⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 488 029 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **91119735.8**

(51) Int. Cl.5: **G03C 1/09**, G03C 1/10

㉒ Date of filing: **19.11.91**

㉚ Priority: **19.11.90 JP 311544/90**

㊸ Date of publication of application:
03.06.92 Bulletin 92/23

(84) Designated Contracting States:
DE FR GB NL

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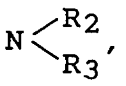
(54) Silver halide photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material comprising at least one silver halide emulsion layer on a support, wherein silver halide grains contained in the silver halide emulsion layer are chemically sensitized by selenium sensitizer, and the silver halide emulsion layer contains a compound represented by the following formula (I), and/or the oxidized product thereof:
formula (I)

$X_1 - A - X_2$

where X_1 and X_2 each represent OR_1 or



$$N\begin{matrix}\diagup R_2 \\ \diagdown R_3\end{matrix},$$

wherein R_1 represents a hydrogen atom or a group capable of changing into a hydrogen atom through hydrolysis, R_2 and R_3 each represent a hydrogen atom, alkyl, aryl, heterocylic, alkylsulfonyl, arylsulfonyl, heterocyliccarbonyl, alkylcarbonyl, arylcarbonyl, sulfamoyl, or carbamoyl, and A represent substituted or unsubstituted allylene group, in at least one of X_1, X_2 and A the hydrogen atom contained therein is substituted by an adsorption accelerating group to a silver halide grain.

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The present invention relates to a silver halide photographic light-sensitive material.

Generally, silver halide emulsions for use in silver halide photographic light-sensitive materials are subjected to chemical sensitization using various chemicals, in order to have desired sensitivities, desired gradation, and the like. Typical examples of chemical sensitizations are: sulfur sensitization, selenium sensitization, noble-metal sensitization such as gold sensitization, reduction sensitization, and any possible combination of these sensitizations.

In recent years, there has been an increasing demand for silver halide photographic light-sensitive material which has high sensitivity and high sharpness and which can be developed at high speed. To meet this demand, many attempts have been made to improve the sensitization methods.

Of the sensitization methods, various methods of selenium-sensitization are disclosed in U.S. Patents 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320069, 3,408,196, 3,408,197, 3,442,653, 3,420,670, and 3,591,385, French Patents 2,693,038 and 2,093,209, JP-B 52-34491, JP-B 52-34492, JP-B 53-295, JP-B 57-22090, JP-A 59-180536, JP-A 59-185330, JP-A 59-181337, JP-B 59-187338, JP-A 59-192241, JP-A 60-150046, JP-A 60-151637, JP-A 61-246738, British Patents 255,846 and 861,984, and H.E. Spencer et al., Journal of Photogra phic Science, Vol. 31, pp. 158-69, 1983.

Various pressures are applied to photographic light-sensitive materials coated with silver halide. For example, negative film for ordinary photography is bent when it is taken up into a cartridge or loaded into a camera, and is pulled in a camera to be fed, frame by frame.

On the other hand, sheets of film for use in printing or X-ray photography are handled directly by hands, and are often bent or folded by hands.

Light-sensitive material of any kind receives a high pressure when it is cut or processed.

When various forces are applied to photographic light-sensitive material in such a way, a force is applied to the silver halide grains through the gelatin used as binder for the grains or the plastic film used as support. As is known in the art, when a pressure is applied to silver halide grains, the photographic properties of the material change. This is reported in detail in, for example, K.B. Mather, J. Opt. Soc. Am., 38 , 1054 (1948); P. Faelens and P. de Smet, Sci, et Ind. Phot., 25, No. 5, 178 (1954); and P. Faelens, J. Phot. Sci, 2, 105 (1954).

Hence it is greatly demanded that photographic light-sensitive material be provided whose photographic properties are not influenced by the pressure applied to it.

Various methods of improving the pressure resistance of photographic light-sensitive material are known. One of them is to add a plasticizer, such as a polymer or an emulsion compound, to the photographic light-sensitive material, in order to prevent a pressure from acting on the grains in the emulsion. Another method is to reduce the ratio of the silver halide to the gelatin, both contained in the silver halide emulsion, so as to prevent a pressure from acting on the grains in the emulsion.

British Patent 738,618, for example, discloses the use of heterocyclic compound; British Patent 738,637 discloses the use of alkylphthalate; and British Patent 738,639 discloses the use of alkylester. Further, U.S. Patent 2,960,404 describes the use of polyvalent alcohol; U.S. Patent 3,121,606 discloses the use of caroxyalkyl cellulose. JP-A-49-5017 discloses the use of paraffin and carboxylate. JP-B-53-28086 describes the use of alkylacrylate and organic acid.

In the method of adding a plasticizer to photographic light-sensitive material, however, the amount in which to use the plasticizer is limited since an excessive amount would decrease the mechanical strength of emulsion layers. When gelatin is used in an increased amount, the sharpness and the speed of development will inevitably decrease. In view of this, any known method cannot achieve desired advantages completely.

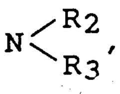
The object of the present invention is to provide a silver halide photographic light-sensitive material which is high sensitive and has a reduced slight scratch fogging and excels in pressure resistance.

The inventors hereof conducted intensive studies on silver halide photographic light-sensitive materials, and successfully made the the silver halide photographic light-sensitive materials, specified below, which fulfill the above-mentioned object.

(1) A silver halide photographic light-sensitive material comprising at least one silver halide emulsion layer on a support, wherein silver halide grains contained in the silver halide emulsion layer are chemically sensitized by selenium sensitizer, and the silver halide emulsion layer contains a compound represented by the following formula (I), and/or the oxidized product thereof: formula (I)

X_1 - A - X_2

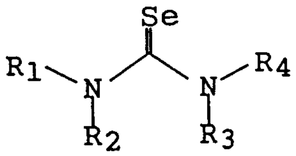
where X_1 and X_2 each represent OR_1 or



wherein R_1 represents a hydrogen atom or a group of changing into a hydrogen atom through hydrolysis, R_2 and R_3 each represent a hydrogen atom, alkyl, aryl, heterocylic, alkylsulfonyl, arylsulfonyl, heterocyliccarbonyl, alkylcarbonyl, arylcarbonyl, sulfamoyl, or carbamoyl, and A represents substituted or unsubstituted allylene group, in at least one of X_1, X_2 and A the hydrogen atom contained therein is substituted by an adsorption accelerating group to a silver halide grain.

(2) The silver halide photographic light-sensitive material described in (1), wherein the silver halide grains are chemically sensitized by at least one of selenium sensitizers represented by the following formula (II):

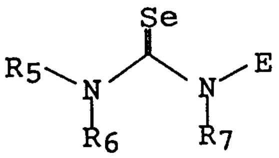
formula (II)



where R_1, R_2, R_3, and R_4 each represent alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, and sulfamoyl.

(3) The silver halide photographic light-sensitive material described in (2), wherein the selenium sensitizer represented by formula (II) is represented the following formula (III):

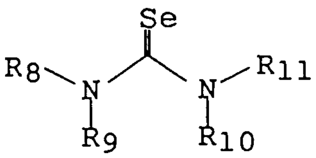
formula (III)



where R_5, R_6, R_7, and E each represent alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, and sulfamoyl, and the E represents a group having Hammett constant σp of at least -0.1.

(4) The silver halide photographic light-sensitive material described in (1), wherein the silver halide grains are chemically sensitized by at least one of selenium sensitizers represented by the following formula (IV):

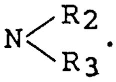
formula (IV)



where R_8, R_9, R_{10}, and R_{11} each represent hydrogen atom, alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxy carbonyl, carbamoyl, and sulfamoyl, and at least one pair of R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, and R_{11} and R_8 are bonded to each other, forming a ring.

The present invention will now be described in detail. First, the compound of formula (I), used in the present invention, will be described.

In the formula (I), i.e., X_1 - A - X_2, X_1 and X_2 are OR_1 or



$$N\langle^{R_2}_{R_3}.$$

Here, R_1 is a hydrogen atom or a group capable of changing into a hydrogen atom through hydrolysis. R_2 and R_3 are a hydrogen atom, alkyl group, aryl group, heterocylic group, alkylsulfonyl group, arylsul fonyl group, heterocylic carbonyl group, alkylcarbonyl group, arylcarbonyl group, sulfamoyl group, or carbamoyl group.

A is substituted or unsubstituted allylene group. In at least one of X_1, X_2 and A, the hydrogen atom contained therein is substituted by a group which accelerates the adsorption to a silver halide grain.

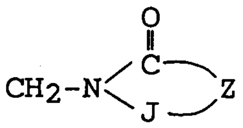
More specifically, A is a substituted or unsubstituted allylene group (e.g., phenylene or naphtylene). Examples of the substituted allylene group are: halogen atom (fluorine, chlorine, bromine), alkyl group (preferably, one having 1 to 20 carbon atoms), aryl group (preferably, one having 6 to 20 carbon atoms), alcoxy group (preferably, one having 1 to 20 carbon atoms), aryloxy group (preferably, one having 6 to 20 carbon atoms), alkylthio group (preferably, one having 1 to 20 carbon atoms), arylthio group (preferably, one having 6 to 20 carbon atoms), acyl group (preferably, one having 2 to 20 carbon atoms), acylamino group (preferably, alkanoylamino group having 1 to 20 carbon atoms or benzoylamino group having 6 to 20 carbon atoms), nitro group, cyano group, oxycarbonyl group (preferably, alkoxycarbonyl group having 1 to 20 carbon atoms or aryloxycarbonyl group having 6 to 20 carbon atoms), carboxy group, sulfo group, hydroxy group, ureido group (preferably, alkylureido group having 1 to 20 carbon atoms or arylureido group having 6 to 20 carbon atoms), sulfonamido group (preferably, alkylsulfonamido group having 1 to 20 carbon atoms or arylsulfonamido group having 6 to 20 carbon atoms), sulfamoyl group (preferably, alkylsulfamoyl group having 1 to 20 carbon atoms or arylsulfamoyl group having 6 to 20 carbon atoms), acyloxy group (preferably, one having 1 to 20 carbon atoms), amino group (unsubstituted amino, preferably alkyl group having 1 to 20 carbon atoms, or secondary or tertiary amino group substituted by aryl group having 6 to 20 carbon atoms), carbonic ester group (preferably, alkylcarbonic ester group having 1 to 20 carbon atoms or arylcarbonic ester group having 6 to 20 carbon atoms), sulfonyl group (preferably, alkylsulfonyl group having 1 to 20 carbon atoms or arylsulfonyl group having 6 to 20 carbon atoms), sulfinyl group (preferably, alkylsulfinyl group having 1 to 20 carbon atoms or arylsulfinyl group having 6 to 20 carbon atoms), and heterocyclic group (pyridine, imidazole, furan, and the like).

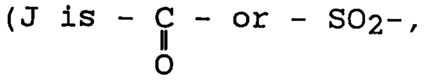
If the compound of formula (I) has two or more substituted groups, these groups can either be identical or different. In the case where two substituted groups are ones substituted on adjacent carbon atoms of benzene ring, they are combined, forming 5-, 6- or 7-membered carbon ring or heterocyclic ring which is either saturated or unsaturated.

Examples of the ring-forming compounds are: cyclopentane, cyclohexane, cycloheptane, cyclopentene, cyclohexadiene, cycloheptadiene, indan, norbonane, norbornene, benzene, pyridine, and the like. These can have substituting groups.

Total carbon atoms in the substituted groups is preferably 1 to 20, more preferably 1 to 10.

Examples of group R_1, which can change into a hydrogen atom through hydrolysis, are - COR_4 (R_4 is alkyl group, either substituted or unsubstituted, aryl group, either substituted or unsubstituted, or anino group, either substituted or unsubstituted),





$$(J \text{ is } -\underset{\underset{O}{\|}}{C}- \text{ or } -SO_2-,$$

Z is a plurality of atoms required to form at least one 5- or 6-membered heterocyclic ring).

R_2 and R_3 are hydrogen atoms, substituted or unsubstituted alkyl group, substituted or unsubstituted heterocyclic group, substituted or unsubstituted alkylsulfonyl group, substituted or unsubstituted arylsulfonyl group, substituted or unsubstituted heterocyclic sulfonyl group, substituted or unsubstituted alkylcarbonyl group, substituted or unsubstituted arylcarbonyl group, substituted or unsubstituted heterocyclic carbonyl group, substituted or unsubstituted sulfamoyl group, or substituted or unsubstituted carbamoyl group. Preferably, R_2 and R_3 are hydrogen atoms, substituted or unsubstituted alkyl group, substituted or unsubstituted heterocyclic group, substituted or unsubstituted heterocyclicsulfonyl group, substituted or unsubstituted heterocycliccarbonyl group, substituted or unsubstituted sulfamoyl group, or substituted or unsubstituted carbamoyl group. R_2 and R_3 can either be identical or different. They can be combined, thus forming nitrogen-containing hetero ring. (For example, they are: morpholino group, pyperrilidino group, pyrrolidino group, or imidazolyl group.)

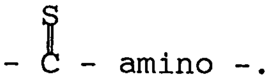
Examples of substituting groups on R_2 and R_3 are those exemplified above as substituting groups A.

The group accelerating the adsorption to the silver halide is one identified by the following formula:

$$Y \text{-(} L \text{)-}_m$$

where Y is the group accelerating the adsorption to silver halide, L is a divalent bonding group, m is 0 or 1. Examples of group Y accelerating the adsorption to silver halide are: thioamido group, mercapto group, group having a disulfide bond, and 5- or 6-membered nitrogen-containing heterocyclic group. The heterocyclic group can form a part of a sensitizing dye.

The thioamido group represented by Y is a divalent group identified by



$$-\overset{\overset{\displaystyle S}{\|}}{C}-\text{amino}-.$$

It can be a part of a cyclic structure, or noncyclic thioamido group. The thioamido adsorption-accelerating group for use in the present invention can be selected from those which are disclosed in, for example, U.S. Patents 4,030, 925, 4,031,127, 4,080,207, 4,245,037, 4,255,511, 4,266,013, and 4,176,364, Research Disclosure, Vol. 151, No. 15162 (November 1976), and Research Disclosure, Vol. 176, No. 17626 (December 1978).

Examples of the noncyclic thioamido group are thioureido group, thiourethane group, and dithiocarbamic ester group. Examples of the cyclic thioamido group are 4-thiazoline-2-thione, 4-midazoline-2-thione, 2-thiohydantoine, rhodanine, thiobarbituric acide, tetrazoline-5-thione, 1,2,4-triazoline-3-thione, 1,3,4-thiaziazoline-2-thione, 1,3,4-oxadiazoline-2-thione, benzimidazoline-2-thione, benzyoxazoline-2-thione, and benzothiazoline-2-thione. These cyclic thiamido groups can be further substituted.

The mercapto group represented by Y is aliphatic mercapto group, aromatic mercapto group, or heterocyclic mercapto group. (When -SH group is bonded to the carbon atom located adjacent to nitrogen atom, it corresponds to cyclic thioamido group which is a tautomer of the mercapto group. Specific examples of this group are identical to those mentioned above.)

The 5- or 6-membered nitrogen-containing heterocyclic group, also represented by Y, is a 5-membered or 6-membered nitrogen-containing hetero ring consisting of nitrogen, oxygen, sulfur, and carbon atoms. Desirable examples of this group are: benzotriazole, triazole, tetrazole, indazole, benzimidazole, imidazole, benzothiazole, thiazole, benzoxazole, oxazole, thiadiazole, oxadiazole), and triazine, and the like. Any of these group can be substituted by an appropriate substituent group, such as a group of atoms which is required for forming a sensitizing dye.

The sensitizing dye can be selected from the dyes disclosed in F.M. Hamer, "Heterocyclic Compounds - Cyanine Dyes and Related Compounds," John Wiley & Cons, Inc., New York, London, 1964.

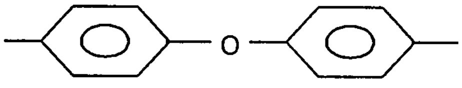
The substituent group can be one described for R_2, R_3, or R_4.

Of the groups generally represented by Y, a preferable one is cyclicthiamido group (i.e., a mercapto-substituted, nitrogen-containing heterocyclic ring, such as 2-mercaptothiazole, 3-mercapto-1,2,4-triazole, 5-mercaptotetrazole, 2-mercapto-1,3,4-oxadiazole, or 2-mercapto-1,3,4-benzyoxazole), or nitrogen-containing heterocyclic group (e.g., benzotriazole, benzimida zole, or indazole).

Two or more $Y \text{(} L \text{)}m$ groups can substitute; they can either be identical or different.

