive material, the application of the material, the temperature of the washing water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineers", Vol. 64, PP. 248 - 253 (May, 1955). In the multi-stage counter-current scheme disclosed in this reference, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of time, however, bacteria multiply and floating substances may be adversely attached to the light-sensitive material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate, and germicides such as benzotriazole described in Hiroshi Horiguchi et al., "Chemistry of Antibacterial and Antifungal Agents", (1986), Sankyo Shuppan, Eiseigijutsu-Kai ed., "Sterilization, Anti-bacterial, and Antifungal Techniques for Microorganisms", (1982), Kogyogijutsu-Kai, and Nippon Bokin Bokabi Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents", (1986), can be used.

The pH of the water for washing the photographic light-sensitive material of the present invention is 4 to 9, and preferably, 5 to 8. The water temperature and the washing time can vary in accordance with the properties and applications of the light-sensitive material. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15 ° C to 45 ° C, and preferably, 30 seconds to 5 minutes at 25 ° C to 40 ° C. The light-sensitive material of the present invention can be processed directly by a stabilizing agent in place of washing. All known methods described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used in such stabilizing processing.

In some cases, stabilizing is performed subsequently to washing. An example is a stabilizing bath containing a dye stabilizing agent and a surface-active agent to be used as a final bath of the photographic color light-sensitive material. Suitable as the dye stabilizing agent are: aldehydes such as formalin and glutaraldehyde, n-methylol compounds, hexamethylenetetramine, and aldehyde sulfite adducts. Various chelating agents and various antifungal agents can be added to this stabilizing bath.

An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

In the processing effected by the automatic developing machine, it is recommendable to add water to each process solution to adjust the concentration thereof in the case where the solution evaporates and its concentration increases.

The silver halide color light-sensitive material of the present invention may contain a color developing agent in order to simplify processing and increases a processing speed. For this purpose, various types of precursors of a color developing agent can be preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597, Schiff base compounds described in U.S. Patent 3,342,599 and Research Disclosure (RD) Nos. 14850 and 15159, an aldol compound described in RD No. 13924, a metal salt complex described in U.S. Patent 3,719,492, and an urethane-based compound described in JP-A-53-135628.

The silver halide color light-sensitive material of the present invention may -contain various 1-phenyl-3-pyrazolidones in order to accelerate color development, if necessary. Typical examples of the compound are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

Each processing solution in the present invention is used at a temperature of 10 ° C to 50 ° C. Although a normal processing temperature is 33 ° C to 38 ° C, processing may be accelerated at a higher temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature.

The silver halide light-sensitive material of the present invention can be applied to thermal development light-sensitive materials described in, for example, U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and European Patent 210,660A2.

The present invention can be applied to various color light-sensitive materials, especially well applied to color reversal light-sensitive material.

The present invention will be described in more detail below by way of its examples, but the present invention is not limited to these examples.

Example 1

(1) Preparation of Emulsions

First, tabular grains for a comparative example, which contain no dislocations, were prepared. An aqueous solution was prepared by dissolving 10 g of potassium bromide and 20 g of inactive gelatin in 3.7 liters of distilled water. To this aqueous solution a 14% potassium bromide aqueous solution and a 20% silver nitrate aqueous solution were added by the double jet method at a constant flow rate over one minute, while thoroughly stirring the aqueous solution. This addition was performed at 40° C. (During this addition (I), 10.00% of all silver was consumed.) Then, a gelatin aqueous solution (17%, 300 cc) was added to the resultant solution, and the resultant mixture was heated to 75° C. Further, 20% silver nitrate aqueous solution was added at a constant flow rate until the pBr value reached 8.40. (During this addition (II), 5.0% of all silver was consumed.) Next, the temperature was raised to 75° C, and 35 cc of 25% NH_3 aqueous solution was added. The resultant solution was left to stand for 15 minutes, and 510 cc of 1N N_2SO_4 was added, thereby neutralizing the solution.

Further, 20% potassium bromide aqueous solution and 33% silver nitrate aqueous solution were added by the double jet method over 80 minutes, while maintaining the temperature at 75° C and the pAg value at 7.80. (During this addition (III), 85% of all silver was consumed.) The total amount of silver nitrate, used in this emulsion, was 425 g. The resultant solution was desalted by the ordinary flocculation method, and was subjected to optimal gold-sulfur sensitization in the presence of sensitizing dyes S-3 and S-4. Thus, comparative Emulsion A of AgBrI tabular grains (AgI = 3.0 mol%) was prepared.

Emulsion A, thus prepared, contained the tabular grains which occupied 98% of all grains contained. These tabular grains had an equivalent-spherical diameter of 0.50 µm and an average diameter/thickness ratio of 5.0.

Direct observation was performed on Emulsion A to detect dislocations, by the method described in Example I-(2) of JP-A-63-220238, by means of a transmission electron microscope. No dislocations were found in Emulsion A.

Emulsions B to F were prepared in the same way as Emulsion A, except that the silver amount ratios in the additions (I) and (III) were changed, and the amount of potassium iodide added at the time of the addition (III) was adjusted, and the pAg value during the addition (III) was adjusted.

Emulsion B had been spectrally sensitized with sensitizing dyes S-5 and S-6. It contained tabular grains which occupied 94% of all grains contained. The tabular grains had an equivalent-sphere diameter of 0.45 µm, an average diameter/thickness ratio of 3.0 and an average AgI content of 4.0 mol%.

Emulsion C had been spectrally sensitized with sensitizing dyes S-5 and S-6. It contained tabular grains which occupied 97% of all grains contained. The babular grains had an equivalent-sphere diameter of 0.55 µm, an average diameter/thickness ratio of 6, and an average AgI content of 2.5 mol%.

Emulsion D had been spectrally sensitized with sensitizing dyes S-5 and S-6. It contained tabular grains which occupied 98% of all grains contained. The tabular grains had an equivalent-sphere diameter of 0.95 µm, an average diameter/thickness ratio of 12 and an average AgI content of 1.5 mol%.

Emulsion E had been spectrally sensitized with sensitizing dyes S-1 and S-2. It contained tabular grains which occupied 96% of all grains contained. The tabular grains had an equivalent-sphere diameter of 0.7 µm, an average diameter/thickness ratio of 4, and an average AgI content of 2.5 mol%.

Emulsion F had been spectrally sensitized with sensitizing dyes S-3 and S-4. It contained tabular grains which occupied 98% of all grains contained. The tabular grains had an equivalent-sphere diameter of 0.8 µm, an average diameter/thickness ratio of 8.5, and an average AgI content of 2.5 mol%.

Emulsions B to F were examined for dislocations, in the same way as Emulsion A. No dislocations were found in Emulsions B to F.

It will now be explained how to prepare tabular grains having dislocations. Emulsion G was prepared in the same way as Emulsion A, except for the following points. Potassium iodide was removed from the halogen solution used in the addition (III), and the addition (III) was effected, with the pAg value maintained at 8.4. Addition of silver nitrate and potassium bromide was interrupted during the addition (III), at the time 45% of all silver was consumed. The temperature was lowered to 55° C, and potassium bromide was added, thereby adjusting the pAg value to 9.4. Then, 1250 mℓ of 1% potassium iodide aqueous solution were added over 120 seconds. Thereafter, the remaining part of the addition (III) were performed over 50 minutes.

