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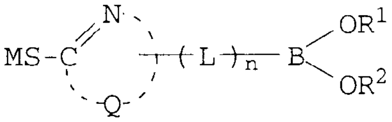
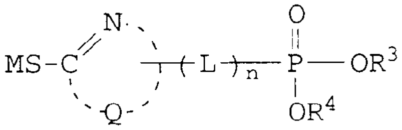
(54) Silver halide photographic light sensitive materials

(57) A silver halide photographic light sensitive material is disclosed, which comprises a support and provided thereon, a light sensitive silver halide emulsion layer containing selenium, tellurium or reduction sensitized silver halide grains, wherein said light sensitive silver halide emulsion layer or another hydrophilic colloid layer on said silver halide emulsion layer side contains a compound represented by the following formula (I) or (II) :

formula [I]



formula [II]



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Description

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material, and more particularly to a silver halide photographic light sensitive material which gives high sensitivity, reduced fog and reduced fluctuation of photographic properties during storage.

BACKGROUND OF THE INVENTION

The silver halide photographic light-sensitive material is superior to any other light-sensitive materials in terms of high sensitivity, high resolution and cost. However, since the silver halide photographic light-sensitive material employs chemical reaction, there is a problem in that photographic properties during storage are likely to fluctuate. I is impossible to completely prevent the fluctuation of the photographic properties, but many attempts to minimize the fluctuation have been tried by many researchers.

As a method of minimizing fluctuation during storage or during development, particularly fog, a method of adding heterocyclic compounds such as 1-phenyl-5-mercaptotetrazoles, benzotriazoles, benzimidazoles or indazoles in a light sensitive material or in processing solutions is known, and is disclosed in US Patent Nos. 3,295,976, 3,376,310, 3,615,616, 3,071,465, 3,420,664, 2,403,927, 3,157,509, 3,082,088, 3,137,578, 3,148,066, 3,511,663, 3,106,467, 3,420,670, 1,763,990 and 2,271,229, British Patent Nos. 919,061, 768,438, 271,475 and 1,344,548, German Patent Nos. 617,712, 708,424, 635,769 and 2,205,539, Belgian Patent Nos. 671,402 and Japanese Patent O.P.I. Publication No. 50-37436/1985. Recently, extensive studies on 1-phenyl-5-mercaptotetrazoles, benzotriazoles have been made, compounds disclosed in Japanese Patent Publication Nos. 61-23542/1986, 61-47415/1986 and 63-65137/1988, Japanese Patent O.P.I. Publication No. 59-71047/1984 and Japanese Patent Publication No. 2-25494/1990 have been proposed. However, these compounds still have problems in which minimization of photographic property fluctuation during storage is insufficient or photographic sensitivity is lowered.

Recently, demand for a silver halide photographic light sensitive material of high sensitivity has been strong, and as new methods for high sensitivity, usage of tabular silver halide grains or introduction of selenium or tellurium sensitization or reduction sensitization has been attempted. However, these methods increase sensitivity but tend to increase undesirable fog. Therefore, a technique for minimizing fog maintaining high sensitivity and for enhancing storage stability has been desired.

SUMMARY OF THE INVENTION

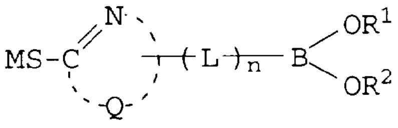
An object of the invention is to provide a silver halide photographic light sensitive material which gives high sensitivity, reduced fog, and reduced fluctuation of photographic properties during storage.