The divalent bonding group represented by L is a carbon atom, a nitrogen atom, a sulfur atom, or an oxygen atom, or a group of atoms including an atom or atoms of at least one of the elements named. More specifically, the divalent bonding group is alkylene group, alkenylene group, alkynylene group, allylene group, -0-, -S-, -NH-, -N=, -CO-, or $-SO_2-$, or any possible combination thereof. (These groups can have a

substituted group or groups.) To be still more specific, the divalent bonding group can be selected from those identified by the following formulas:
-CONH-, -NHCONH-, $-SO_2NH-$, -COO-, -NHCOO-,



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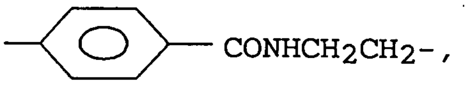
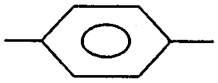


$-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$,



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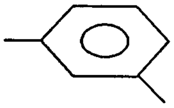

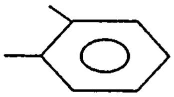

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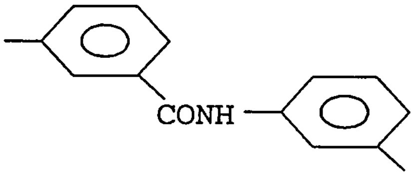

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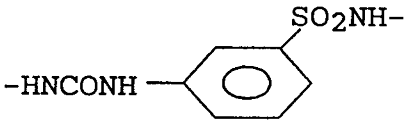

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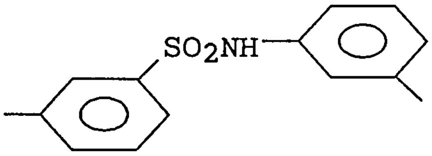

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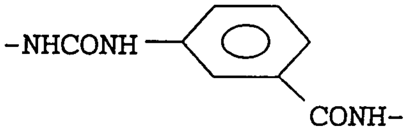

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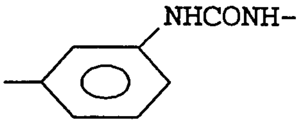
-NHCONHCH$_2$CH$_2$CONH-,



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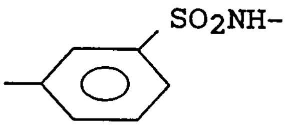

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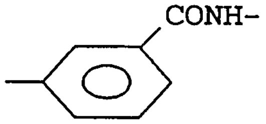

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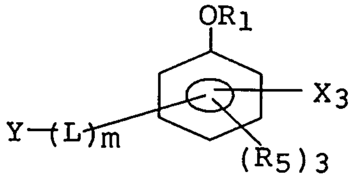
$-CH_2CH_2SO_2NH-$, $-CH_2CH_2CONH-$

The groups, exemplified above, can be substituted by appropriate substituent groups. The substituent groups can be those represented for A. Of the compounds identified by the formula (I), preferable are those represented by the following formula (V):

formula (V)



where R_1, Y, L, and m are identical to those included in formula (I), X_3 is identical to X_1 and X_2 included in formula (I), R_5 is a hydrogen atom or a group which can substitute the hydrogen atom on a benzene ring. The group, which can substitute, is selected from those substituting groups represented for $\underline{A}$. R_5s is either identical or different.

It is desirable that X_3 substitute at an ortho site or a para site of OR_1. Of the groups represented by X_3, $-OR_1$ is preferred, and more preferably R_1 is a hydrogen atom.

The compound of formula (I) can either contain the oxidized product thereof or consist the oxidized product thereof. It is assumed that most compounds identified by formula (I) contain the oxidized product formed through natural oxidation by air and the like. The term "oxidized product" is p-quinones if the compound of formula (I) is hydroquinones, or o-quinone if the compound is catechols.

Preferable examples of the compound identified by formula (I) are shown in Table A which is part of the present specification. Nevertheless, compounds of formula (I) for use in the invention are not limited to those illustrated in Table A.

A typical example of a method of synthesizing the compound identified by formula (I) will now be described.

Synthesis of Compound I-11

First, 23.8 g (0.1 mol) of 5-phenylbenztriazole carbonate, 25.2 g (0.11 mol) of 2-(4-aminophenyl)-ethylhydroquinone, and 100 ml of DMAC were stirred together for 5 hours in an oil bath maintained at 120°C (external temp.), in the presence of a nitrogen flow. Next, DMAC was distilled out under a reduced pressure, and 200 ml of methanol was added to the stirred mix ture. As a result, a small amount of by-product, or black crystals, remained. The insoluble part was filtered out by means of suction filtering. Then, the methanol was distilled under a reduced pressure, there by obtaining a reaction product. The reaction product was singly separated and refined in a silica-gel column (chloroform/methanol = 4/1). The methanol was washed, thereby obtaining the target compound I-11 at a yield of 14.4% (38.5%). Compound I-11, thus synthesized had a melting point of 256 to 257°C.

Preferably, the compound represented by formula (I) is added in an amount of 1×10^{-7} mol to 1×10^{-2} mol per mol of the silver halide contained in the silver halide photographic light-sensitive material according to the present invention. More preferably, the compound is added in an amount ranging from 1×10^{-6} to 5×10^{-3} mol per mol of the silver halide.

The compound of formula (I) can be added to a hydrophilic colloid solution, preferably to a solution of silver halide emulsion. If the compound is to be added to a silver halide emulsion solution, it can be added at any time prior to the start of chemical sensitization of the silver halide grains, or at any time before the coating of the silver halide emulsion solution.

The selenium sensitization, which is performed by using a selenium sensitizer according to the invention, will now be described.

The selenium sensitization is carried out in the method hitherto known. That is, a labile selenium compound and/or an unlabile selenium compound is added to silver halide emulsion. Then, the emulsion is stirred for a predetermined time at high temperature, preferably at 40°C or more. It is desirable that the selenium sensitization disclosed in JP-B-44-15748, wherein use is made of a labile selenium sensitizer, be performed in the present invention. Specific examples of the labile selenium sensitizer are: aliphatic isoseleno cyanates such as arylisoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarbonic acids and esters, and selenophosphates. Of these labile selenium sensitizers, the following ones are preferred in particular:

I. Colloid Metallic Selenium

II. Organic Selenide (i.e., compound wherein selenium atoms are double-bonded to the carbon atoms of an organic compound by covalent bonding)

a. Isoselenocyanates

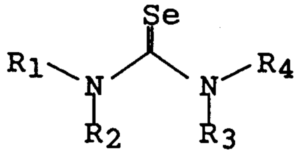
Aliphatic isoselenocyanates such as allylisoselenocyanate and the like.

b. Selenoureas (including enol-type ones)

Selenourea, alphatic selenoureas such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dioctyl, tetramethyl, N-(β-carboxyethyl)-N', N'-dimethyl, N,N-dimethyl, diethyl, and dimethyl selenourea; aromatic selenoureas having one or more aromatic groups such as phenyl and tolyl; and heterocyclic selenoureas having heterocyclic groups such as pyridyl and benzothiazolyl.

Preferably, in the present invention, the selenium sensitizer represented by the following formula (II) is used as the selenium sensitizer:

formula (II)



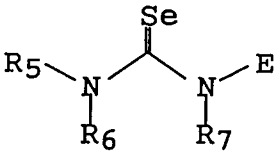
This formula (II) will be explained. In this formula, R_1, R_2, R_3, and R_4 are substituted or unsubstituted alkyl group (e.g., methyl, ethyl, n-propyl, t-butyl, isopropyl, n-octyl), substituted or unsubstituted cycloalkyl group (e.g., cyclopentyl, cyclohexyl, 2-methyl cyclohexyl), substituted or unsubstituted alkenyl group (e.g., aryl, 2-butenyl, 3-pentenyl), substituted or unsubstituted alkynyl group (e.g., propargyl, 3-pentenyl), substituted or unsubstituted aralkyl group (e.g., benzyl group, phenetyl), substituted or unsubstituted aryl group (e.g., phenyl, naphtyl, 4-methylphenyl), substituted or unsubstituted heterocyclic group (e.g., pyridyl, thienyl, furyl, imidazolyl, piperidyl, morphoryl), substituted or unsubstituted acyl group (e.g., acetyl, benzoyl, formyl, pivaroyl, carboxy group, substituted or unsubstituted alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), substituted or unsubstituted aryloxycarbonyl group (e.g., phenoxycarbonyl), substituted or unsubstituted carbamoyl group (e.g., carbamoyl, dimethylcarbamoyl, propylcarbamoyl), and substituted or unsubstituted sulfamoyl group (e.g., sulfamoly, N-methylsulfamoyl).

Examples of substituent groups for R_1, R_2, R_3, and R_4, which can have substituent groups, are as specificied below:

Alkyl group (e.g., methyl, ethyl, t-butyl), cycloalkyl group (e.g., cyclopentyl, cyclohexyl), alkenyl group (e.g., aryl group, 3-pentenyl), alkynyl group (e.g., propargyl, 3-pentenyl), aralkyl group (e.g., benzyl, phenetyl), aryl group (e.g., phenyl, naphtyl, 4-methylphenyl), heterocyclic group (e.g., pyridyl, thienyl, furyl, imidazolyl, piperdyl, mor phoryl, benzyriazolyl, teteraazaindenyl, indolyl), acyl group (e.g., acetyl, benzoyl, formyl, pyvaroyl, carboxy group, alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), aryloxycarbonyl group (e.g., phenoxycarbonyl), acyloxy group (e.g., acetoxy, benzoyloxy), amino group (e.g., unsubstituted amino, dimethylamino, ethylamino), ammonio group (e.g., trimethylammonio), acylamino group (e.g., acetylamino, benzoylamino), carbamoyl group (e.g., carbamoyl, dimethylcarbamoyl, propylcarbamoyl), sulfonylamino group (e.g., benzenesulfoamido), and sulfamoyl group (e.g., sulfamoly, N-methylsulfamoyl), alkoxy group (e.g., methoxy, ethoxy, isopropoxy), aryloxy group (e.g., phenoxy), alkylthio group (e.g., methylthio, ethylthio), arylthio group (e.g., phenyl thio), sulfonyl group (e.g., mecyl, benzenesulfonyl), sulfinyl group (e.g., methylsulfinyl, ethylsulfinyl), sulfo group, sulfino group, hydroxy group, halogen group (e.g., fluoro, chloro, bromo), cyano group, nitro group, ureido group (e.g., ureido, N'-methylureiodo), phosophono group, mercapto group.

Of the compounds represented by formula (II), the one represented by the following formula (III), is preferred:

formula (III)



where R_5, R_6, R_7, and E are alkyl group, cycloalkyl group, alkenyl group, alkynyl group, aralkyl group, aryl group, heterocyclic group, acyl group, carboxy group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, and sulfamoyl group. (E is a group having Hammett constant σp of at least -0.1.)

Formula (III) will be explained in detail.

R_5, R_6, and R_7 are of the same significance as R_1, R_2, R_3, and R_4 included in formula (II).

E is a group having Hammett constant σp of -0.1 or more, preferably 1 or less. (As for the definition of Hammett constant, see Journal of Medicinal Chemistry, Vol. 16, p. 304 (1973), and Vol. 20, p. 304 (1977).) Specific examples of group E are: substituted or unsubstituted alkyl group (e.g., chloromethyl, trifluoromethyl, acetonyl), substituted or unsubstituted cycloalkyl group (e.g., cyclopentyl), substituted or unsubstituted alkenyl group (e.g., 1-chloro-3-butenyl, 1-chloro-4-octetyl), substituted or unsubstituted alkynyl group (e.g., 1-chloro-3-butynyl, 1-chloro-4-octynyl), substituted or unsubstituted aralkyl group (e.g., benzyl), substituted or unsubstituted aryl group (e.g., phenyl, pentafluorophenyl), substituted or unsubstituted heterocyclic group (e.g., 4-pyridyl, 2-benzoxazolyl, 1-ethyl-2-benzimidazolyl), substituted or unsubstituted acyl group (e.g., acetyl, formyl, benzoyl, pivaroyl, carboxy group, substituted or unsubstituted alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), substituted or unsubstituted aryloxycarbonyl group (e.g., phenoxycarbonyl), substituted or unsubstituted carbamoyl group (e.g., carbamoyl, dimethylcarbamoyl, propylcarbamoyl), and substituted or unsubstituted sulfamoyl group (e.g., sulfamoyl, methylsulfamoyl).

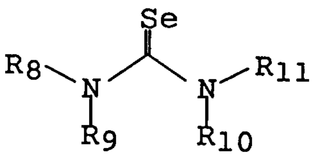
Substituent group of R_5, R_6, R_7, and E are of the same significance as the substituent group of R_1, R_2, R_3, and R_4 included in formula (II).

Preferably, R_5, R_6, and R_7, all shown in formula (III), are substituted or unsubstituted alkyl group, substituted or unsubstituted aryl group, substituted or unsubstituted heterocyclic group, or substituted or unsubstituted acyl group. E, also shown in formula (III), is a group having Hammett constant σp of 0.3 or more. Preferably, E is substituted or unsubstituted heterocyclic group, substituted or unsubstituted acyl group, substituted or unsubstituted carbamoyl group, substituted alkyl group, or substituted aryl group.

More preferably, R_5, R_6, and R_7 are substituted or unsubstituted alkyl group, substituted or unsubstituted aryl group, or substituted or unsubstituted acyl group, and E is acyl group having Hammett constant σp of 0.5 or more.

In the present invention, a selenium compound represented by the following formula (IV) can be used as a preferable selenium sensitizer:

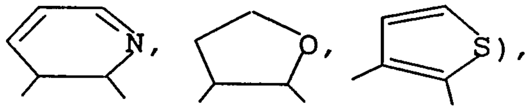
formula (IV)



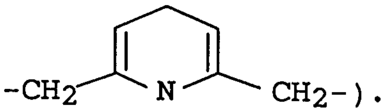
Formula (IV) will be explained in detail.

In formula (IV), R_8, R_9, R_{10}, and R_{11} are hydrogen atoms, substituted or unsubstituted alkyl group (e.g., methyl, ethyl, n-propyl, t-butyl, isopropyl, n-octyl), substituted or unsubstituted cycloalkyl group (e.g., cyclopentyl, cyclohexyl, 2-methylcyclohexyl), substituted or unsubstituted alkenyl group (e.g., aryl, 2-butenyl, 3-pentenyl), substituted or unsubstituted alkynyl group (e.g., propargyl, 3-pentynyl), substituted or unsubstituted aralkyl group (e.g., benzyl group, phenetyl), substituted or unsubstituted aryl group (phenyl, naphtyl, 4-methylphenyl), substituted or unsubstituted heterocyclic group (e.g., pyridyl, thienyl, furyl, imidazolyl, piperdyl, morphoryl), substituted or unsubstituted acyl group (e.g., acetyl, benzoyl, formyl, pivbaroyl, carboxy group, substituted or unsubstituted alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), substituted or unsubstituted aryloxycarbonyl group (e.g., phenoxycarbonyl), carbamoyl group (e.g., carbamoyl, dimethylcarbamoyl, propylcarbamoyl), or substituted or unsubstituted sulfamoyl group (e.g., sulfamoyl, methylsulfamoyl).

Groups, which combine with one another, forming a ring, are substituted or unsubstituted alkylene group (including ether group, thioether group, substituted or unsubstituted amino group, such as methylene group, ethylene group, propylene group, butylene group, hexylene group, 1-methylethylene group, $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2NHCH_2CH_2-$), substituted or unsubstituted alalykylene group (e.g., benzylidene), substituted or unsubstituted arylene group (e.g., phenylene, naphtylene), substituted or unsubstituted heterocyclic bonding group (e.g.,



or bonding group formed by combining these groups (e.g.,



Substituent groups for R_8, R_9, R_{10}, and R_{11} can be the same substituent groups described for R_1, R_2, R_3, and R_4 included in formula (II).

In formula (IV), the ring formed by R_8 and R_9, the ring formed by R_9 and R_{10}, the ring formed by R_{10} and R_{11}, and the ring formed by R_{11} and R_8 are preferably 4- to 8-membered rings. R_8, R_9, R_{10}, and R_{11} are preferably hydrogen atoms, substituted or unsubstituted alkyl group, substituted or unsubstituted aryl group, substituted or unsubstituted heterocyclic group, substituted or unsubstituted acyl group, and substituted or unsubstituted carbamoyl group.

In formula (IV), the ring formed by R_8 and R_9, the ring formed by R_9 and R_{10}, the ring formed by R_{10} and R_{11}, and the ring formed by R_{11} and R_8 are more preferably 5- or 6-membered rings, and R_8, R_9, R_{10}, and R_{11} are more preferably hydrogen atoms, substituted or unsubstituted alkyl group, and substituted or unsubstituted acyl group.

Specified examples of the the compounds for use in the present invention are will be shown in Table B which is part of the present specification. Nonetheless, the compounds for use in the invention are not limited to those illustrated in Table B.

The compounds identified by formulas (II), (III), and (IV) can be synthesized by the methods known in the art. More specifically, they can be synthesized by the method disclosed in Saul Patai, "The Chemistry of Organic Selenium and Tellurium Compounds," Vol. 2, pp. 255-258 (1987).

Typical examples of the methods of synthesizing the compounds represented by formulas (II), (III) and (IV) will now be described.

1. Synthesis of Compound II-1

1-(1) Synthesis of N-acetyl-N,N',N'-trimethylthiourea

First, 37 g of acetic anhydride was added to 400 ml of toluene solution containing 40 g of N,N,N'-trimethylthiourea. Further, 0.5 ml of concentrated sulfuric acid was added to the resultant mixture, while the mixture was being stirred, thereby obtaining a reaction liquid. The reaction liquid was heated to 80 ° C, and was stirred for 6 hours. Thereafter, the liquid was cooled to room temperature. Then, 400 ml of water was added to the cooled reaction liquid. Water phase was extracted from the reaction liquid. Common salt was added to the water phase, thereby preparing saturated saline solution. Further, extraction was performed with acetonitrile. The layer of acetonitril was dried with magnesium sulfate and condensed, thereby obtaining 42 g of the target compound, which was oil-like substance.

1-(2) Synthesis of N-acetyl-N,N',N',S-tetramethyl thiouronium iodide

The N-acetyl-N,N',N'-trimethylthiourea (42 g) obtained by method 1-(1) was dissolved in 90 g of methyl iodide, preparing a solution. This solution was stirred for 8 hours at room temperature, thereby obtaining crystal. The crystal was filtered out, and washed with chloroform, thus obtaining 23 g of the target compound.

1-(3) Synthesis of Compound II-1

First, 2.0 g of selenium was added to 150 ml of dried ethanol in a nitrogen atmosphere, thus preparing a solution. The solution was cooled to 0 ° C. Then, 1.0 g of sodium boron hydride was added to the cooled solution, while the solution was being stirred. Gas was instantly generated, but was no longer generated in a few minutes. The solution was further stirred for several minutes at room temperature, thereby obtaining pale red NaHSe solution. Next, 50 ml of ethanol solution containing 4.0 g of N-acetyl-N,N',N',S-tetramethyl thiouronium iodide was added to the pale red solution. The resultant solution was left to stand for 20 hours at room temperature. Glacial acetic acid was added to the solution, reducing the acidity thereof. Thereafter, the solution was concentrated to 10 ml under a reduced pressure.