Emulsions H to L were prepared in the same way as Emulsion G, except for those points except for which Emulsion B to F were prepared in the same way as Emulsion A.

Emulsions G to L were identical to Emulsions A to F, respectively, in terms of the content of tabular grains, the equivalent-sphere diameter, average diameter/thickness ratio and AgI content of the tabular grains. Emulsions G to L were examined for dislocations, in the same way as Emulsion A. It was found that 50% or more (in number) of the grains contained in each of Emulsions G to L had 10 or more dislocation lines each.

A method of measuring the density of dislocation lines, and a method of measuring the dislocation density distribution among grains will be described. The density of dislocation lines is, by definition, the number of dislocation lines existing in one grain. It is determined by preparing a series of photographs of each grain, taken at different angles to the path of incident electrons, detecting the dislocation lines in each of these photographs, and counting the dislocation lines detected in each grain. Many dislocation lines are assumed to exist in a grain if they are arranged too densely to count. The dislocation density distribution among grains is obtained by measuring the dislocation-line densities of 200 or more grains, preferably 300 or more grains, and determining the frequency distribution of these densities.

Preparation of Sample 101

A multilayered color light-sensitive material constituted by layers having the following compositions was formed on an undercoated 127 µm thick triacetylcellulose film support, thereby preparing Sample 101. Numerals below indicate an addition amount per m^2. Note that the effects of the added compounds are not limited to those described here.

Layer 1: Antihalation layer	
Black colloidal silver	silver 0.20 g
Gelatin	1.9 g
Ultraviolet absorbent U-1	0.04 g
Ultraviolet absorbent U-2	0.1 g
Ultraviolet absorbent U-3	0.1 g
Ultraviolet absorbent U-4	0.1 g
Ultraviolet absorbent U-6	0.1 g
High-boiling organic solvent Oil-1	0.1 g
Solid dispersion of fine crystals of dye E-1	0.1 g

Layer 2: Interlayer	
Gelatin	0.40 g
High-boiling organic solvent Oil-3	0.1 g
Dye D-4	0.4 mg

Layer 3: Interlayer	
Surface-fogged and internally fogged fine grain silver bromoiodiede emulsion (average grain size: 0.06 µm, variation coefficient: 18%, AgI content: 1 mol%)	silver 0.05 g
Gelatin	0.4 g

Layer 4: Low-speed red-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-1 and S-2 (spherical grains having an average grain size of 0.3 µm, and AgI content of 4.5 mol%)	silver 0.5 g
Gelatin	0.8 g
Coupler C-1	0.15 g
Coupler C-2	0.05 g
Coupler C-9	0.05 g
High-boiling organic solvent Oil-2	0.1 g

Layer 5: Medium-speed red-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-1 and S-2 (spherical grains having an average grain size of 0.4 µm, and AgI content of 3.5 mol%)	silver 0.5 g
Gelatin	0.8 g
Coupler C-1	0.2 g
Coupler C-2	0.05 g
Coupler C-3	0.2 g
High-boiling organic solvent Oil-2	0.1 g

Layer 6: High-speed red-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-1 and S-2 (spherical grains having an average grain size of 0.7 µm, and AgI content of 2.5 mol%)	silver 0.4 g
Gelatin	1.1 g
Coupler C-1	0.3 g
Coupler C-3	0.7 g
Additive P-1	0.1 g

Layer 7: Interlayer	
Gelatin	0.6 g
Additive M-1	0.3 g
Color-mixing inhibitor Cpd-K	2.6 mg
Ultraviolet absorbent U-1	0.1 g
Ultraviolet absorbent U-6	0.1 g
Dye D-1	0.02 mg

Layer 8: Interlayer	
Surface-fogged and internally fogged silver bromoiodide emulsion (average grain size: 0.06 µm, variation coefficient: 16%, AgI content: 0.3 mol%)	silver 0.02 g
Gelatin	1.0 g
Additive P-1	0.2 g
Color-mixing inhibitor Cpd-N	0.1 mg
Color-mixing inhibitor Cpd-A	0.1 mg

Layer 9: Low-speed green-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-3 and S-4 (spherical grains having an average grain size of 0.3 µm, and AgI content of 4.0 mol%)	silver 0.5 g
Gelatin	0.5 g
Coupler C-7	0.05 g
Coupler C-8	0.02 g
Compound Cpd-B	0.03 g
Compound Cpd-E	0.02 g
Compound Cpd-F	0.02 g
Compound Cpd-G	0.02 g
Compound Cpd-H	0.02 g
High-boiling organic solvent Oil-1	0.1 g
High-boiling organic solvent Oil-2	0.1 g

Layer 10: Medium-speed green-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-3 and S-4 (spherical grains having an average grain size of 0.5 µm, and AgI content of 3.0 mol%)	silver 0.4 g
Gelatin	0.6 g
Coupler C-7	0.2 g
Coupler C-8	0.1 g
Compound Cpd-B	0.03 g
Compound Cpd-E	0.02 g
Compound Cpd-F	0.05 g
Compound Cpd-G	0.05 g
Compound Cpd-H	0.05 g
High-boiling organic solvent Oil-2	0.01 g

Layer 11: High-speed green-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-3 and S-4 (spherical grains having an average grain size of 0.8 µm, and AgI content of 2.5 mol%)	silver 0.5 g
Gelatin	1.0 g
Coupler C-4	0.3 g
Coupler C-8	0.1 g
Compound Cpd-B	0.08 g
Compound Cpd-E	0.02 g
Compound Cpd-F	0.02 g
Compound Cpd-G	0.02 g
Compound Cpd-H	0.02 g
High-boiling organic solvent Oil-1	0.2 g
High-boiling organic solvent Oil-2	0.2 g

Layer 12: Interlayer	
Gelatin	0.6 g
Dye D-1	0.1 g
Dye D-2	0.05 g
Dye D-3	0.07 g

Layer 13: Yellow filter layer	
Yellow colloidal silver	silver 0.07 g
Gelatin	1.1 g
Color-mixing inhibitor Cpd-A	0.01 g
High-boiling organic solvent Oil-1	0.01 g
Solid dispersion of fine crystals of dye E-2	0.05 g

Layer 14: Interlayer	
Gelatin	0.6 g

Layer 15: Low-speed blue-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-5 and S-6 (spherical grains having an average grain size of 0.45 µm, and AgI content of 4.0 mol%)	silver 0.6 g
Gelatin	0.8 g
Coupler C-5	0.6 g

Layer 16: Medium-speed blue-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-5 and S-6 (spherical grains having an average grain size of 0.55 µm, and AgI content of 2.5 mol%)	silver 0.5 g
Gelatin	0.9 g
Coupler C-5	0.7 g