The concentrated solution was extracted with chloroform and water, thereby obtaining a chloroform layer. The chloroform layer was concentrated, dried, and solidified. The resultant crystal was recrystallized with a mixture solvent consisting of 15 ml of ethyl acetate and 10 ml of hexane, whereby 2.3 g of compound II-1 was prepared.

The target compound, thus prepared, exhibited nuclear magnetic resonance spectrum, mass spectrum, and composition, which coincided with the estimated ones. This compound was synthesized at a yield of 80%, and had a melting point of 87 to 88 ° C.

2. Synthesis of Compound III-29

2-(1) Synthesis of N,N'-dimethylethylenethiouronium iodide

First, 30 g of methyl iodide was added to acetone solution containing 20 g of N,N'-dimethyl ethylene thiourea. The resultant solution was stirred for 8 hours at room temperature, thereby forming crystals. The crystal were filtered out and washed with acetone, whereby the target compound was obtained in an amount of 32 g.

2-(2) Synthesis of Compound III-29

The target compound, III-29, was obtained in an amount of 2.0 g from 4.0 g of the N,N'-dimethylethylene thiouronium iodide prepared in method 2-(1). The target compound exhibited nuclear magnetic resonance spectrum, mass spectrum, and composition, which coincided with the estimated ones. Compound III-29 was synthesized at a yield of 76%, and had a melting point of 144 to 145 ° C.

The other compounds shown in Tables A and B can be synthesized by similar methods.

No cases have been hitherto reported, in which the compound of formula (II), (III) or (IV) is used as a selenium-sensitization agent. It was therefore very difficult to predict the sensitization power of these compounds or the fogging and other photographic properties caused by the compound of formula (II), (III) or (IV). However, the use of the compounds of formulas (II), (III) and (IV) actually imparted remarked photographic properties to silver halide photographic photosensitive materials.

The amount of selenium-sensitizer agent used according to the invention depends on its composition, the silver halide grains to be sensitized, the conditions of chemically-ripening the grains, and the like. In most cases, the selenium sensitizer is used in an amount of 10^{-8} to 10^{-4} mol per mol of silver halide, preferably 10^{-7} to 10^{-5} mol per mol of silver halide.

The conditions, under which to chemically sensitize silver halide grains with the selenium-sensitizing agent of this invention, are not limited in particular. It is desirable, however, that the pAg value be 6 to 11, preferably 7 to 10, an more preferably 7 to 9.5, and that the temperature be 40 to 95 ° C, preferably 50 to 85 ° C.

According to the present invention, it is preferable that the chemical sensitization be performed immediately after silver halide grains have been formed during the manufacture of the emulsion.

Further, in the present invention, it is desirable that a noble metal sensitizer, such as tellurium, gold, platinum, palladium, iridium, be used along with the selenium compound. In particular, gold sensitization should preferably be applied, together with selenium sensitization. More precisely, chloroauric acid, potassium chloroaurate, potassium arurithiocyanate, gold sulfide, gold selenide, and the like can be used as sensitizers, in an amount of 10^{-7} to 10^{-2} mol per mol of silver halide.

In the present invention, it is desirable that sulfur sensitization be applied, too. More specifically, known labile sulfur compounds, such as thiosulfates (e.g., hypo), thioureas (e.g., diphenylthiourea, triethylthiourea, arylthiourea), and rhodanines, can be used in an amount of 10^{-7} to 10^{-2} mol per mol of silver halide.

Moreover, with the present invention it is possible to apply reduction sensitization, along with selenium sensitization. More specifically, stannous chloride, aminoiminomethanesulfonic acid, hydrazine derivaltive, borane derivative, silane compound, polyamine compound, and the like can be used.

According to the invention, it is desirable that selenium sensitization be performed in the presence of a silver halide solvent. Preferable examples of the silver halide solvent are: thiocyanate (e.g., potassium thiocyanate); thioether compound (e.g., the compounds disclosed in U.S. Patents 3,021,215 and 3,271,157, JP-B-58-30571, and JP-A-60-136736, in particular, 3-,6-dithia-1,8-octanediol); tetra-substituted thiourea compound (e.g., the compounds disclosed in JP-B-59-11892 and U.S. Patent 4,221,863, in particular, teteramethyl thiourea); thione compound disclosed in JP-B-60-11341; mercapto compound disclosed in JP-B63-29727; mesoionic compound disclosed in JP-A-60-163042; selenoether compound disclosed in U.S. Patent 4,782,013; telluroether compound disclosed in JP-A-2-118566; and sulfite. Of these solvents, thiocyanate, thioether compound, tetra-substituted thiourea compound, and thione compound are particularly preferable. The solvent is used in an amount of 10^{-5} to 5×10^{-2} mol per mol of silver halide.

The silver halide for use in the present invention is preferably silver bromide, silver iodide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, or silver chloride.

The silver halide grains used in the invention are regular crystals such as octoheral ones, or irregular crystals such as spherical ones or tabular ones. Alternatively, a mixture of regular grains and irregular grains can be used. Nonetheless, it is desirable that irregular silver halide grains be used in the present invention.

The silver halide grains for use in the invention can consist of either a single homogeneous phase or two different phases, i.e., a core and a shell covering the core. Further, the silver halide grains can be those of, for example, neagative-type emulsion, wherein an latent image is formed chiefly on the surfaces of the grains, or those of, for example, inner latent-image type emulsion or pre-fogged direct reverse emulsion, wherein an latent image is formed mainly within the grains. Preferably, the grains are of the type in which a latent image is formed mainly on their surfaces.

The silver halide emulsion for use in the present invention contains tabular grains which have a thickness of 0.5 microns or less, preferably 0.3 microns or less, and a diameter of 0.6 microns or more, and in which those having an average aspect ratio of 5 or more occupy 50% or more of the total projection area. Alternatively, the emulsion can be monodispesant emulsion having a statistical variation coefficient of 20% or less (the variation coefficient being S/d, where S is standard deviation of the projection area in terms of circule-equivalent diameter, and d is the diameter of the grains). Still further, use can be made of a mixture of at least one regular-grain emulsion and at least one monodispersant emulsion.

The photographic emulsion used in the present invention can be manufactured by various methods. Examples of these methods are disclosed in, for example, P. Glafkides, "Chime et Physique Photographique," Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry," Focal Press, 1966; V.L. Zeilikman et al., "Making and Coating Photographic Emulsion," Focal Press, 1964.

To control the growth of the grains, a solvent for silver halide can be used. Examples of this solvent are ammonia, potassium rhodanide, antimony rhodanide, thioether compound (e.g., those disclosed in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439, and 4,276,374), thion compound (e.g., those disclosed in JP-A-53-144319, JP-A-53-82408, and JP-A55-77737), amine compound (e.g., those disclosed in JP-A-54,100717).

In the present invention, the silver halide grains can be grown or physically ripened, in the presence of of cadmium salt, zinc salt, thallium salt, iridium salt or a complex salt thereof, rhodium salt or complex salt thereof, iron salt or complex salt thereof.

It is recommendable that gelatin be contained, as binder or protective colloid, in the emulsion layers and interlayers of the light-sensitive material according to the present invention. Instead, hydrophilic colloid can be used. Examples of hydrophilic high-molecular substances are: gelatin derivative; graft polymer formed of gelatin and other high-molecular substance; protain such as albumin and casein; celluose derivative such as hydroxyethyl celluose, carboxymethyl celluose, and cellulose sulfate ester; sugar derivative such as sodium alginate and starch derivative; and monomer or polymer such as polyvinyl alcohol, polyvinylalcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, and polyvinyl pyrazole.

The gelatin for use in the invention can be general-purpose gelatin, gelatin for processing lime stone, acid-processed gelatin, or enzyme-processed gelatin, such those disclosed in Bull. Soc. Sci. Phot. Japan, No. 16, p. 30 (1966). The gelatin subjected to hydrolysis can be used.

The light-sensitive material according to the present invention has hydrophilic colloid layers forming photogratic light-sensitive layers or back layers. These colloid layers can contain an inorganic or organic layer-hardening agent. Specific examples of the layer-hardening agent are chromium salt, aldehyde salt (e.g., formaldehyde, glyoxazal, glutaraldehyde, N-methylol-series compound (e.g., dimethylol urea). Preferably, active halogen compounds (e.g., 2,4-dichlor-6-hydroxy-1,3,5-triazine and its soldium salt), and active vinyl compounds (e.g., 1,3-bisvinylsulfonyl-2-propanol, 1,2-bis(vinylsufonyl acetoamide) ethane, bis-(vinylsulfonyl methyl) eter, and vinyl-series polymer having vinylsulfonyl group at side chains) are used, since they hardens hydrophilic colloid, such as gelatin, at high speed, thereby imparting stable photographic properties to the silver halide photographic light-sensitive material. N-carbamoly pyridium salts (e.g., (1-

morphorlinocarbonyl-3-pyridinio) methanesulfonate), or halloamidium salts (e.g., 1-(1-chloro-1-pyridinomethylene) pyrrolidium 2-naphthalenesulfonate) can also be used, since they can harden hydrophilic colloid at high speed, too.

The silver halide emulsion for use in this invention can be subjected to spectral sensitization with methyn dyes or the like. Examples of these dyes are: cyanine dye, merocyanine dye, composite cyanine dye, composite merocyanine dye, holopolar cyanine dye, hemicyanine dye, styryl dye, and hemioxonol dye. In particular, the dyes belonging to cyanine dye, merocyanine dye, and composite merocyanine dye are very useful. In these dyes, use can be made of any nucleus usually used in cyanine dye as a basic heterocyclic nucleus. Examples of the nucleus are: a pyrroline nucleus, an oxazoline nucleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, and a pyridine nucleus. Other examples are: a nucleus which has an alicyclic hydrocarbon ring fused to any one of the nuclei named above, and a nucleus which has an aromatic hydrocarbon ring fused to any one of the above-mentioned nuclei, such as a indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxadole nucleus, a naphthoxzole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. These nuclei can have a substituent group on its carbon atom.

Nuclei having a ketomethylene structure can be used in a merocyanine dye or a composite merocyanine dye. Among these nuclei are 5- or 6-membered heterocyclic nuclei, such as a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus can be used as a nucleus having a ketomethylene structure.

The sensitizing dyes, mentioned above, can be used singly or in combination. The use of two or more sensitizing dyes, in combination, is desirable, in order to achieve supersensitization. The emulsion can contain, in addition to a sensitizing dye or dyes, a dye incapable of performing spectral sensitization or a substance absorbing virtually no light and capable of performing supersensitization. Examples of the dye of this type are aminostylbenzene compound (e.g., those disclosed in, for example, U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensate (e.g., those disclosed in U.S. Patent 3,743,510), cadmium salt, azaindene compound, and the like. The combinations of dyes, which are disclosed in U.S. Patents 3,615,613, 3,615,641, 3,617,295, and 3,635,721 are particularly useful.

The silver halide photographic emulsion for use in the present invention can contain various compounds, so that it may not suffer from fogging or its photographic properties may remain stable, during its manufacture or during its storage. Examples of such compounds, known as antifoggands or stabilizers, are: benzothiazolium salt, nitroimidazoles, nitrobenzyimidazoles, chlorobenzyimidazoles, bromobenzyimidazoles, mercaptothizoles, mercaptobenzothiazoles, mercaptobenzyimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole); mercaptopyrizines; mercaptotriazines, thioketo compounds such as oxadolinethione; azaindines (e.g., triazaindine, tetraazaindine (in particular, 4-hydroxy substituted (1, 3, 3a, 7) tetraazaindine), and pentaazaindine; and benzenethisulfonic acid, benzenesulfinic acid, benzenesulfonic acid amide.

The light-sensitive material according to the invention can contain a coating aid and one or more sufactants. Surfactants are used for various purposes, for preventing electric charging, for improving sliping property, for dispersing the emulsion, for preventing adhesion, and for improving photographic properties (e.g., development speed, degree of contrast, degree of sensitization).

The hydrophilic colloid layers of the light-sensitive material according to the invention can contain a water-soluble dye used as filter dye or for various purposes such as prevention of irradiation or halation. Examples of this dye are oxonol dye, hemioxonol dye, styryl dye, merocyanine dye, antraquinone dye, azo dye. Other dyes, such as cyanine dye, azomethyn dye, triarylmethane dye, phthalocyanine dye, are also useful. Further, an oil-suluble dye can be emulsified by means of in-water oil-dispersion method and then be added to the hydrophilic colloid layers.

The present invention can be applied to multi-layer color photographic material which comprises a support and at least two emulsion layers formed on the support and having different spectral sensitivities. The multilayer color photographic material of this invention has at least one red-senstive emulsion layer, at least one green-sensitive emulsion layer, and at least one blue-sensitive emulsion layer -- all formed above the support. These emulsion layers can be arranged in any order desired. Preferably, however, the red-sensitive layer, the green-sensitive layer, and the blue-sensitive layer are arranged in this order from the side of the support. Alternatively, it is desired that the blue-sensitive layer, the red-sensitive layer, and the green-sensitive layer are arranged in this order from the side of the support. In this invention, emulsion layers sensitive to the same color can be each formed of two or more layers having different sensitivities, to have an increased sensitivity. Further, three emulsion layers can be combined, thereby forming a layer having an improved graininess. Moreover, a non-light-sensitive layer can be interposed between any two adjacent emulsion layers sensitive to the same color. Still further, an emulsion layer sensitive to a color can be interposed between any adjacent emulsion layers sensitive to another color. Furthermore, a reflection layer containing fine silver halide grains can be provided below a high-sensitive layer, particularly, a layer highly sensitive to blue, thereby to improve the photographic properties of the photographic light-sensitive material.

Generally, a red-sensitive emulsion layer, a grteen-sensitive emulsion layer, and a blue-sensitive emulsion layer contain a cyan-forming coupler, a magenta-forming coupler, and a yellow-forming coupler, respectively. Nevertheless, different combinations of emulsion layers can be formed in the present invention. For example, infrared-sensitive layers can be combined into a light-sensitive material for use in pseudo-color photography and semiconductor laser-beam exposure.

Various color couplers can be used in the photographic light-sensitive material according to the present invention. Examples of the color couplers are disclosed in the patents set forth in Research Disclosure No. 17643, VII-C to VII-G, and are listed in the following table:

Additives	RD No.17643	RD No.18716
1. Chemical sensitizers	page 23	page 648, right column
2. Sensitivity increasing agents		do.
3. Spectral sensitizers, supersensitizers	pages 23-24	page 648, right column to page 649, right column
4. Brighteners	page 24	
5. Antifoggants and stabillzers	pages 24-25	page 649, right column
6. Light Absorbent, filter dye, 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 stabilizer	page 25	
9. Hardening agents	page 26	page 651, left column
10. Binder	page 26	do.

Additives	RD No.17643	RD No.18716
11. Plasticizers, lubricants	page 27	page 650, right column
12. Coating aids, surface active agents	pages 26-27	do.
13. Antistatic agents	page 27	do.

In order to prevent degradation in photographic properties, which may otherwise be caused by formaldehyde gas, a compound which can react with, and can set, formaldehyde described in U.S. Patent 4,411,987 or 4,435,503, is preferably added to the light-sensitive material.

It is desirable that the photographic emulsion of this invention be used in color light-sensitive materials. Various color couplers can be used. Specific examples are disclosed in the patents set forth in the above-mentioned Research Disclosure No. 17643, VII-C to VII-G.

Preferred examples of a yellow coupler are described in, e.g., U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961 JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, and 4,511,649, and EP 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone and pyrazoloazole compounds, and more preferably, those compounds described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, and 4,556,630, and WO (PCT) 88/04795.

Examples of a cyan coupler are phenol and naphthol couplers, and preferably, those described in, e.g., U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, EPs 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658.

Typical examples of a polymerized dye-forming coupler are described in U.S. patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, and British Patent 2,102,173, and EP 341,188A.

Preferable examples of a colored coupler for correcting unnecessary absorption of a colored dye are those described in Research Disclosure No. 17643, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368. It is advisable to use a coupler disclosed in U.S. Patent 4,774, 181 which releases a fluorescent dye at the time of coupling, the fluorescent dye correcting unnecessary absorption of a colored dye, or a coupler disclosed in U.S. Patent 4,777,120 which contains, as a releasing group, a dye-precursor group able to react with the developing agent to form a dye.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,570, and West German Patent Application (OLS) No. 3,234,533.

Typical examples of polymerized dye-forming couplers are disclosed in, for example, U.S. Patents 3,451,820, 4,080,211, 4,367,288, 4,409,320 and 4,576,910, and British Patent 2,102,137.

Couplers releasing a photographically useful residue group on coupling can also be preferably used in the present invention. DIR couplers which releases a development inhibitor are preferably those described in the patents cited in the above-mentioned Research Disclosure No. 17643, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, and JP-A-63-37346, and U.S. Patents 4,248,962 and 4,782,012.

Couplers, which are particularly preferable for use in the present invention, are such bleaching accelerator releasing couplers as described in JP-B-61-201247 or Research Disclosure No. 11449 (October 1973). These are preferably used in the red-sensitive silver halide emulsion layer located near the support, and can release β-mercapto propionic acid from the releasing group of phenol-type or, more preferably, naphthol-type coupler residual. These couplers serve to prevent insufficient desilverization which may take place when the light-sensitive material of the invention, containing a tabular-grain emulsion, is subjected to high-speed development.

Examples of a coupler which can be used in the light-sensitive material of the present invention are competing couplers described in, for example, U.S. Patent 4,130,427; poly-equivalent coupler disclosed in, for example, U.S. Patents 4,283,427, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler leasing redox compound, or a DIR redox relasing redox compound, described in, for example, JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which turns to a colored form after being released, disclosed in EPs 173,302A and 313,308A; bleaching accelerator releasing couplers described in, for example, RD. No. 24241; a ligand releasing coupler disclosed in, for example, U.S. Patent 4,553,477; a leuco dye releasing coupler disclosed in JP-A-63-75747; and a fluorescent dye releasing coupler disclosed in U.S. Patent 4,774,181.

It is desirable that the color light-sensitive material of the invention contain various antiseptic or antifungal agents, such as 1,2-benzisochiazoline-3-one, n-butyl-p-hydroxybenzoate, phenol, 4-chlor-3, 5-dimethylphenol, 2-phenoxylethanol, 2-(4-thiazolyl) benzoimidazole.

Examples of a support suitable for use in this invention are described in the above-mentioned RD. No. 17643, page 28 and ibid., No. 18716, page 647, right column to page 648, left column.

The hydrophilic colloid layers in the color photographic light-sensitive material according to the invention preferably have a total thickness of 28 μm or less, more preferably 23 μm or less, most preferably 20 μm or less. It is preferred that the hydrophilic colloid layers has a swelling speed $T_{1/2}$ of 30 seconds or less, preferably 20 seconds or less. The thickness of the colloid layers is one measured after these layers had been left to stand for two days at 25 °C at relative humidity of 55%. The swelling speed $T_{1/2}$ can be measured by the techniques known in the art, by means of, for example, a swellometer of the type which A. Green et al. describe in Photographic Science and Engineering, Vol. 19, No. 2, pp. 124-129. The swelling speed $T_{1/2}$ is the period of time which a colloid layer requires to swell to half the saturated thickness, i.e., 90% of the maximum swollen thickness when it is immersed in a color developing liquid at 30 °C for 3 minutes and 15 seconds.

The swelling speed $T_{1/2}$ can be adjusted by adding a proper amount of a hardening agent to gelatin which is used as a binder, or by changing the conditions under which each colloid layer is allowed to age after it has been coated. It is desirable that each hydrophilic colloid layer be swollen to a swelling ratio of 150 to 400%, said swelling ratio calculated as follows:

$$(Tmax - T)/T$$

where T is the thickness of the colloid layer mentioned above, and Tmax is the maximum swollen thickness the layer can have when treated under the above-mentioned conditions.

The color photographic light-sensitive materials of the present invention can be developed by the ordinary processes as described, for example, in the above-described Research Disclosure, No. 17643, pages 28 and 29 and ibid., No. 18716, page 651, left to right columns.

In order to perform reversal development, black-and-white development is carried out, and then color development is effected. 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 combination.

The 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 determined over a broad range in accordance with the properties of the light-sensitive material (e.g., a property determined by the substances used such as couplers), 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).

According to the above-described multi-stage counter-current scheme, 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 the produced floating substances may be undesirably 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, "Chemistry of Anti-bacterial and Antifungal Agents", 1986, published by Sankyo Shuppan, Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", 1982, published by Kogyo Gijutsukai, and Nippon Bokin Bobabi 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 photosensitive material of the present invention can be processed directly by a stabilizer 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 process.

Satabilization is performed in some cases, after the water-washing, in, for example, a formalin bath which is used as final bath of the color photographic light-sensitive materials.

EXAMPLE 1

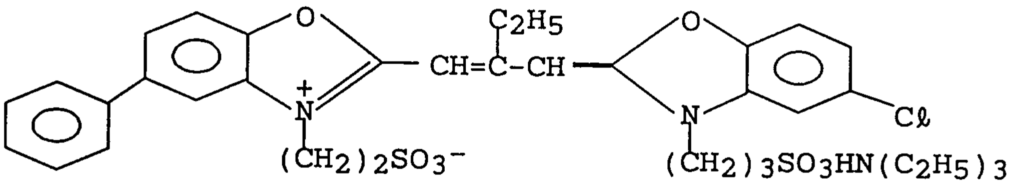
Preparation of Emulsion E

One liter (1000 mℓ) of aqueous solution containing 10.5 g of gelatin and 3.0 g of KBr was stirred at 60° C. An aqueous solution of silver nitrate ($AgNO_3$, 8.2 g), and an aqueous solution of halides (KBr, 5.7 g; KI, 0.35 g) were added to the aqueous solution thus stirred, over a period of 1 minutes by double jet method. Further, 21.5 g of gelatin was added to the resultant solution, and the solution was heated to 75° C. Thereafter, an aqueous solution of silver nitrate ($AgNO_3$, 136.3 g) and an aqueous solution of halides (KBr and 4.2 mol% of KI based on KBr) were added to the heated solution, over a period of 51 minutes by the double jet method, thus accelerating the flow of the additive solutions. In this process, the silver potential was maintained at 0 mV with respect to the saturated calomel electrode for first 46 minutes, and was changed to 90 mV thereafter. The solution was cooled to 40° C. Then, an aqueous silver nitrate solution ($AgNO_3$, 3.2 g) and a KI aqueous solution (KI, 2.3 g) were added to the cooled solution, over a period of 5 minutes by the double jet method. Further, an aqueous silver nitrate solution ($AgNO_3$, 25.4 g) and a KI aqueous solution were added to the solution, over a period of 5.35 minutes by the double jet method, while maintaining the silver potential at -50 mV with respect to the saturated calomel electrode, thereby preparing an emulsion. The emulsion was desalted and added with gelatin. Then, the emulsion was processed, adjusting its pH value and pAg value to 5.5 and 8.8, respectively. This emulsion (hereinafter referred to as "emulsion E") contained tabular grains having an average sphere-equivalent diameter of 1.21 μm, an average thickness of 0.197 μm, an average aspect ratio of 6.14, and a variation coefficient in circule equivalent diameter of 17%.

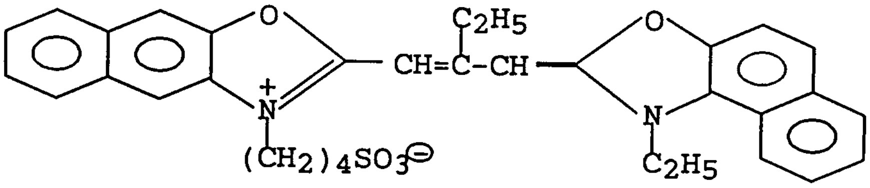
Emulsion E was subjected gold-sulfur sensitization in the following way. First, emulsion E was heated to 64° C. Next, three sensitizing dyes, Dye-1, Dye-2, and Dye-3, identified by the following formulas, were added to heated emulsion E, in an amount of 4.7×10^{-4} mol/mol Ag, in an amount of 1.4×10^{-4} mol/mol

Ag, and in an amount of 2.0 × 10^{-4} mol/mol Ag, respectively.

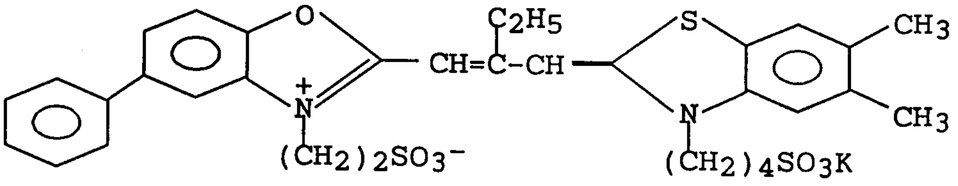
Dye-1



Dye-2

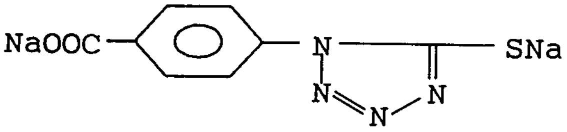


Dye-3



Then, the antifoggant idenfified by the following formula was added to emulsion E in an amount of 5 × 10^{-5} mol/mol Ag. Also, sodium thiosulfate, chloroaulate, and potassium thiocyanate are sequentially added to the emulsion E in an amount of 8.0 × 10^{-6} mol/mol Ag, an an amount of 1.0 × 10^{-5} mol/mol Ag, and in an amount of 3.0 × 10^{-3} mol/mol Ag. Emulsion E was thereby chemically sensitized appropriately. (The phrase "sensitized appropriately" means that the emulsion is chemically sensitized such that it will exhibit the highest possible photosensitivity when exposed to light for 1/100 second.) The emulsion, thus chemically sensitized, shall be called "emulsion E-1" hereinafter.

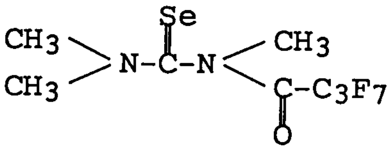
(Antifoggant)



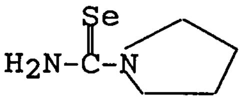
Further, emulsion E was subjected gold-sulfurselenium sensitization in the following way. First, emulsion E was heated to 64 °C. Next, the sensitizing dyes, Dye-1, Dye-2, and Dye-3 were added to heated emulsion E, in an amount of 4.7 × 10^{-4} mol/mol Ag, in an amount of 1.4 × 10^{-4} mol/mol Ag, and in an amount of 2.0 × 10^{-4} mol/mol Ag, respectively. Then, the above-identified antifoggant was added to emulsion E in an amount of 1 × 10^{-4} mol/mol Ag. Also, sodium thiosulfate, chloroaulate, potassium thiocyanate, and N,N-dimethylselenourea are sequentially added to the emulsion E in an amount of 6.4 × 10^{-6} mol/mol Ag, an an amount of 1.3 × 10^{-5} mol/mol Ag, in an amount of 3.0 × 10^{-3} mol/mol Ag, and in an amount of 1.6 × 10^{-6}

mol/mol Ag, respectively. Emulsion E was thereby chemically sensitized appropriately, fomring emulsion E-2.

Still further, emulsion E was subjected gold-sulfur-selenium sensitization in the same way as described in the preceding paragraph, except that the below-identified selenium sensitizing agent was used in place of N,N-dimethylselenourea, thereby preparing emulsion E-3.



Moreover, emulsion E was subjected gold-sulfur-selenium sensitization in the same way as in the first-described gold-sulfur-selenium sensitization, except that the below-identified sensitizing agent was used in place of N,N-dimethylselenourea, thereby preparing emulsion



E-4.

Layers having the compositions specified below were coated, one upon another, on undercoated, celluose triacetate film supports, thereby forming samples 101 to 104 of a multi-layer color light-sensitive material. Emulsion E-1 was used in sample 101; emulsion E-2 was used in sample 102; emulsion E-3 was used in sample 103; and emulsion E-4 was used in sample 104.

Compositions of Layers:

The amounts coated are represented in units of g/m^2. The amount of silver halide coated is specified in terms of the amount of silver used per square meter. The amounts of sensitizing dyes coated are specified in terms of the number of mols per mol of silver halide used in the same layer.

Samples 101 to 104

Layer 1: Antihalation Layer	
Black Colloidal Silver	Silver 0.18
Gelatin	1.40

Layer 2: Interlayer	
2,5-di-t-pentadecylhydroquinone	0.18
EX-1	0.070
EX-3	0.020
EX-12	2.0×10^{3}
U-1	0.060
U-2	0.080
U-3	0.10
HBS-1	0.10
HBS-2	1.020
Gelatin	1.04

Layer 3: 1st Red-Sensitive Emulsion Layer	
Emulsion A	Silver 0.25
Emulsion B	Silver 0.25
Sensitizing Dye-I	6.9×10^{-5}
Sensitizing Dye-II	1.8×10^{-5}
Sensitizing Dye-III	3.1×10^{-4}
EX-2	0.34
EX-10	0.020
U-1	0.070
U-2	0.050
U-3	0.070
HBS-1	0.060
Gelatin	0.87

Layer 4: 2nd Red-Sensitive Emulsion Layer	
Emulsion G	Silver 1.0
Sensitizing Dye-I	5.1×10^{-5}
Sensitizing Dye-II	1.4×10^{-5}
Sensitizing Dye-III	2.3×10^{-4}
EX-2	0.40
EX-3	0.050
EX-10	0.015
U-1	0.070
U-2	0.050
U-3	0.070
Gelatin	1.30

Layer 5: 3rd Red-Sensitive Emulsion Layer	
Emulsion D	Silver 1.60
Sensitizing Dye-I	5.4×10^{-5}
Sensitizing Dye-II	1.4×10^{-5}
Sensitizing Dye-III	2.4×10^{-4}
EX-2	0.097
EX-3	0.010
EX-4	0.080
HBS-1	0.035
HBS-2	0.015
Gelatin	1.63

Layer 6: Interlayer	
EX-5	0.040
HBS-1	0.020
Gelatin	0.80

Layer 7: 1st Green-Sensitive Emulsion Layer	
Emulsion A	Silver 0.15
Emulsion B	Silver 0.15
Sensitizing Dye-IV	3.0×10^{-5}
Sensitizing Dye-V	1.0×10^{-5}
Sensitizing Dye-VI	3.8×10^{-4}
EX-1	0.021
EX-6	0.26
EX-7	0.030
EX-8	0.025
HBS-1	0.10
HBS-3	0.010
Gelatin	0.63

Layer 8: 2nd Green-Sensitive Emulsion Layer	
Emulsion C	Silver 0.45
Sensitizing Dye-IV	2.1×10^{-5}
Sensitizing Dye-V	7.0×10^{-5}
Sensitizing Dye-VI	2.6×10^{-4}
EX-6	0.094
EX-7	0.026
EX-8	0.018
HBS-1	0.16
HBS-3	0.8×10^{-3}
Gelatin	0.50

Layer 9: 3nd Green-Sensitive Emulsion Layer	
Emulsion E-1, E-2 or E-3	Silver 1.20
Sensitizing Dye-1	4.7×10^{-4}
Sensitizing Dye-2	1.4×10^{-4}
Sensitizing Dye-3	2.0×10^{-4}
EX-1	0.025
Ex-11	0.10
EX-13	0.015
Compound I-9 in Table A	2.7×10^{-5}
HBS-1	0.25
HBS-2	0.10
Gelatin	1.54

Layer 10: Yellow Filter Layer	
Yellow Colloidal Silver	Silver 0.05
EX-5	0.080
HBS-1	0.030
Gelatin	0.95

Layer 11: 1st Blue-Sensitive Emulsion layer	
Emulsion A	Silver 0.080
Emulsion B	Silver 0.070
Emulsion F	Silver 0.070
Sensitizing Dye-VII	3.5×10^{-4}
EX-8	0.042
EX-9	0.72
HBS-1	0.28
Gelatin	1.10

Layer 12: 2nd Blue-Sensitive Emulsion Layer	
Emulsion G	Silver 0.45
Sensitizing Dye-VII	2.1×10^{-4}
EX-9	0.15
EX-10	7.0×10^{-3}
HBS-1	0.050
Gelatin	0.78

Layer 13: 3rd Blue-Sensitive Emulsion Layer	
Emulsion H	Silver 0.77
Sensitizing Dye-VII	2.2×10^{-4}
EX-9	0.20
HBS-1	0.070
Gelatin	0.69

Layer 14: 1st Protective Layer	
Emulsion I	Silver 0.20
U-4	0.11
U-5	0.17
HBS-1	5.0×10^{-2}
Gelatin	1.00

Layer 15: 2nd Protective Layer	
H-1	0.40
B-1 (diameter: about 1.7 µm)	5.0×10^{-2}
B-2 (diameter: about 1.7 µm)	0.10
B-3	0.10
S-1	0.20
Gelatin	1.20

All layers mentioned above contained W-1, W-2, W-3, B-4, B-5, F-1, F-2, F-3, F-4, F-5, F-6, F-8, F-9, F-10, F-11, F-12, F-13, iron salt, lead salt, gold salt, platinum salt, iridium salt, and rhodium salt, so that they may have improved storage stability, pressure-resistance, antifugal property, antibacterial property, anti-charging property and coating property.

The particulars of emulsions A to I are shown in the following table, and the compounds specified above are identified in Table C, by their names or their structural formulas.

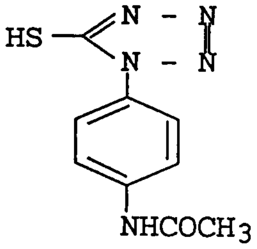
Emulsion	Mean AgI Content (%)	Average Grain Diameter (µm)	Variation Coefficient of the Diameter(%)	Diameter/thickness	Silver Content (AgI Content (%))
A	4.0	0.45	27	1	Core/Shell = 1/3(13/1), Double-Structure Grains
B	8.9	0.70	14	1	Core/Shell = 3/7(25/2), Double-Structure Grains
C	10	0.75	30	2	Core/Shell = 1/2(24/3), Double-Structure Grains
D	16	1.05	35	2	Core/Shell = 4/6(40/0), Double-Structure Grains
F	4.0	0.25	28	1	Core/Shell = 1/3(13/1), Double-Structure Grains
G	14.0	0.75	25	2	Core/Shell = 1/2(42/0), Double-Structure Grains
H	14.5	1.30	25	3	Core/Shell = 37/63(34/3), Double-Structure Grains
I	1	0.07	15	1	Spherical Grains

Preparation of Sample 105

Sample 105 was prepared which was identical to sample 103, except that layer 9 did not contained compound I-9.

Preparation of Sample 106

Sample 106 was prepared which was identical to sample 103, except that the below-identified compound was used in layer 9, in equimolar amount, instead of compound I-9.



Preparation of Sample 107

Sample 107 was prepared which was identical to sample 103, except that compound I-17 shown in Table A was used in layer 9, in equimolar amount, instead of compound I-9.

Samples 101 to 107, thus obtained, were left to stand for 14 hours at 40 ° C at reltive humidity of 70%. Thereafter, they were exposed to white light for 1/100 second, using a wedge. Samples 101 to 107, thus exposed, were developed by the method specified below, and subjected to density measuring. The results were as is shown in Table 2.

Method

Process	Time	Temp.	Quantity Replenished*	Tank Vol.
Clor Development	2 min.45 sec.	38	33 ml	20L
Bleaching	6 min.30 sec.	38	25 ml	40L
Washing	2 min.10 sec.	24	1200 ml	20L
Fixing	4 min.20 sec.	38	25 ml	30L
Washing 1	1 min.05 sec.	24	**	10L
Washing 2	1 min.00 sec.	24	1200 ml	10L
Stabilization	1 min.05 sec.	38	25 ml	10L
Drying	4 min.20 sec.	55	--	--

Note*: Quantity per meter of a 35 mm-wide sample.