Layer 17: High-speed blue-sensitive emulsion layer	
Silver bromoiodide emulsion spectrally sensitized with sensitizing dyes S-5 and S-6 (spherical grains having an average grain size of 0.95 µm, and AgI content of 1.5 mol%)	silver 0.4 g
Gelatin	1.2 g
Coupler C-6	0.9 g

Layer 18: First protective layer	
Gelatin	0.7 g
Ultraviolet absorbent U-1	0.04 g
Ultraviolet absorbent U-2	0.01 g
Ultraviolet absorbent U-3	0.03 g
Ultraviolet absorbent U-4	0.03 g
Ultraviolet absorbent U-5	0.05 g
Ultraviolet absorbent U-6	0.05 g
High-boiling organic solvent Oil-1 Formalin scavengers	0.02 g
Cpd-C	0.2 g
Cpd-I	0.4 g
Dye D-3	0.05 g
Compound Cpd-N	0.02 g

Layer 19: Second protective layer	
Colloidal silver	silver 0.1 mg
Fine grain silver bromoiodide emulsion (average grain size: 0.06 µm; AgI content: 1 mol%)	silver 0.1 g
Gelatin	0.4 g

Layer 20: Third protective layer	
Gelatin	0.4 g
Polymethylmethacrylate (average grain size: 1.5 µm)	0.1 g
Copolymer of methylmethacrylate and acrylic acid in the ratio of 4:6 (av. grain size: 1.5 µm)	0.1 g
Silicone oil	0.03 g
Surfactant W-1	3.0 mg
Surfactant W-2	0.03 g

In addition to the above compositions, additives F-1 to F-8 were added to all of the emulsion layers. Furthermore, in addition to the above compositions, gelatin hardener H-1 and surfactants W-3, W-4, W-5, W-6, and W-7 for coating and emulsification were added to each layer.

Further, as antiseptic and mildewproofing agents, phenol, 1,2-benzisothiazoline-3-one, 2-phenoxyethanol, and phenethyl alcohol were added.

The compounds used in Sample 101 will be specified in Table I later presented.

Samples 102 to 124 were prepared in the same way as Sample 101, except that tabular grains were used in stead of spherical grains as is shown in Table 1 to 3 (presented later), and that DIR compounds were added as is specified in Tables 1 to 3. The DIR compound Cpd-D used in some of Samples 102 to 124 will be specified in Table A (presented later).

Samples 101 to 124 were tested by the method described below, to determine their sensitivities and sharpnesses.

Samples 101 to 124 were exposed for 1/100 second to white light applied through a wedge from a light source whose color temperature had been adjusted to 4800° K, and were subjected to the developing process which will be specified below. They were evaluated for their sensitivities in terms of yellow density, magenta density and cyan density.

Samples 101 to 124 were also subjected to the following sharpness test.

The samples were exposed to gray light applied through a wedge designed to measure black/white rectangular-wave MTF value, by means of a photometer whose color temperature had been adjusted to 4800° K. Then, they were subjected to the developing process which will be specified below. They were evaluated for their MTF values, i.e., the MTF values of the color-sensitive layers at 30 cycles/mm.

The results of the test will be explained.

The results of the test on Samples 101 to 109 were as is shown in Table 4. Samples 102 to 109 were identical to Sample 101, except in that comparative DIR compound Cpd-D or DIR compound I-(1) of this invention was added to layer 9, and that tabular grain emulsions A, C, and D, each having no dislocations, or the tabular grains of the invention which contains dislocations was used in layers 15, 16 and 17 (i.e., blue-sensitive layers).

As is evident from Table 4, Samples 107 to 109, the blue-sensitive layers of which contained tabular grains having dislocations, exhibited high yellow sensitivity. Table 4 also indicates that the emulsion of tabular grains having dislocations had a higher sensitivity than the emulsion containing tabular grains having the same size but having no dislocations. Hence, an emulsion needs to contain tabular grains having dislocations in order to meet the demand for a high sensitivity. As for sharpness, Table 4 shows that any layer located below the blue-sensitive layers which used the tabular grain emulsion exhibited a greater sharpness (i.e., a greater magenta or cyan sharpness) than the corresponding layer of a sample using spherical grains only. The yellow sharpness of the blue-sensitive layers using the tabular grain emulsion was insufficient unless a DIR compound was used. The sharpness of any sample using the comparative DIR compound was greater than that of any sample using spherical grains or tabular grains having no dislocations, but was less than that of any sample using tabular grains having dislocations. Apparently, the emulsion containing tabular grains having dislocations and the DIR compound of this invention, used in combination, enhanced sharpness remarkably.

The results of the test on Samples 110 to 115 were as is shown in Table 5. In Samples 110 to 115, the emulsion used in layer 10, i.e., the medium-speed green-sensitive layer, was changed, and the comparative DIR compound Cpd-D or the DIR compound I-(1) of this invention was added to layer 10. As in the case of Samples 101 to 109, the emulsion containing tabular grains having dislocations had high sensitivity, and served to enhance the sharpness of any layer using the tabular grains and also the sharpness of the layer located below that layer.

The results of the test on Samples 116 to 124 were as is shown in Table 6. Of these samples, Samples 119 to 124 were the most preferred embodiment of the invention, In Samples 116 to 124, the emulsions used in layers 10, 11, 15, 16, and 17, were changed, and DIR compounds were added to layers 2 and 7. As is evident from Table 6, any sample using the tabular grains of this invention which had dislocations, and containing the DIR compound of this invention, had high sensitivity and excelled in sharpness.

The steps of processing Samples 101 to 124 were as follows:

Steps	Time	Temperature-
First development	6 min.	38°C
Washing	2 min.	38°C
Reversing	2 min.	38°C
Color Development	6 min.	38°C
Control	2 min.	38°C
Bleaching	6 min.	38°C
Fixing	4 min.	38°C
Washing	4 min.	38°C
Stabilization Drying	1 min.	Normal temp.

The compositions of the respective processing solutions used in processing Samples 101 to 124 were as follows.

(First development solution)	
Water	700 mℓ
Pentasodium nitrilo-N N,N-trimethylenephosphonate	2 g
Sodium sulfite	20 g
Hydroquinone monosulfonate	30 g
Potassium carbonate (monohydrate)	30 g
1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2 g
Potassium bromide	2.5 g
Potassium thiocyanate	1.2 g
Potassium iodide (0.1% solution)	2.0 mg
Water to make	1000 mℓ

(Reversing solution)	
Water	700 mℓ
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	3 g
Stannous chloride dihydrate	1 g
p-aminophenol	0.1 g
Sodium hydroxide	8 g
Glacial acetic acid	15 mℓ
Water to make	1000 mℓ

(Color developing solution)	
Water	700 mℓ
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	3. g
Sodium sulfite	7 g
Sodium triphosphate (dodecahydrate)	36 g
Potassium bromide	1 g
Potassium iodide (0.1% solution)	90 mg
Sodium hydroxide	3 g
Citrazinic acid	1.5 g
N-ethyl-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g
3,6-dithiaoctan-1,8-diol	1 g
Water to make	1000 mℓ