Note**: A counnter-flow from stage 2 to stage 1.

The compositions of the process solutions used were as follows:

Color Developing Solution		
	Mother Solution	Replenisher
Diethylenetriaminepentaacetic acid	1.0 g	1.1 g
1-hydroxyethylidene-1,1-diphosphonic Acid	3.0 g	3.2 g
Sodium Sulfite	4.0 g	4.4 g
Potassium Carbonate	30.0 g	37.0 g
Potassium Bromide	1.4 g	0.7
Potassium Iodide	1.5 mg	--
Hydroxylamine Sulfate	2.4 g	2.8 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylalinine Sulfate	4.5 g	5.5 g
Water to make	1.0 L	1.0 L
pH	10.05 g	10.10 g

Bleaching Solution		
	Mother Solution	Replenisher
Sodium Iron (III) Eithylenediaminetetraacetate (Trihydrate)	10.0 g	120.0 g
Disodium Ethylenediaminetetraacetate	10.0 g	11.0 g
Ammonium Bromide	140.0 g	160.0 g
Ammonium Nitrate	30.0 g	35.0 g
Ammonia Water	6.5 mg	4.0 mg
Water to make	1.0 L	4.0 L
pH	6.0	5.7

Fixing Solution

	Mother Solution	Replenisher
Sodium Ethylenediaminetetraacetate	0.5 g	0.7 g
Sodium sulfite	7.0 g	8.0 g
Sodium bisulfite	5.0 g	5.5 g
Ammonium Thiosulfate Aqueous Solution (70%)	170 mℓ	200.0 mℓ
Water to make	1.0 L	1.0 L
pH	6.7	6.6

Stabilizing Solution:

Formalin (37%)	2.0 mℓ	3.0 mℓ
Polyoxyehtylene-p-monononylphenylether (average polymerization degree = 10)	0.3 g	0.45 g
Disodium Ethylenediaminetetraacetate	0.05 g	0.08 h
Water to make	1.0 L	1.0 L
pH	5.8-8.0	5.8-8.0

Samples 101 to 107 were subjected to pressure-resistance test in the following manner. The samples were left to stand for at least 3 hours in an atmosphere having relative humidity of 55%. Then, in the same atmosphere, a load of 4 g was applied to each sample with a stylus having a diameter of 0.1 mm, and the stylus was moved at speed of 1 cm/sec, thereby scratching the surface of the emulsion layer. Samples 101 to 107 were develop and subjected to density measuring, which was performed by means of an aperture having a diameter of 25 µm.

The results of the test were as is shown in Table 1.

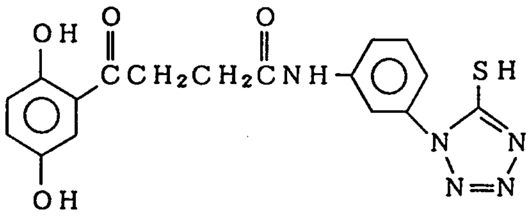
Table 1

	Sensitivity of Green-sensitive Layer	Fogging Density Increased by Scratcking
Sample 101(Comp.Ex.)	100	0.14
Sample 102(Pres.Inv.)	126	0.15
Sample 103(Pres.Inv.)	126	0.13
Sample 104(Pres.Inv.)	126	0.14
Sample 105(Comp.Ex.)	118	0.35
Sample 106(Comp.Ex.)	120	0.38
Sample 107(Pres.Inv.)	126	0.14
Note: The sensitivity is represented in terms of the reciprocal of that exposure amount at which a density is higher by 0.2 than the fogging density of a magenta image.		

As evident from Table 1, the silver halide photosensitive materials according to the present invention had high sensitivity and slight scratch fogging (i.e., an increase in fogging density, resulting from scratching). In view of this, the present invention achieved remarkable advantages.

Table A

I − 1



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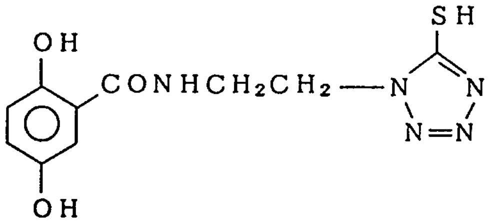
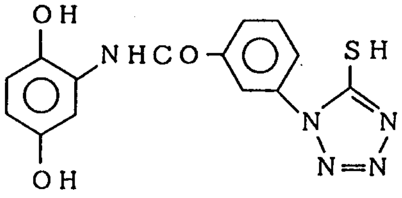
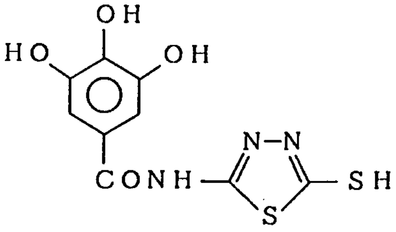


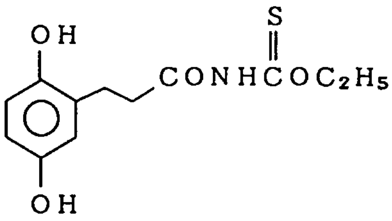
I − 3



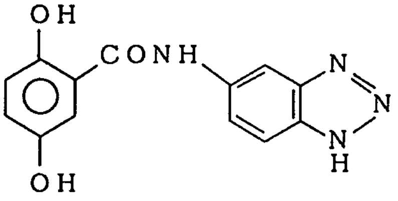
I − 4



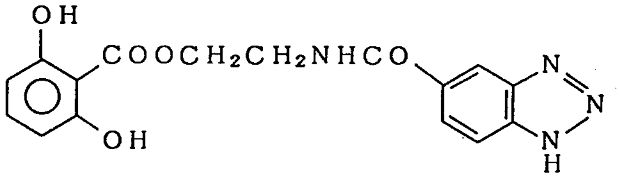
I − 5



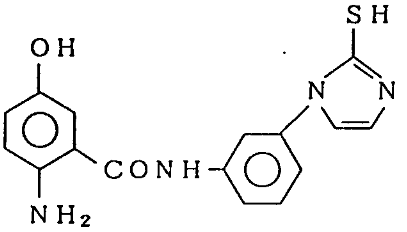
I − 6



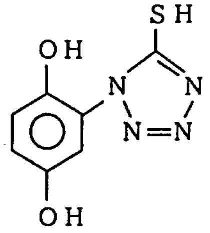
I − 7



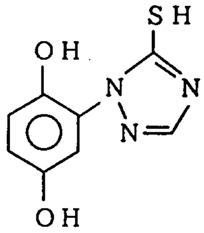
I − 8



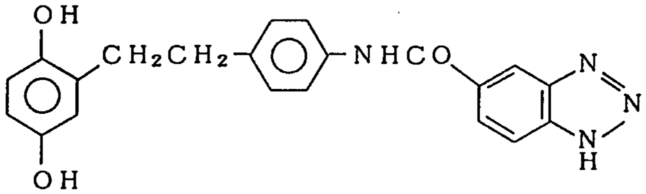
I－9



I－10



I－11



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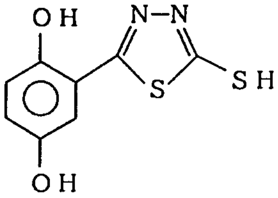
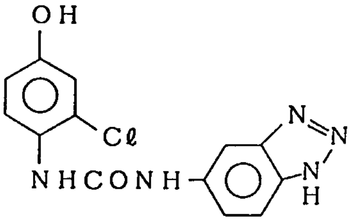
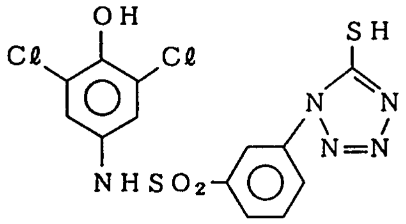


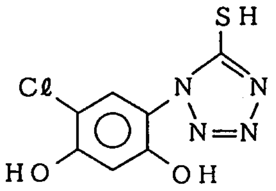
I－13



I－14



I－15



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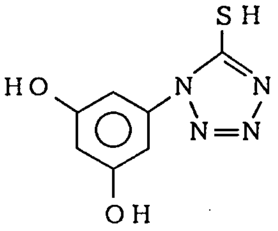

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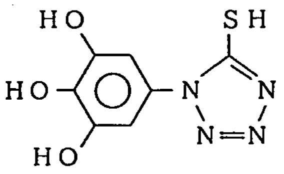

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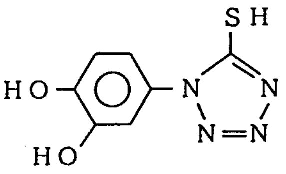

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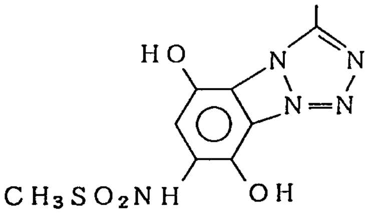
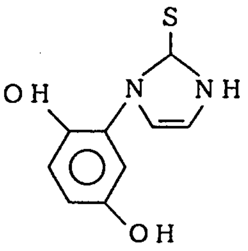
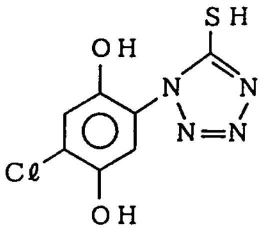


I－20



I－21



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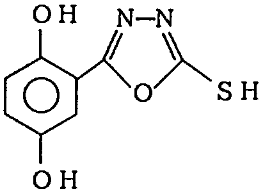

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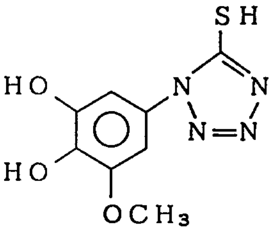

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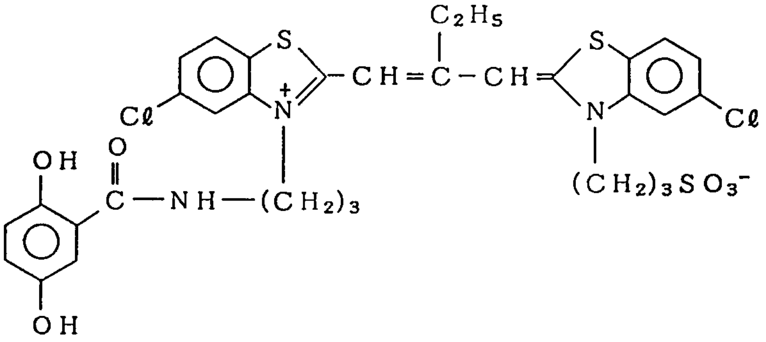
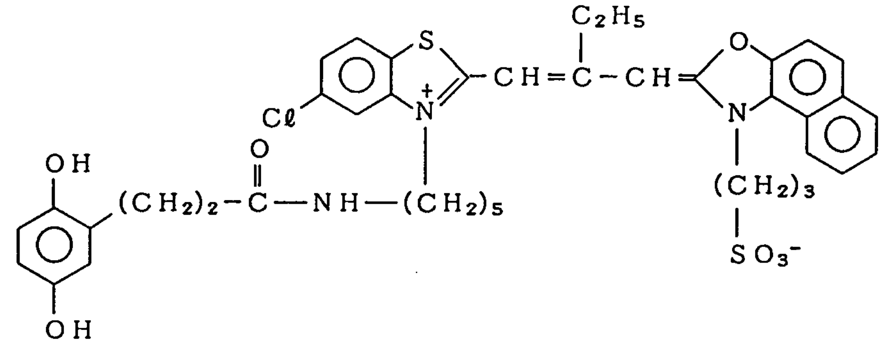
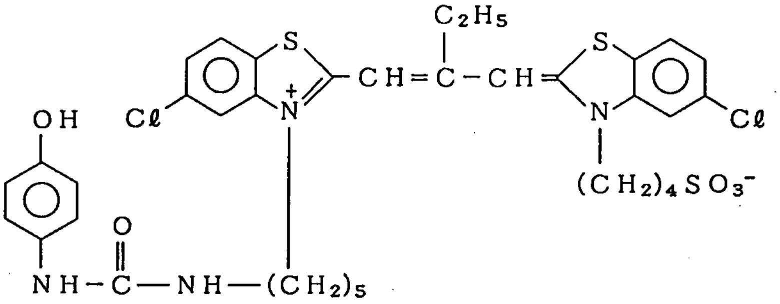


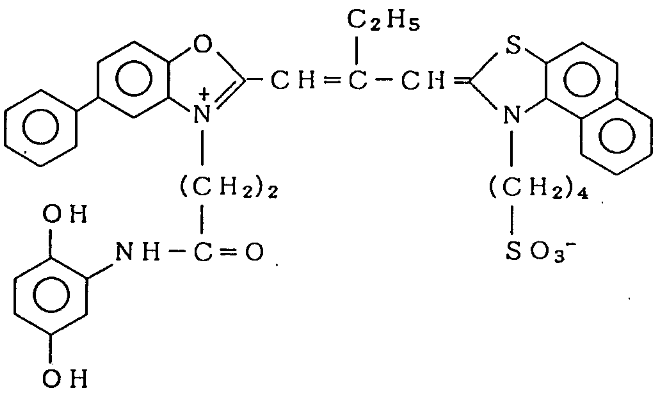
I－25


C2H5
S
O
Cl
N+
N
O
OH
(CH2)2－C—NH—(CH2)5
(CH2)3
SO3-
OH
CH=C－CH

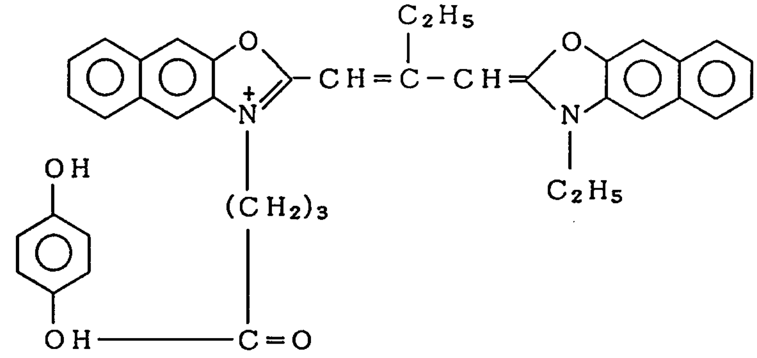
I－26


C2H5
S
S
CH=C－CH
Cl
N+
N
Cl
OH
(CH2)4SO3-
O
NH－C—NH—(CH2)5

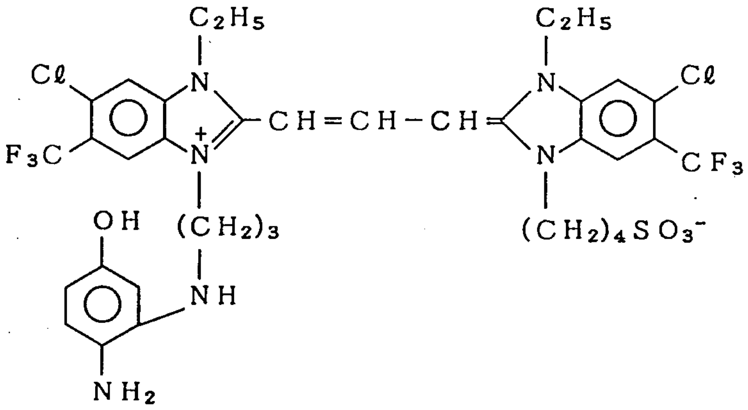
I－27


C2H5
O
S
CH=C－CH
N+
N
(CH2)2
(CH2)4
OH
NH－C=O
SO3-
OH

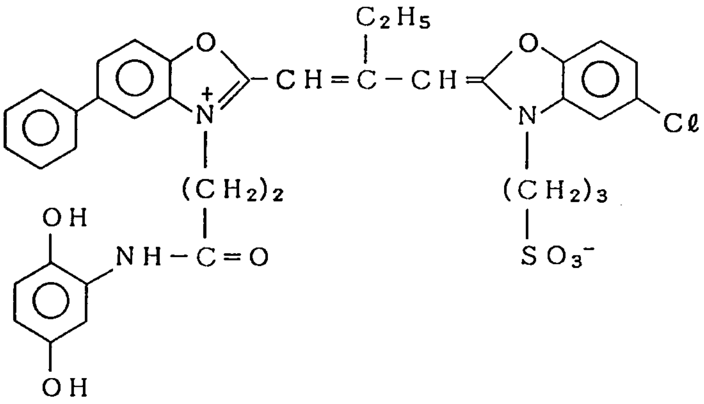
I－28



I－29



I－30



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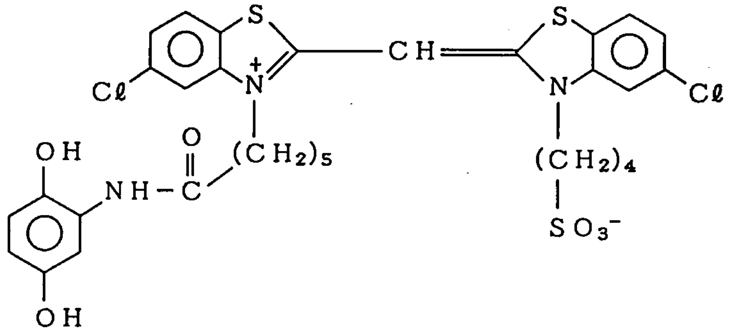
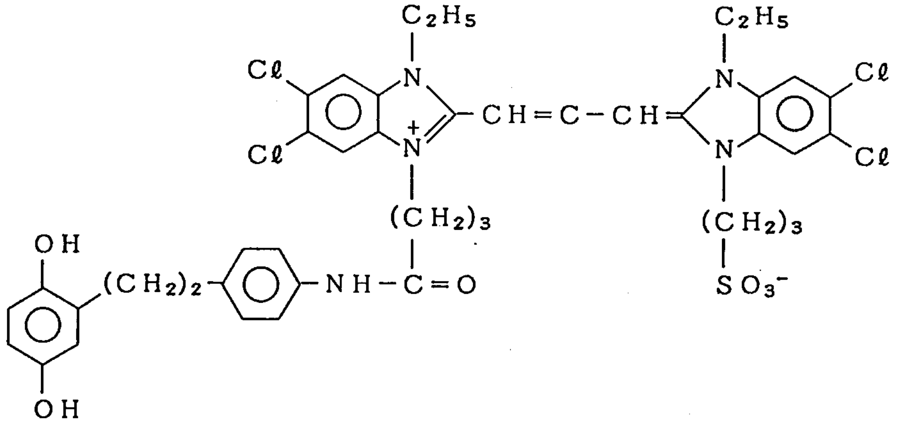
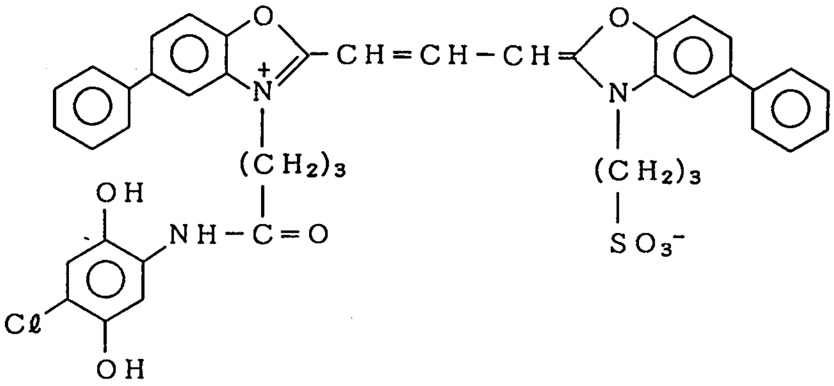