(Control solution)	
Water	700 mℓ
Sodium sulfite	12 g
Sodium ethylenediamine tetraacetate (dihydrate)	8 g
Thioglycerol	0.4 mℓ
Glacial acetic acid	3 mℓ
Water to make	1000 mℓ

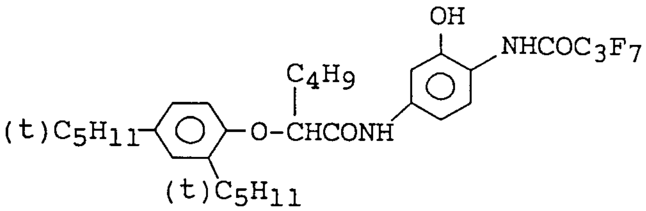
(Bleaching solution)	
Water	800 mℓ
Sodium ethylenediaminetetraacetate (dihydrate)	2 g
Ammonium Fe (III) ethylenediaminetetraacetate (dihydrate)	120 g
Potassium bromide	100 g
Water to make	1000 mℓ

(Fixing solution)	
Water	800 mℓ
Sodium thiosulfate	80.0 g
Sodium sulfite	5.0 g
Sodium bisulfite	5.0 g
Water to make	1000 mℓ

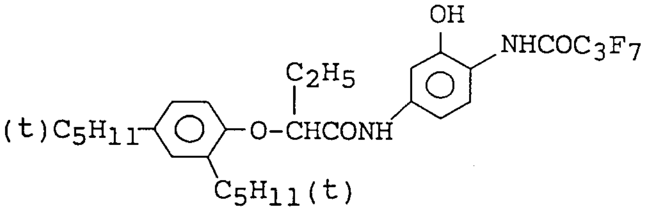
(Stabilizing Solution)	
Water	800 mℓ
Formalin (37 wt%)	5.0 mℓ
Fuji Drywell (Surfactant manufactured by Fuji Photo Film Co., Ltd.)	5.0 mℓ
Water to make	1000 mℓ

Table I

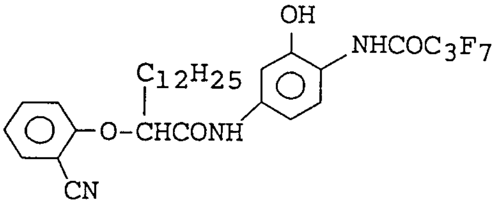
C-1



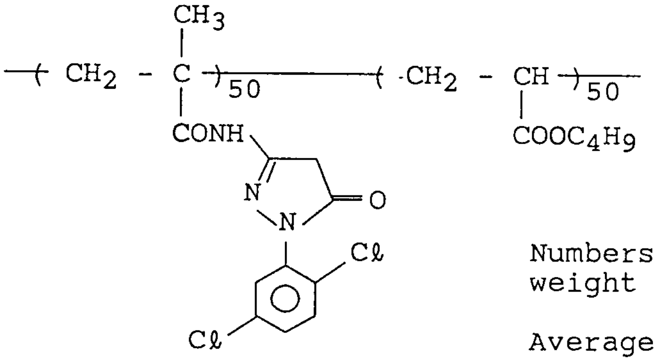
C-2



C-3



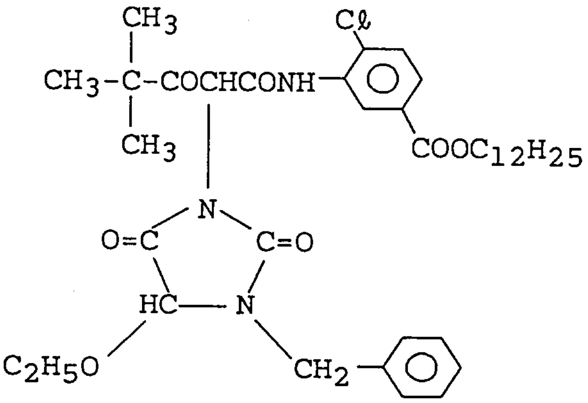
C-4



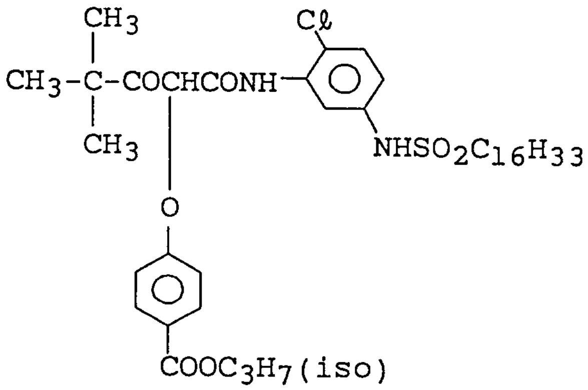
Numbers indicate weight percent

Average molecular weight: about 25,000

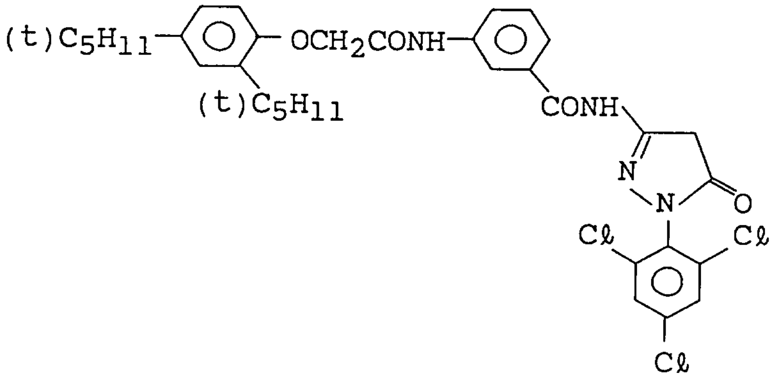
C-5



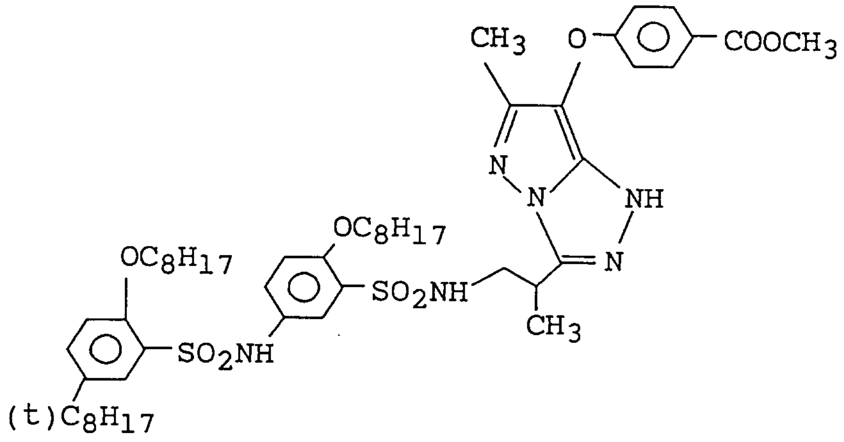
C-6



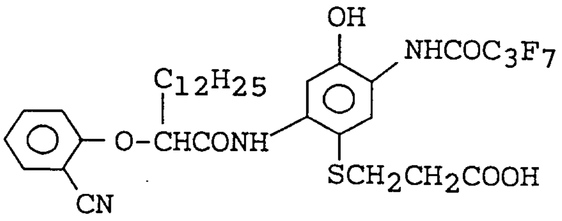
C-7



C-8



C-9



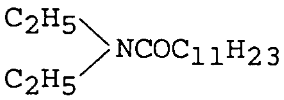
Oil-1

Dibutylphthalate

Oil-2

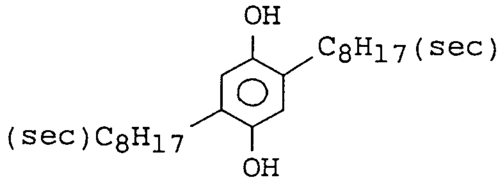
Tricresylphosphate

Oil-3

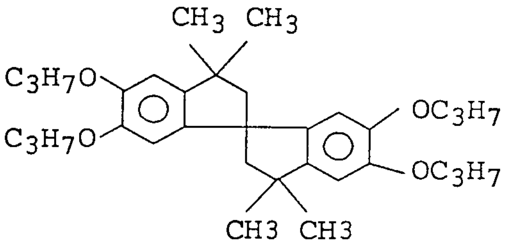


$(C_2H_5)_2NCOC_{11}H_{23}$

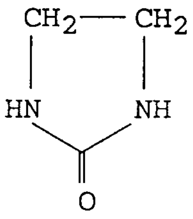
Cpd-A



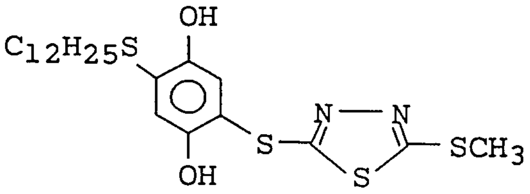
Cpd-B



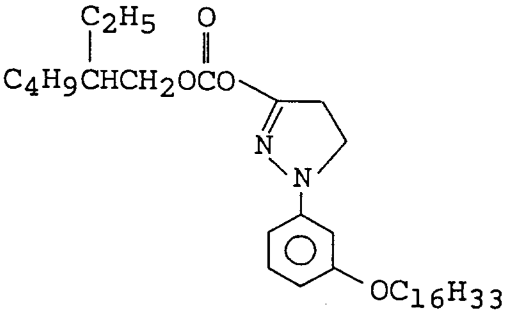
Cpd-C



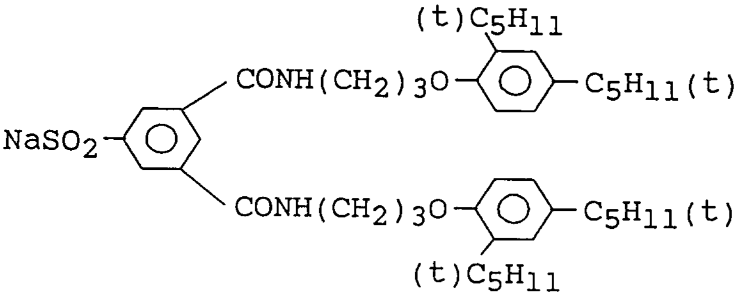
Cpd-D



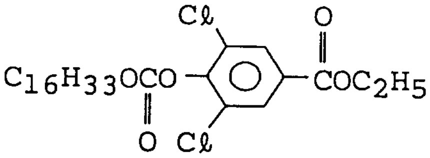
Cpd-E



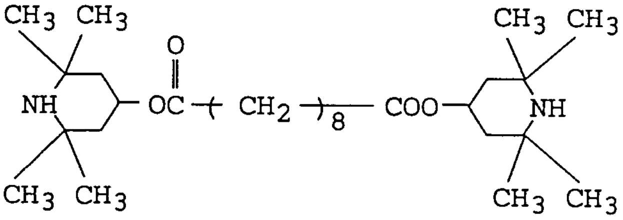
Cpd-F



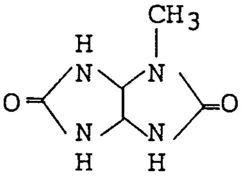
Cpd-G



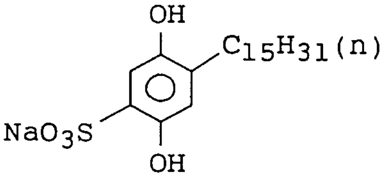
Cpd-H



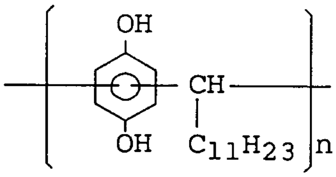
Cpd-I



Cpd-K

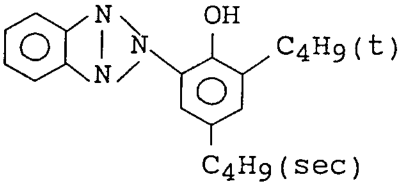


Cpd-N

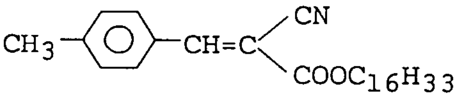


Average molecular weight: 9,000

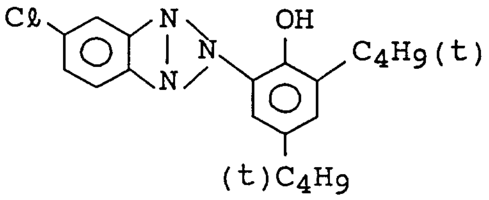
U-1



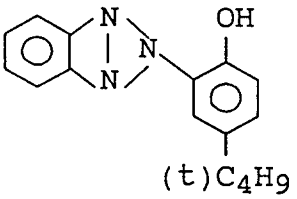
U-2



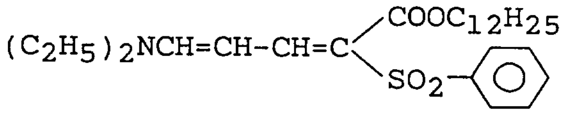
U-3



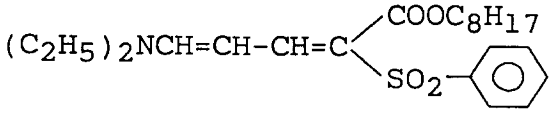
U-4