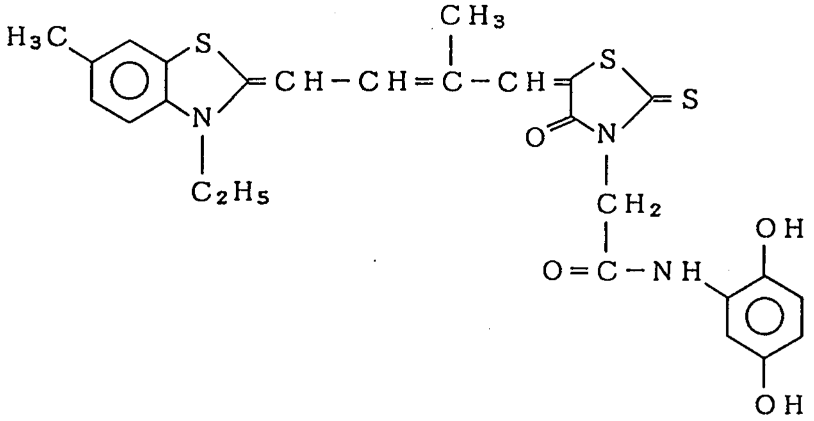
I－32



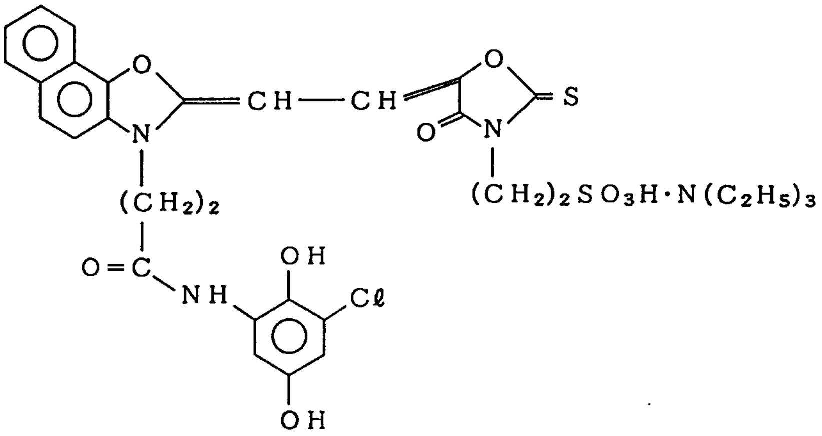
I－33



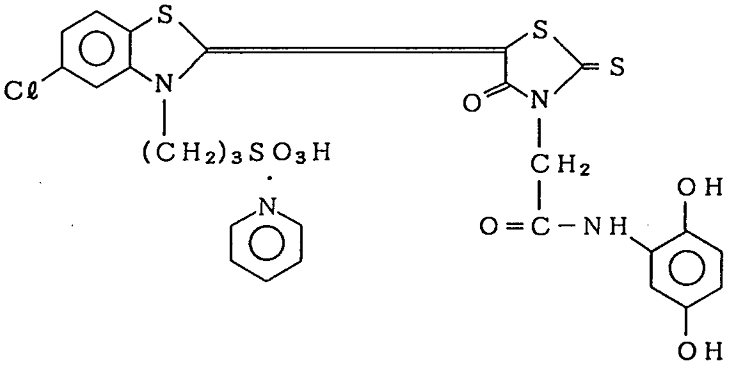
I－34



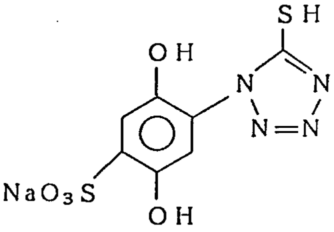
I－35


O
N
CH
CH
O
S
O
N
(CH2)2
(CH2)2SO3H·N(C2H5)3
O=C
NH
OH
Cl
OH

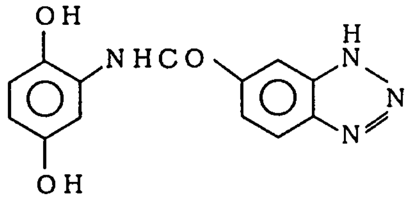
I－36


S
N
Cl
S
S
O
N
(CH2)3SO3H
N
CH2
O=C−NH
OH
OH

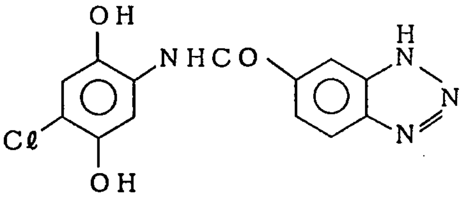
I－37


SH
OH
N
N
N=N
NaO3S
OH

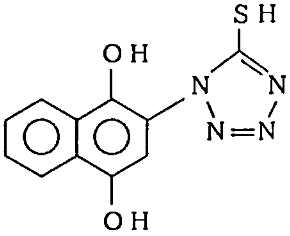
I－38



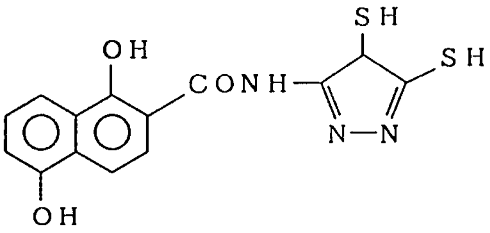
I－39



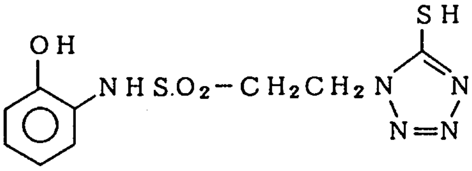
I－40



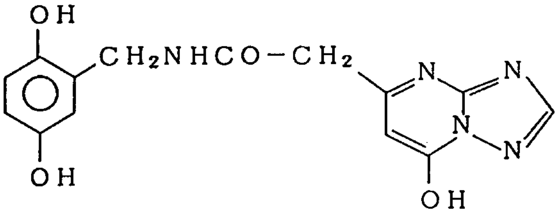
I－41



I－42



I－43



I－44

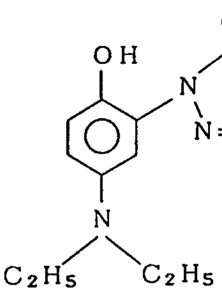
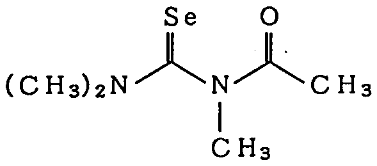
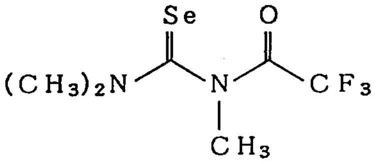


Table B

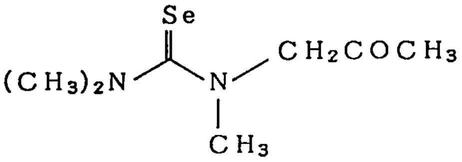
II − 1



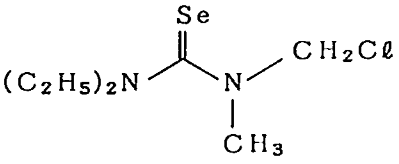
II − 2



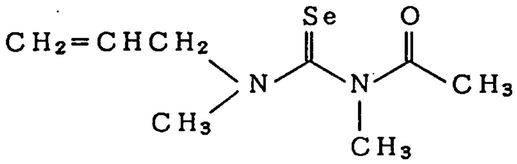
II − 3



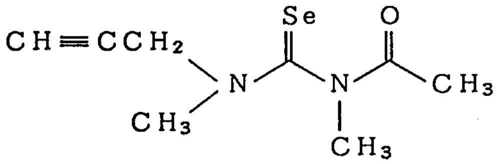
II − 4



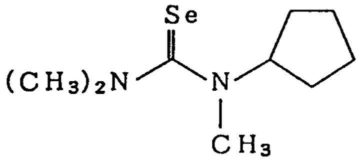
II − 5



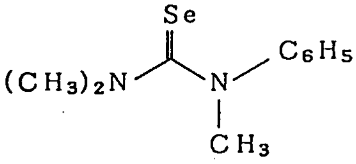
II − 6



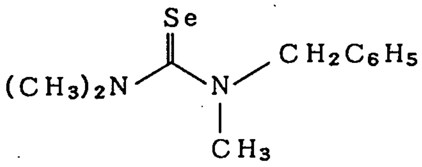
II − 7



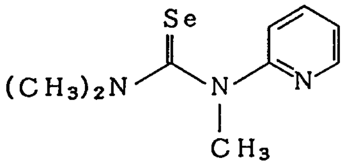
II − 8



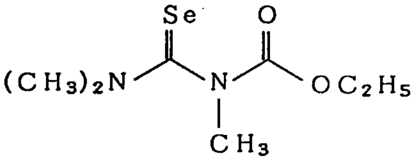
Ⅱ－９



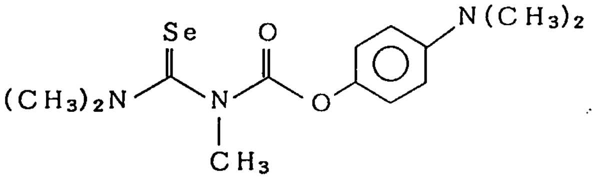
Ⅱ－１０



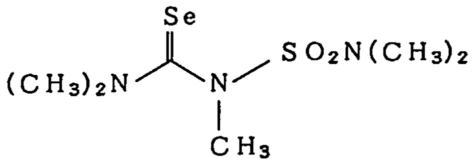
Ⅱ－１１



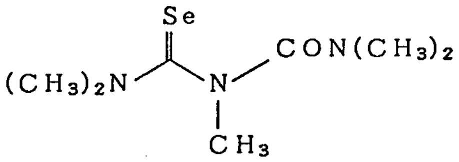
Ⅱ－１２



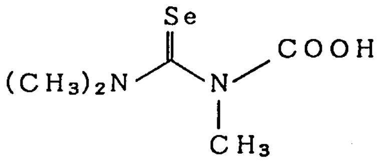
II－13



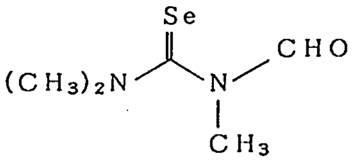
II－14



II－15



II－16



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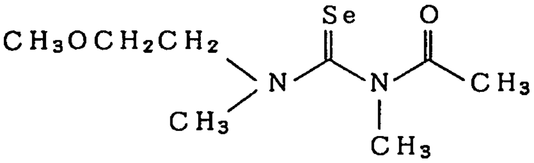
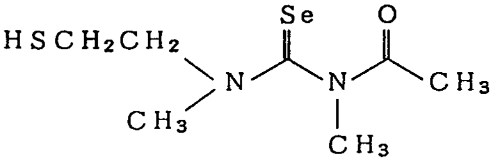
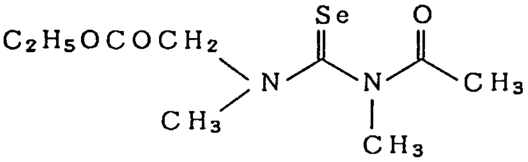


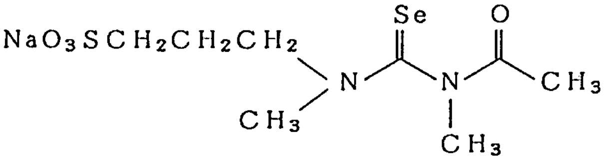
II－１８



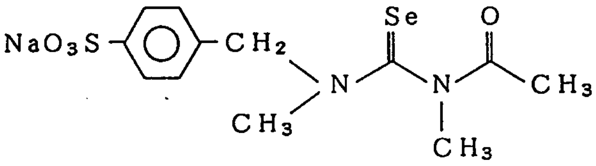
II－１９



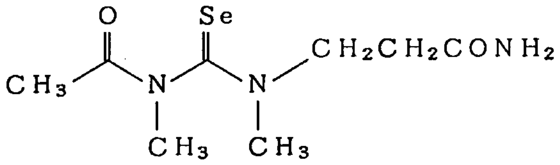
II－２０



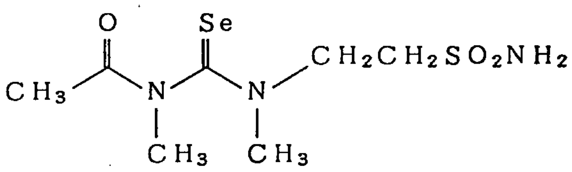
II − 2 1



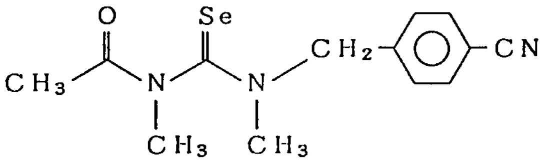
II − 2 2



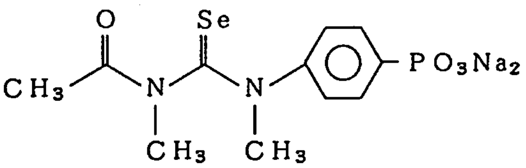
II − 2 3



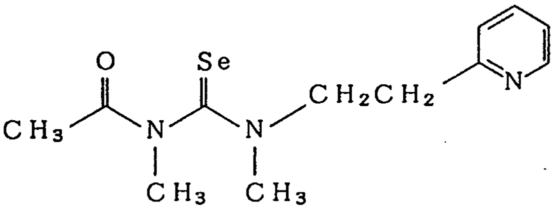
II − 2 4



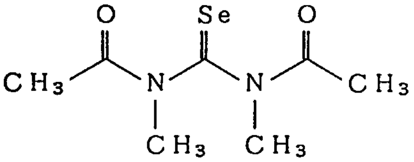
II－25



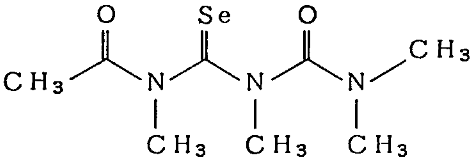
II－26



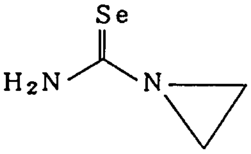
II－27



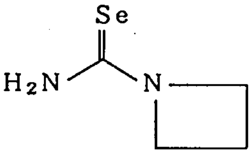
II－28



Ⅲ－1



Ⅲ－2



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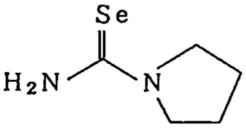
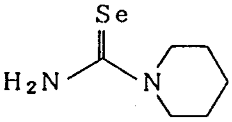
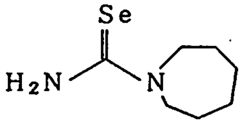


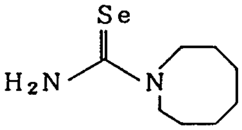
Ⅲ－4



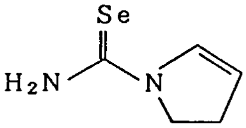
Ⅲ－5



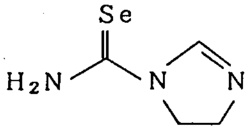
Ⅲ－6



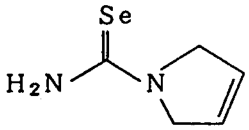
Ⅲ－7



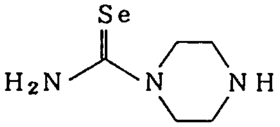
Ⅲ－8



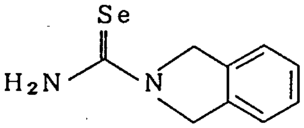
Ⅲ－９



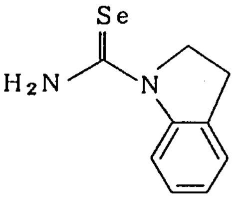
Ⅲ－１０



Ⅲ－１１



Ⅲ－１２



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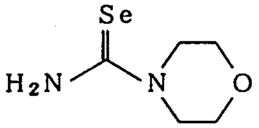
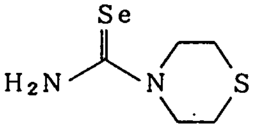
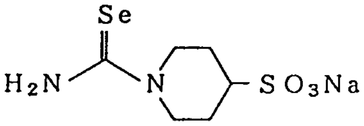