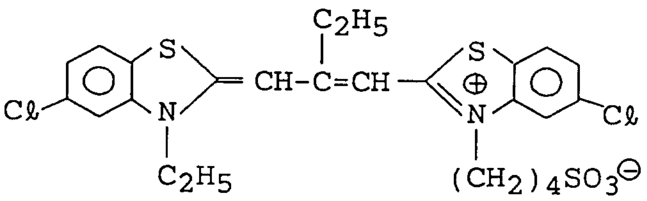
U-5



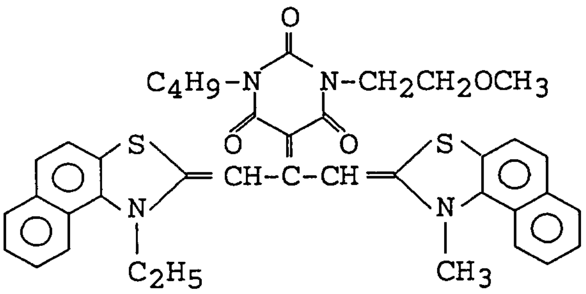
U-6



S-1

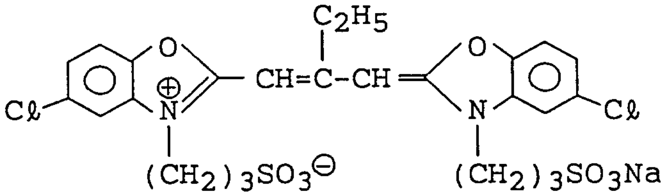


S-2



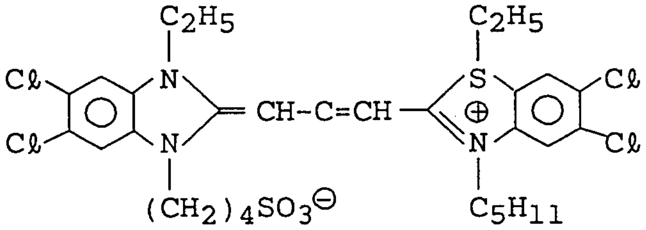
O
C_4H_9-N
N-$CH_2CH_2OCH_3$
S
O
O
S
CH-C-CH
N
N
C_2H_5
CH_3

S-3



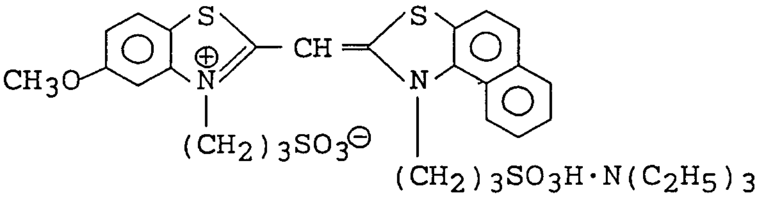
C_2H_5
O
O
CH=C-CH
Cl
⊕N
N
Cl
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3Na$

S-4



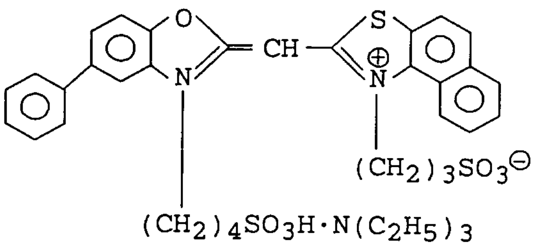
C_2H_5
C_2H_5
Cl
N
S
Cl
CH-C=CH
⊕
Cl
N
N
Cl
$(CH_2)_4SO_3^{\ominus}$
C_5H_{11}

S-5

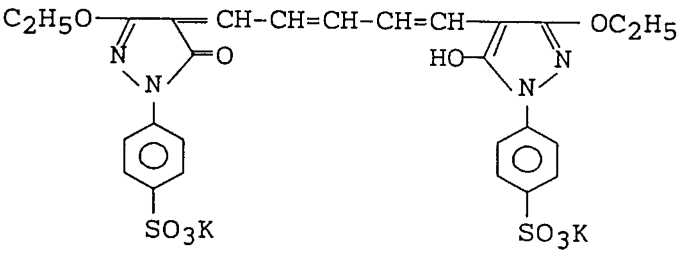


S
S
CH
CH_3O
⊕N
N
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3H \cdot N(C_2H_5)_3$

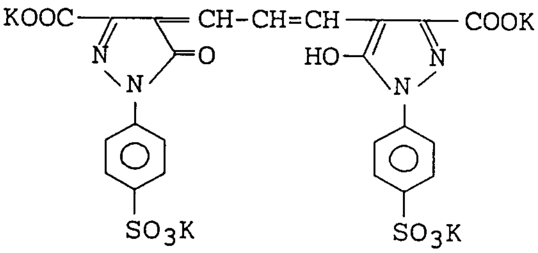
S-6


O
N
CH
S
N
(CH2)3SO3
(CH2)4SO3H·N(C2H5)3

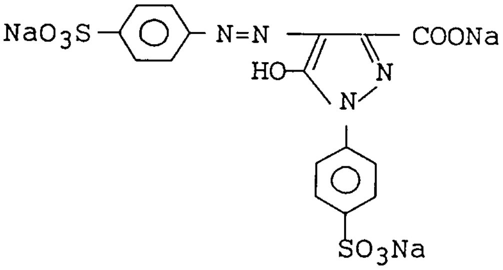
D-1


C2H5O
CH-CH=CH-CH=CH
OC2H5
N
N
O
HO
N
N
SO3K
SO3K

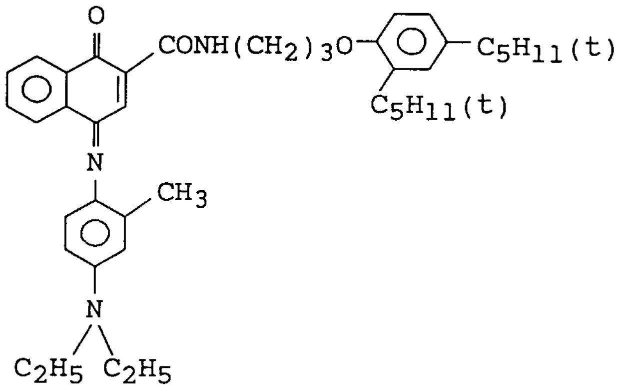
D-2


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

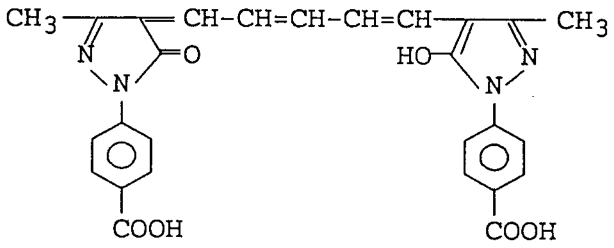
D-3


NaO3S
N=N
COONa
HO
N
N
SO3Na

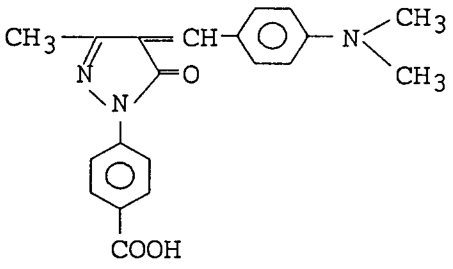
D-4



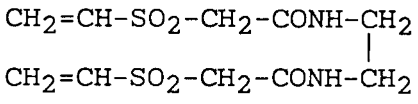
E-1



E-2

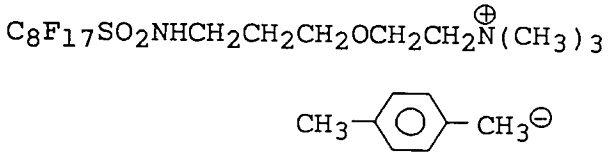


H-1

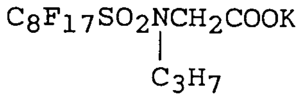


$$\begin{array}{l} CH_2{=}CH\text{-}SO_2\text{-}CH_2\text{-}CONH\text{-}CH_2 \\ \hphantom{CH_2{=}CH\text{-}SO_2\text{-}CH_2\text{-}CONH\text{-}}| \\ CH_2{=}CH\text{-}SO_2\text{-}CH_2\text{-}CONH\text{-}CH_2 \end{array}$$

W-1

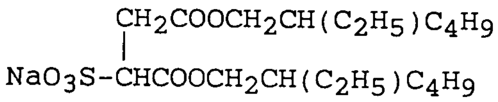


W-2



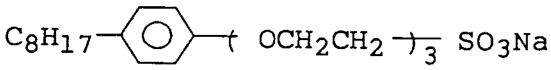
$C_8F_{17}SO_2\underset{\substack{|\\C_3H_7}}{N}CH_2COOK$

W-3

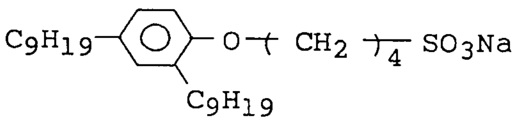


$NaO_3S\text{-}\overset{\substack{CH_2COOCH_2CH(C_2H_5)C_4H_9\\|}}{C}HCOOCH_2CH(C_2H_5)C_4H_9$

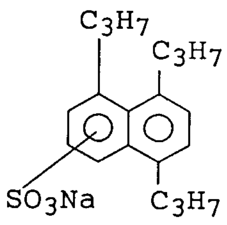
W-4



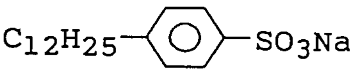
W-5



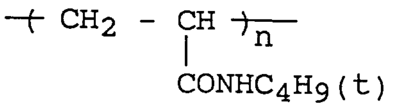
W-6



W-7



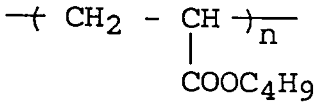
P-1



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

n = 100 - 1000

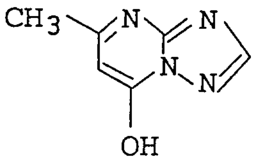
M-1



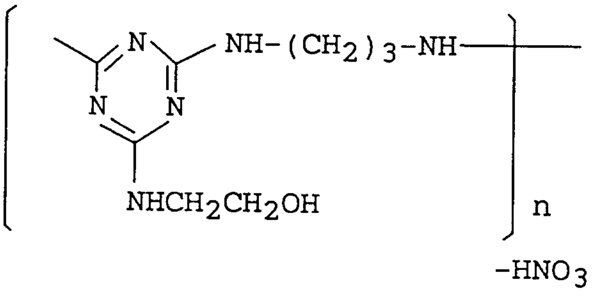
$$-\!\left(\mathrm{CH_2 - \underset{\underset{COOC_4H_9}{|}}{CH}}\right)_n\!-$$

n = 100 - 1000

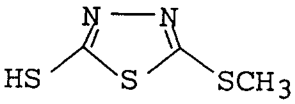
F-1



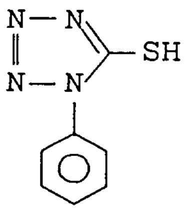
F-2



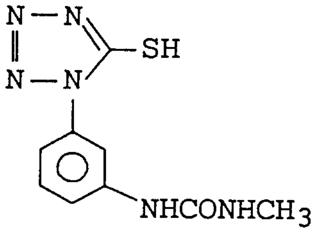
F-3



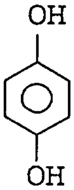
F-4



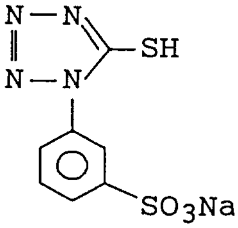
F-5



F-6



F-7



F-8

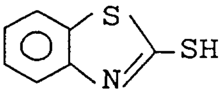


Table 1

Sample No.	DIR Compound	Emulsion
101 (Comparative)	Not used	All light-sensitive emulsions are spherical grain emulsions
102 (Comparative)	Cdp-D 1 mg/m^2 in layer 9	The same as in Sample 101
103 (Comparative)	I-(1) 1 mg/m^2 in layer 9	The same as in Sample 101
104 (Comparative)	The same as in Sample 101	In layer 15, emulsion B of tabular grains having no dislocations In layer 16, emulsion C of tabular grains having no dislocations In layer 17, emulsion D of tabular grains having no dislocations
105 (Comparative)	The same as in Sample 102	The same as in Sample 104
106 (Comparative)	The same as in Sample 103	The same as in Sample 104
107 (Comparative)	The same as in Sample 101	In layer 15, emulsion H of tabular grains having dislocations In layer 16, emulsion I of tabular grains having dislocations In layer 17, emulsion J of tabular grains having dislocations
108 (Comparative)	The same as in Sample 102	The same as in Sample 107
109 (Invention)	The same as in Sample 103	The same as in Sample 107

(Continued)

Table 1

Sample No.	DIR Compound	Emulsion
110 (Comparative)	Cdp-D 1 mg/m^2 in layer 10	The same as in Sample 101
111 (Comparative)	I-(1) 1 mg/m^2 in layer 10	The same as in Sample 101
112 (Comparative)	The same as in Sample 110	In layer 10, emulsion A of tabular grains having no dislocations

Table 2

Sample No.	DIR Compound	Emulsion
113 (Comparative)	The same as in Sample 111	The same as in Sample 112
114 (Comparative)	The same as in Sample 110	Emulsion G of tabular grains having dislocations
115 (Invention)	The same as in Sample 111	The same as in Sample 114
116 (Comparative)	Cdp-D 10 mg/m^2 in layers 2 and 7	In layer 6, emulsion E of tabular grains having no dislocations In layer 10, emulsion A of tabular grains having no dislocations In layer 11, emulsion F of tabular grains having no dislocations In layer 15, emulsion B of tabular grains having no dislocations In layer 16, emulsion C of tabular grains having no dislocations In layer 17, emulsion D of tabular grains having no dislocations
117 (Comparative)	I-(1) 10 mg/m^2 in layers 2 and 7	The same as in Sample 116

(Continued)

Table 2

Sample No.	DIR Compound	Emulsion
118 (Comparative)	The same as in Sample 116	In layer 6, emulsion K of tabular grains having dislocations In layer 10, emulsion G of tabular grains having dislocations In layer 11, emulsion L of tabular grains having dislocations In layer 15, emulsion H of tabular grains having dislocations In layer 16, emulsion I of tabular grains having dislocations In layer 17, emulsion J of tabular grains having dislocations
119 (Invention)	The same as in Sample 117	The same as in Sample 118
120 (Invention)	I-(7) 10 mg/m^2 in layers 2 and 7	The same as in Sample 118
121 (Invention)	I-(22) 10 mg/m^2 in layers 2 and 7	The same as in Sample 118