Ⅲ－１４



Ⅲ－１５



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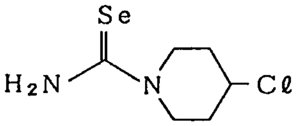
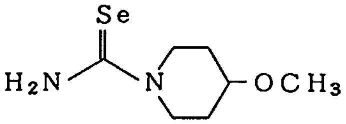


Ⅲ－１７



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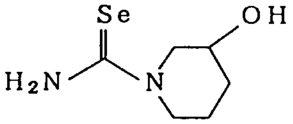
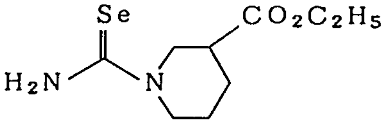
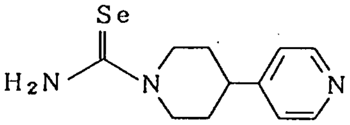


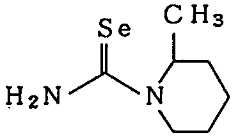
Ⅲ－１９



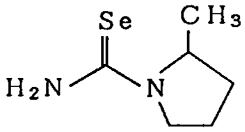
Ⅲ－２０



Ⅲ－２１



Ⅲ－２２



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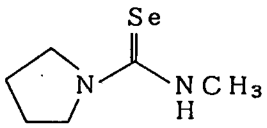

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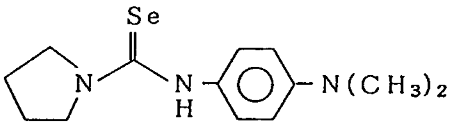

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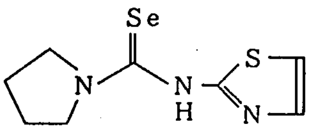

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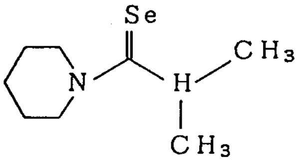

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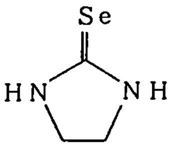

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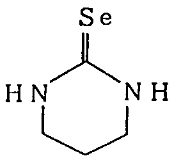

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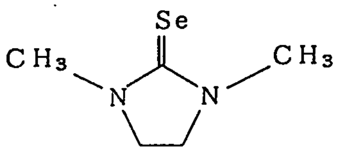

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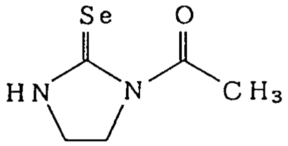

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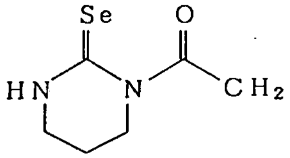

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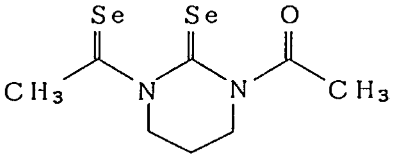

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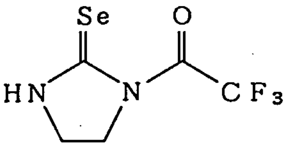
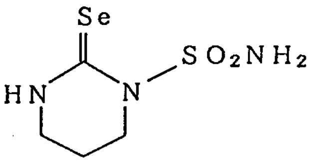


Ⅲ－３４



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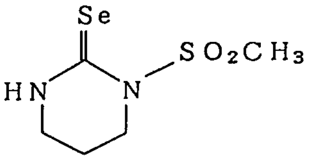

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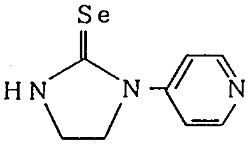
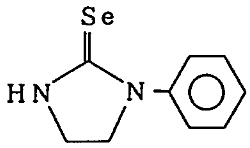


Ⅲ－３７



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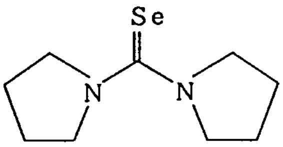
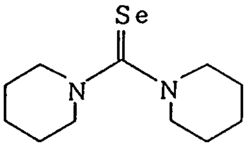
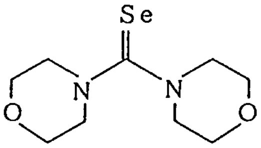


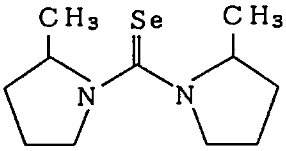
Ⅲ－３９



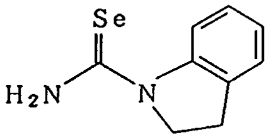
Ⅲ－４０



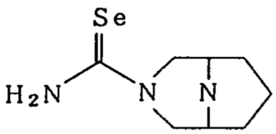
Ⅲ－４１



Ⅲ－４２



Ⅲ－４３



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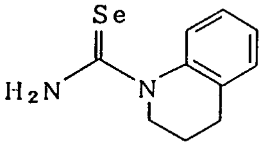

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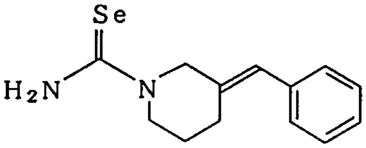

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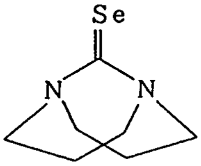

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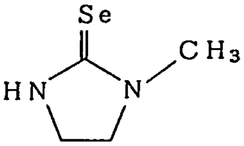
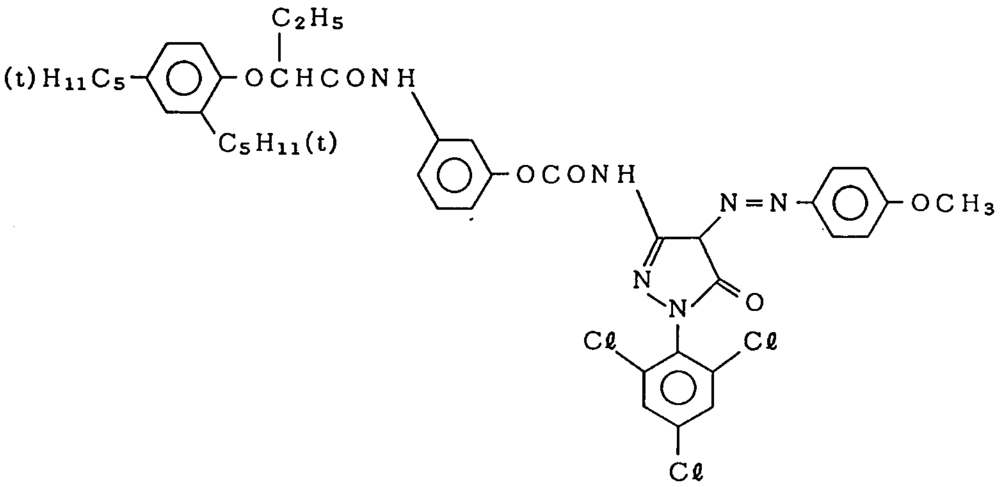
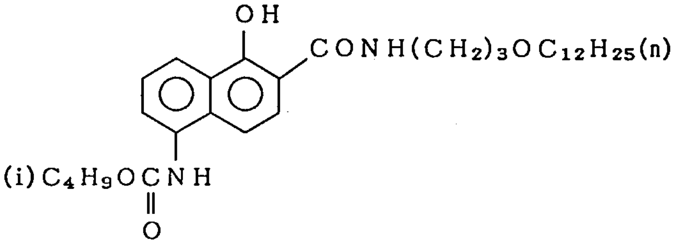