Table 3

Sample No.	DIR Compound	Emulsion
122 (Invention)	I-(52) 10 mg/m^2 in layers 2 and 7	The same as in Sample 118
123 (Invention)	II-(1) 10 mg/m^2 in layers 2 and 7	The same as in Sample 118
124 (Invention)	II-(28) 10 mg/m^2 in layers 2 and 7	The same as in Sample 118

Table 4

Sample No.	Relative yellow sensitivity density : 1.0	Sharpness; MTF value		
		R	G	B
101 (Comparative	100	0.28	0.43	0.74
102 (")	97	0.31	0.50	0.78
103 (")	95	0.35	0.56	0.81
104 (")	103	0.36	0.52	0.75
105 (")	100	0.39	0.58	0.84
106 (")	98	0.44	0.65	0.87
107 (")	128	0.36	0.52	0.73
108 (")	127	0.40	0.58	0.78
109 (Invention)	124	0.44	0.65	0.88

Table 5

Sample No.	Relative yellow sensitivity density : 1.0)	Sharpness; MTF value		
		R	G	B
110 (Comparative)	100	0.30	0.49	0.78
111 (")	97	0.34	0.55	0.81
112 (")	105	0.33	0.54	0.78
113 (")	103	0.37	0.57	0.81
114 (")	132	0.34	0.47	0.78
115 (Invention)	130	0.38	0.59	0.81

Table 6

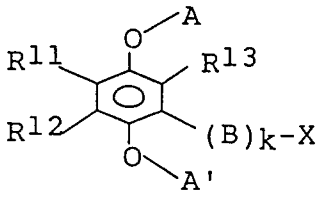
Sample	Relative cyan sensitivity density : 2.0	Relative magenta sensitivity density : 2.0	Relative yellow sensitivity density : 2.0	Sharpness; MTF value		
				R	G	B
116 (Comparative)	100	100	100	0.44	0.63	0.85
117 (")	97	98	98	0.47	0.68	0.87
118 (")	131	132	128	0.46	0.54	0.79
119 (Invention)	129	131	127	0.49	0.68	0.88
120 (")	129	130	127	0.48	0.67	0.87
121 (")	127	129	126	0.50	0.68	0.88
122 (")	130	130	128	0.47	0.67	0.86
123 (")	128	131	128	0.48	0.66	0.86
124 (")	129	131	128	0.48	0.67	0.87

Claims

1. A silver halide color photographic light-sensitive material comprising at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, on a support, at least one silver halide emulsion layer containing

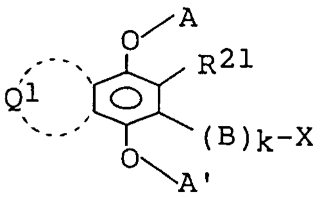
tabular silver halide grains, each having a thickness of less than 0.5 μm, a diameter of 0.3 μm or more, and a diameter/thickness ratio of 2 or more, said tabular silver halide grains occupying at least 50% of the total projected area of all silver halide grains contained in said silver halide emulsion layer, at least 50% in number of said tabular grains having 10 or more dislocations each, and at least one layer in the light-sensitive material containing at least one compound represented by the following formula (I) or (II):

Formula (I)



where R^{11} is R^{14}-N(R^{16})CON(R^{15})-, R^{14}OCON(R^{15})-, $R^{14}SO_2N(R^{15})$-, R^{14}-N(R^{16})$SO_2N(R^{15})$- or R^{17}CO NH-; R^{14} is an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group; each of R^{15} and R^{16} is a hydrogen atom, an alkyl group or an aryl group; R^{17} is an alkyl group having 2 or more carbon atoms in which a heteroatom is not substituted on the carbon atom adjacent to a carbonyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group; each of R^{12} and R^{13} is a hydrogen atom or a substituent group having a Hammett's substituent constant σ_p of 0.3 or less; B is a group releasing X after splitting off from an oxidized form of the hydroquinone nucleus; X is a development inhibitor; k is an integer; and each of A and A' is a hydrogen atom or a group which can be removed by alkali;

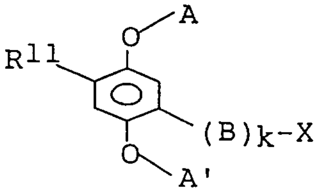
Formula (II)



where Q^1 is an atomic group containing at least one heteroatom, required to form, together with the carbon atoms, a 5- or more-membered heterocyclic ring; R^{21} is a group which can be substituted on the hydroquinone nucleus; and B, X, k, A and A' are idential in meaning to those in the formula (I).

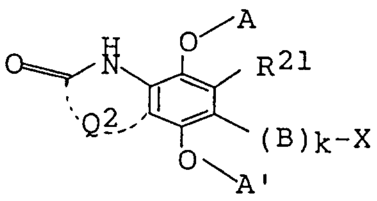
2. The light-sensitive material according to claim 1, characterized in that said compound of formula (I) or (II) is represented by the following formula (IA) or (IIA):

Formula (IA)



where R^{11}, B, X, A, A', and k are identical in meaning to those in the formula (I);

Formula (IIA)



where Q^2 is of the same meaning as Q^1 in the formula (II), and R^{21}, A, A', B, X and k are identical in meaning to those in the formula (II).

3. The light-sensitive material according to claim 1, characterized in that said tabular silver halide grains are made of silver bromoiodide containing 1 to 5 mole% of silver iodide.

4. The light-sensitive material according to claim 1, characterized in that said tabular silver halide grains occupy at least 90% of said total projected area of all silver halide grains contained in said silver halide emulsion layer.

5. The light-sensitive material according to claim 1, characterized in that said tabular silver halide grains have a diameter/thickness ratio of 2 to 12.

6. A method of processing a silver halide color photographic light-sensitive material, comprising subjecting a light-sensitive material of claim 1 to an imagewise exposure, and processing the exposed material by a treating process including a block-and-white developing step.

7. A method of processing a silver halide color photographic light-sensitive material, comprising subjecting a light-sensitive material of claim 2 to an imagewise exposure, and processing the exposed material by a treating process including a block-and-white developing step.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 92 11 7395

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.5)
D,A	EP-A-0 440 195 (FUJI PHOTO FILM) * page 76, line 31 - line 39 * * page 86, line 36 - line 47; example 1 * * page 125, line 5 - line 12; example 4 * * claims * ---	1-7	G03C7/30 G03C7/305
D,A	EP-A-0 282 896 (FUJI PHOTO FILM) * claims; example 2 * ---	1-7	
A	T.H. JAMES 'Theory of the Photographic Process' 1977 , MACMILLAN PUBL. INC. , NEW YORK, US Section II.F: "Dislocations" , pages 19-21 * page 21, column 2, line 11 - line 20 * ---		
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 233 (P-724)(3080) 5 July 1988 & JP-A-63 25 653 (FUJI PHOTO FILM) 3 February 1988 * abstract * * page 341; figure 19 * * page 344; figures I-23 * -----	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 JANUARY 1993	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
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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
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