Table C

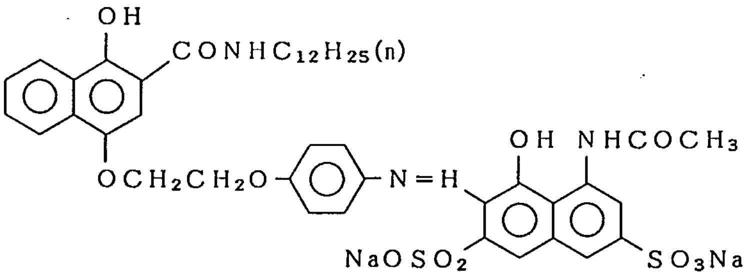
EX-1



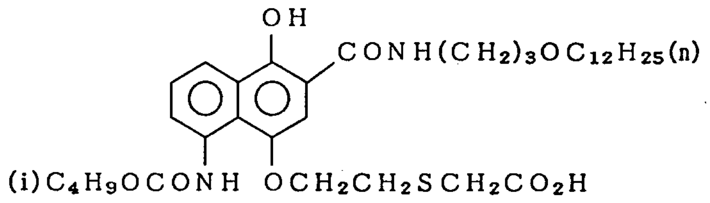
EX-2



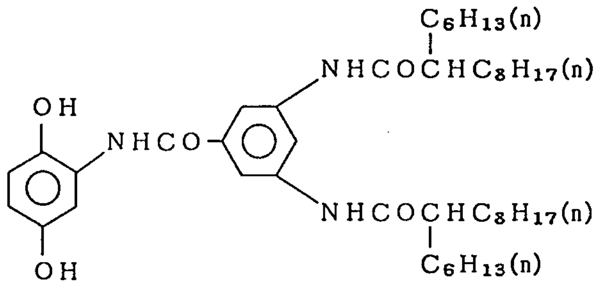
EX-3



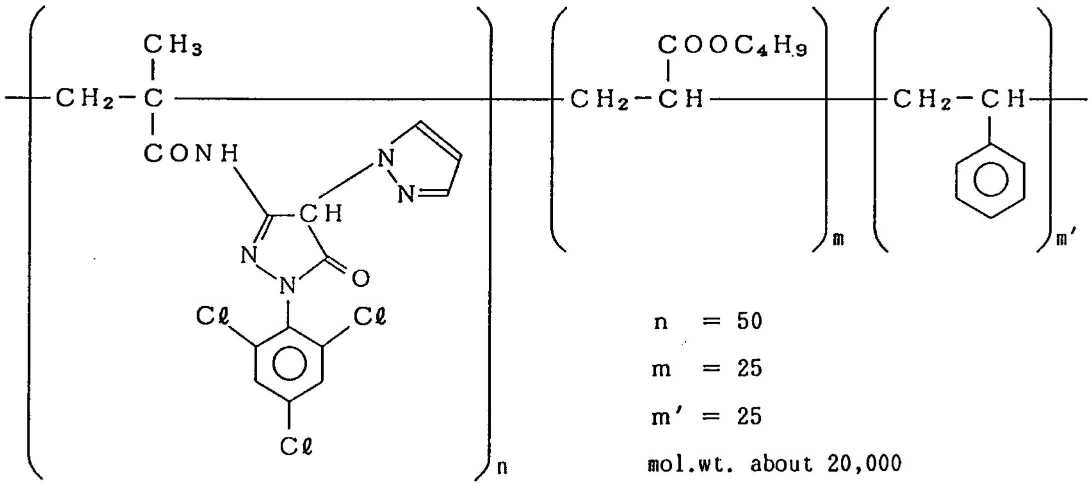
EX-4



EX-5

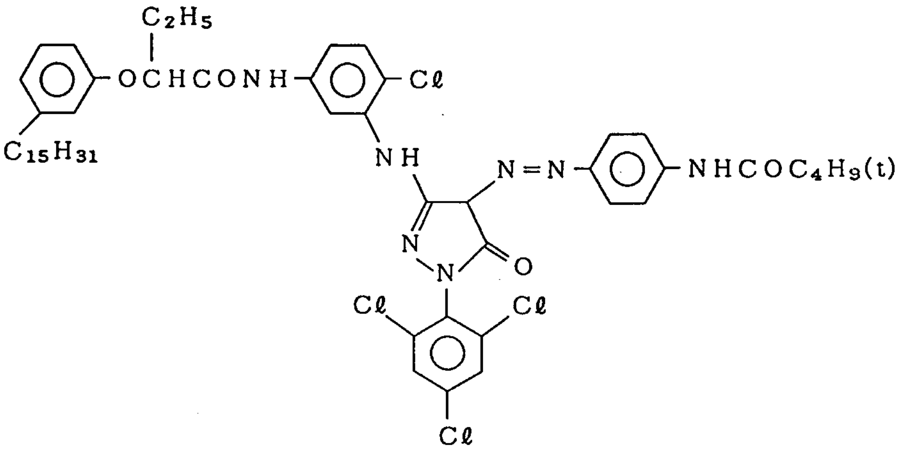


EX-6

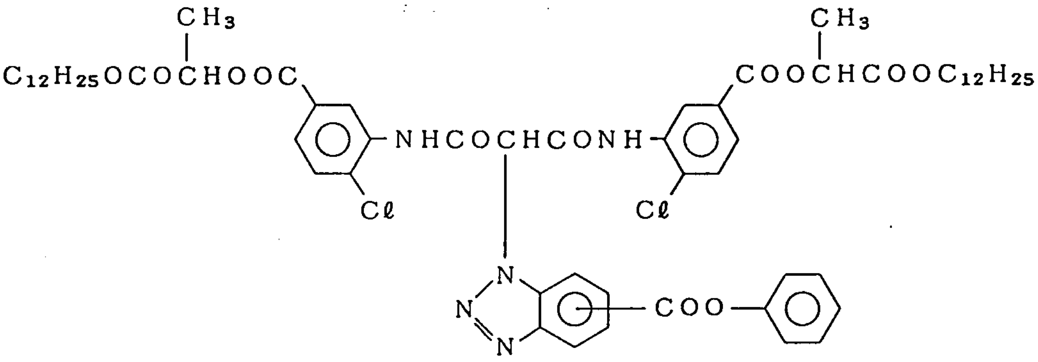


n = 50
m = 25
m' = 25
mol.wt. about 20,000

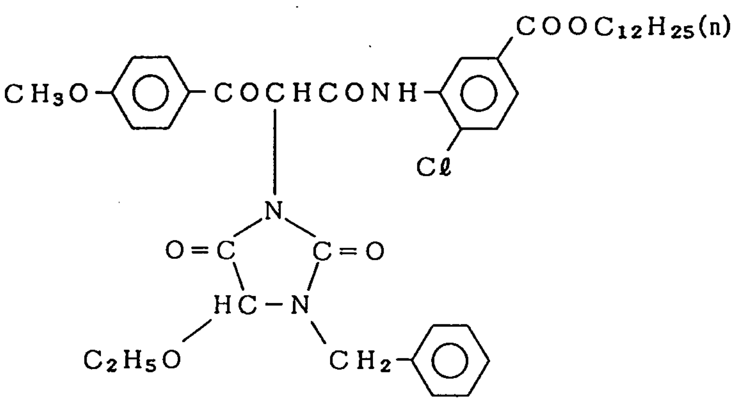
E X − 7


C₂H₅
OCHCONH
Cℓ
C₁₅H₃₁
NH
N=N
NHCOC₄H₉(t)
N
N
O
Cℓ
Cℓ
Cℓ

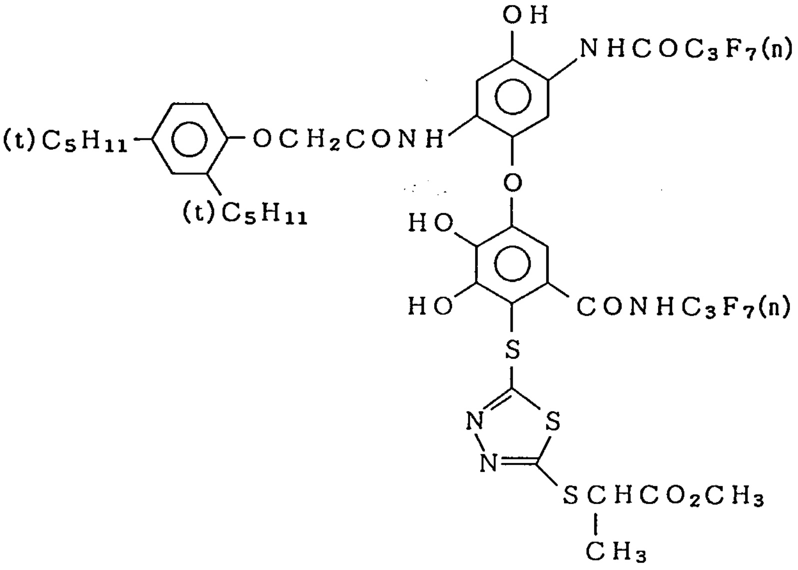
E X − 8


CH₃
C₁₂H₂₅OCOCHOOC
NHCOCHCONH
Cℓ
Cℓ
CH₃
COOCHCOOC₁₂H₂₅
N
N
N
COO

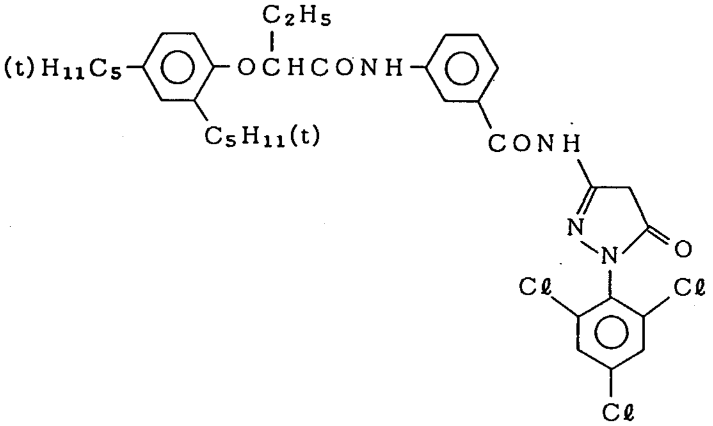
EX−9


COOC12H25(n)
CH3O
COCHCONH
Cℓ
N
O=C
C=O
HC−N
C2H5O
CH2

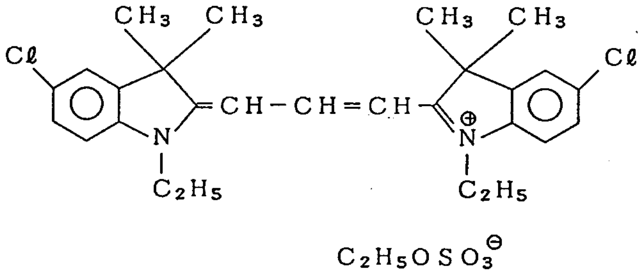
EX−10


OH
NHCOC3F7(n)
(t)C5H11
OCH2CONH
(t)C5H11
O
HO
HO
CONHC3F7(n)
S
N
S
N
SCHCO2CH3
CH3

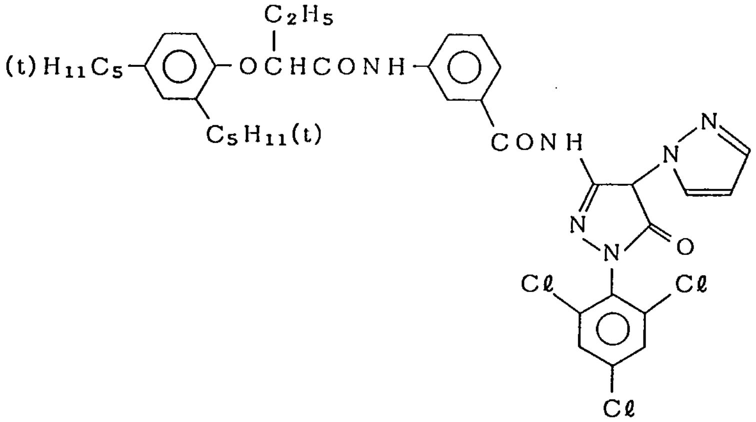
EX-11



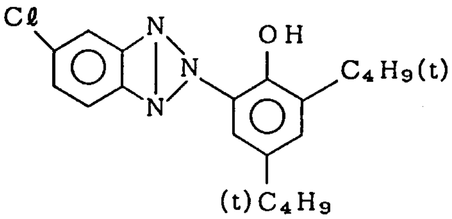
EX-12



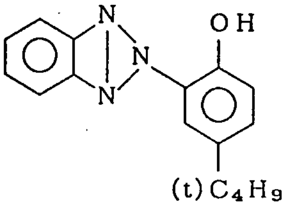
EX-13



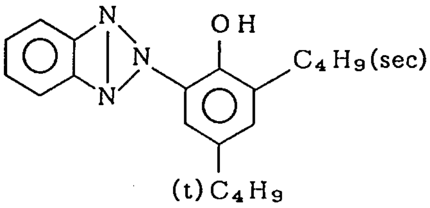
U－1



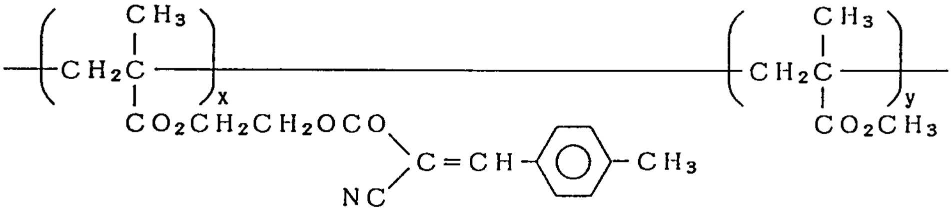
U－2



U－3

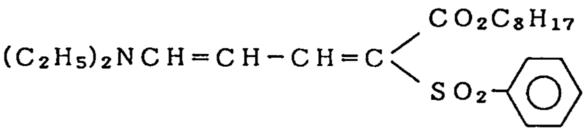


U－4



x : y =70 : 30 (wt%)

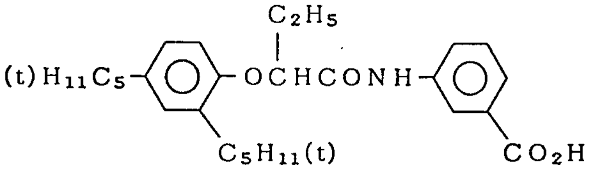
U－5



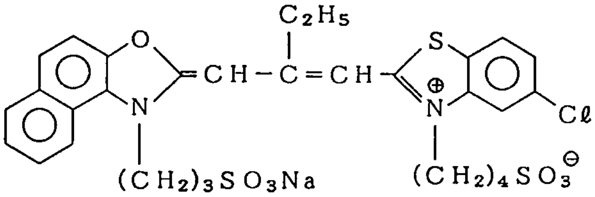
HBS－1　Tricresylphosphate

HBS－2　Di－n－butylphthalate

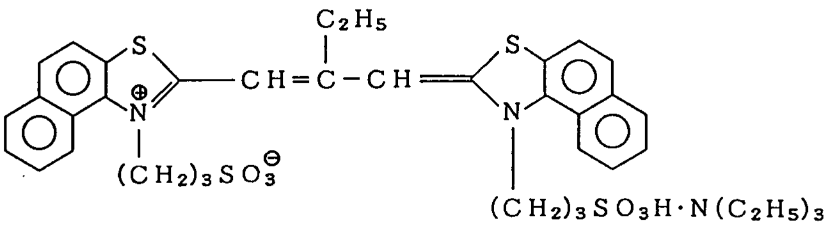
HBS－3



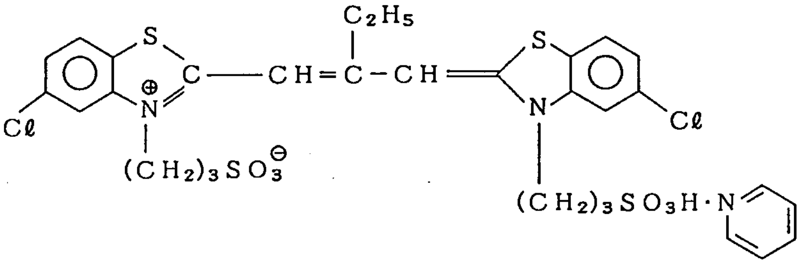
Sensitizing dye I



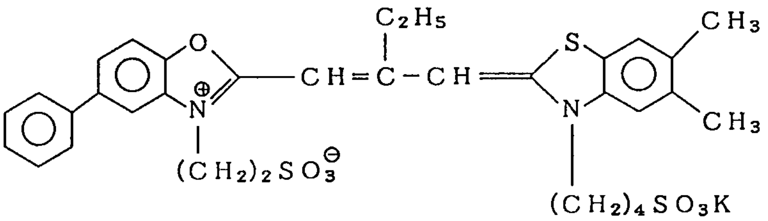
Sensitizing dye II



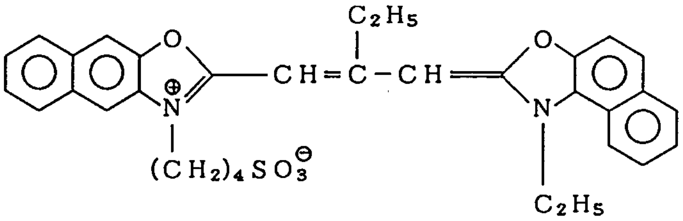
Sensitizing dye III



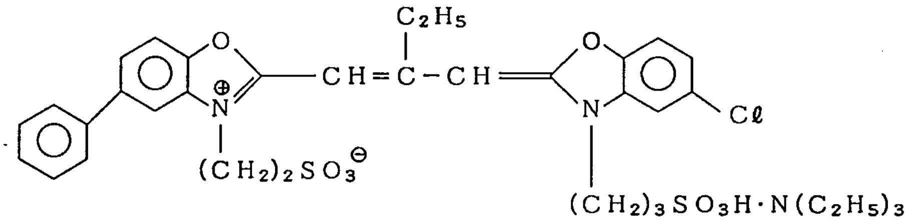
Sensitizing dye IV



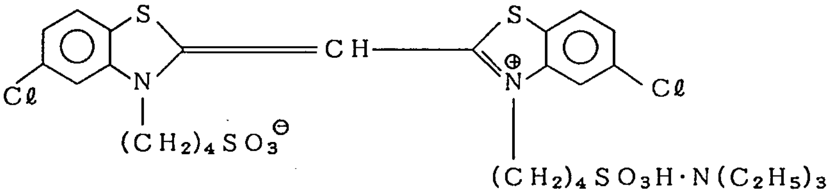
Sensitizing dye V



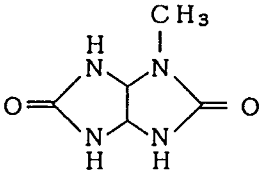
Sensitizing dye VI



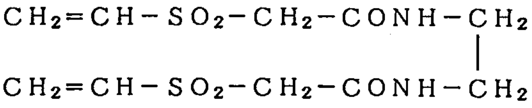
Sensitizing dye VII



S－1

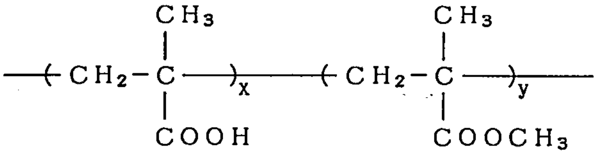


H－1



$$\begin{array}{l} CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \\ \hspace{10em} | \\ CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

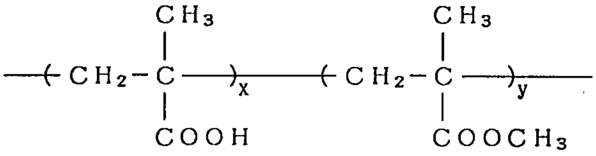
B－1



$$-\!\!\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\!\!-\!\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y\!\!-$$

x／y＝10／90

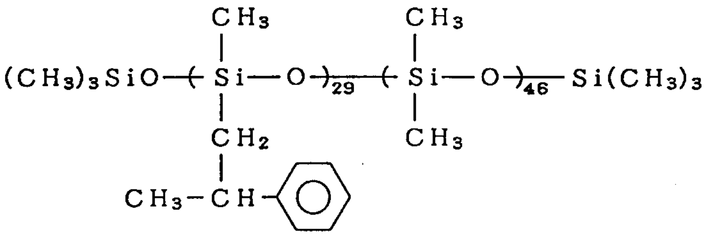
B－2



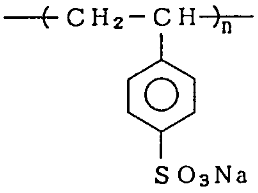
$$-\!\!\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\!\!-\!\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y\!\!-$$

x／y＝40／60

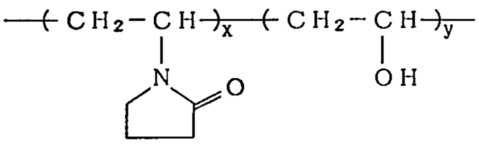
B－3



B－4

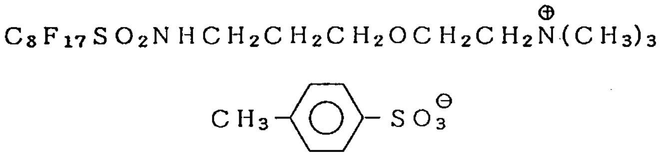


B－5

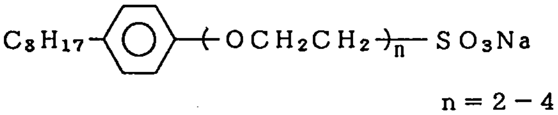


x／y＝70／30

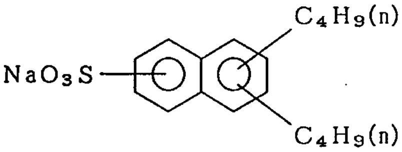
W－1



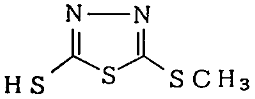
W－2



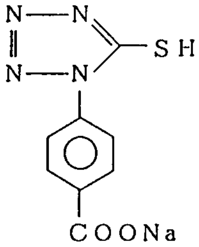
W－3



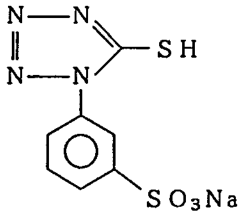
F－1



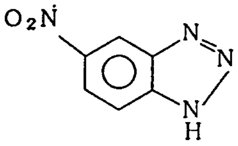
F－2



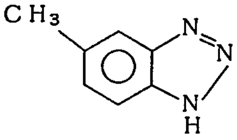
F－3



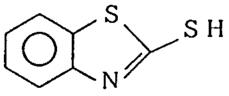
F－4



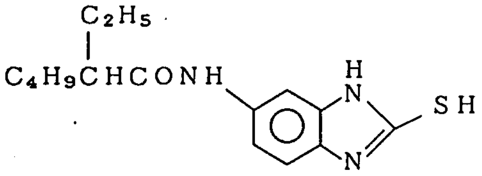
F－5



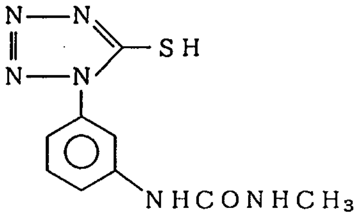
F－6



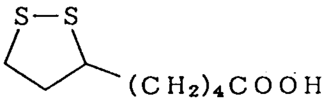
F－7



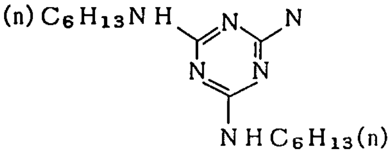
F－8



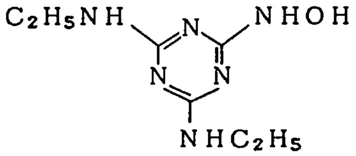
F－9



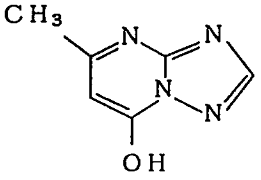
F－10



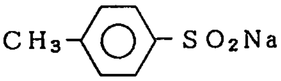
F－11



F－12



F－13

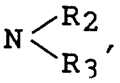


Claims

1. A silver halide photographic light-sensitive material comprising at least one silver halide emulsion layer on a support, wherein silver halide grains contained in the silver halide emulsion layer are chemically sensitized by selenium sensitizer, and the silver halide emulsion layer contains a compound represented by the following formula (I), and/or the oxidized product thereof:
   formula (I)

   X_1 - A - X_2

   where X_1 and X_2 each represent OR_1 or

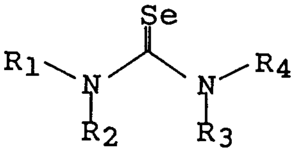
   

   $N\langle^{R_2}_{R_3}$,

   wherein R_1 represents a hydrogen atom or a group capable of changing into a hydrogen atom through hydrolysis, R_2 and R_3 each represent a hydrogen atom, alkyl, aryl, heterocylic, alkylsulfonyl, arylsulfonyl, heterocyliccarbonyl, alkylcarbonyl, arylcarbonyl, sulfamoyl, or carbamoyl, and A represents substituted or unsubstituted allylene group, in at least one of X_1, X_2 and A the hydrogen atom contained therein is substituted by an adsorption accelerating group to a silver halide grain.

2. The silver halide photographic light-sensitive material according to claim 1, characterized in that the silver halide grains are chemically sensitized by at least one of selenium sensitizers represented by the following formula (II):

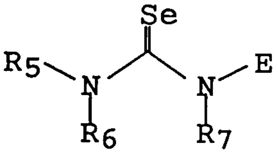
formula (II)



where R_1, R_2, R_3, and R_4 each represent alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, and sulfamoyl.

3. The silver halide photographic light-sensitive material according to claim 2, characterized in that the selenium sensitizer represented by formula (II) is represented the following formula (III):

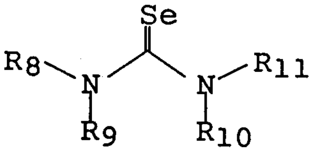
formula (III)



where R_5, R_6, R_7, and E each represent alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, and sulfamoyl, and the E represents a group having Hammett constant σp of at least -0.1.

4. The silver halide photographic light-sensitive material according to claim 1, characterized in that the silver halide grains are chemically sensitized by at least one of selenium sensitizers represented by the following formula (IV):

formula (IV)



where R_8, R_9, R_{10}, and R_{11} each represent a hydrogen atom, alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, heterocyclic, acyl, carboxy, alkoxycarbonyl, aryloxy carbonyl, carbamoyl, and sulfamoyl, and at least one pair of R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, and R_{11} and R_8 are bonded to each other, forming a ring.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9735

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)
Y	US-A-4 810 626 (EASTMAN KODAK COMPANY) * claims 11,14 *	1-4	G03C1/09 G03C1/10
Y	EP-A-0 121 435 (KONISHIROKU PHOTO INDUSTRY COMPANY LTD) * page 8, line 21 - page 9, line 20 * * compounds I-1 - I-9 on p.8/9 * * claims 1,3,4,9,10,13-15 *	1-4	
Y	US-A-4 845 020 (I.ITOH ET AL) * column 8, line 25 - column 16, line 25 * * claims 1-11 *	1-4	
P,X	EP-A-0 452 772 (FUJI PHOTO FILM COMPANY LTD.) * the whole document *	1-4	
E,X	EP-A-0 458 278 (FUJI PHOTO FILM COMPANY LTD.) * Claims and Abstract *	1-4	

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	25 MARCH 1992	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document