DETAILED DESCRIPTION OF THE INVENTION

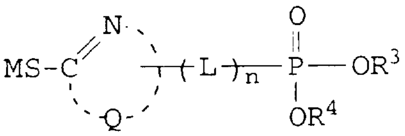
The above object of the invention can be attained by the following constitution:

(1) A silver halide photographic light sensitive material comprising a support and provided thereon, at least one light sensitive silver halide emulsion layer, wherein said at least one light sensitive silver halide emulsion layer contains selenium or tellurium sensitized light sensitive silver halide grains and said at least one light sensitive silver halide emulsion layer or another hydrophilic colloid layer, each layer having a water permeable relation, contains at least one selected from compounds represented by the following formulas (I) and (II):

formula (I)



formula (II)



wherein M represents a hydrogen atom, a metal atom or a quaternary ammonium group; Q represents a non-metal atomic group necessary to form a single or condensed heterocyclic ring containing a carbon atom and a nitrogen atom; L represents a divalent group; n is an integer of 0 to 2; R^1, R^2, R^3 and R^4 independently represent a hydrogen atom, a cation or a substituent; R^1 and R^2 may be the same or different, or combine with each other to form a ring; and R^3 and R^4 may be the same or different or combine with each other to form a ring,

(2) A silver halide photographic light sensitive material comprising a support and provided thereon, at least one light sensitive silver halide emulsion layer, wherein said at least one light sensitive silver halide emulsion layer contains reduction sensitized light sensitive silver halide grains and said at least one light sensitive silver halide emulsion layer or another hydrophilic colloid layer, each layer having a water permeable relation, contains at least one selected from compounds represented by the above formulas (I) and (II), or

(3) A silver halide photographic light sensitive material comprising a support and provided thereon, at least one light sensitive silver halide emulsion layer, wherein said at least one light sensitive silver halide emulsion layer contains light sensitive silver halide grains having an aspect ratio of not less than 2 and said at least one light sensitive silver halide emulsion layer or another hydrophilic colloid layer, each layer having a water permeable relation, contains at least one selected from compounds represented by the above formulas (I) and (II).

The invention will be detailed below.

The compound of the invention represented by formula (I) or (II) will be explained below.

In formula (I) or (II), the metal atom represented by M include Li, Na, K, Mg, Ca, Zn and Ag, the quaternary ammonium includes NH_4, $N(CH_3)_4$, $N(C_4H_9)_4$, $N(CH_3)_2(C_{12}H_{25})$, $N(CH_3)_3(C_{16}H_{33})$, and $N(CH_3)_3(CH_2C_6H_5)$.

The preferable heterocyclic group represented by Q includes an imidazole ring, a pyrazole ring, a triazole ring, a tetrazole ring, an oxazole ring, a thiazole ring, a selenazole ring, a tellurazole ring, an oxadiazole ring, a thiadizole ring, a pyridine ring, a pyrazine ring, and pyrimidine ring and a condensed ring such as a benzoimidazole ring, a benzooxazole ring, a benzothiazole ring. Another preferable heterocyclic group is a tetrazaindene ring.

The preferable divalent group represented by L includes an alkylene group, an arylene group, an aromatic heterocyclic group, an ether group, a thioether group, an imino group, an ester group, an amido group, a sulfonyl group, and a combination thereof.

That is, said divalent group includes an alkylene group, an arylene group, an aromatic heterocyclic divalent group, -O-, -S-, -NH-, -C(=O)O-, -CONH- and $-SO_2-$ and their mixture divalent group.

The more preferable L is an alkylene group, an arylene group, -S-, -CONH- or a combination thereof.

The cation represented by R^1, R^2, R^3 or R^4 includes an inorganic cation such as Na^+, K^+, Li^+, Mg^{2+}, Cg^{2+}, NH_4^+, Na^+, and an inorganic cation such as a trimethylammonium or pyridinium ion. A cation corresponding to a monovalent cation is used in order to neutralize valency, for example, a 1/2 calcium ion is used in the case of a calcium ion.

When R^1, R^2, R^3 and R^4 represent a substituent, the substituent preferably has not more than 10 carbon atoms. The substituent will be shown later.

R^1 and R^2, or R^3 and R^4 may combine with each other, respectively, to form a 1,2-ethylene group or a 1,3-propylene group.

In formla (I) compound, either one of R^1 and R^2 preferably represents a hydrogen atom, and in formla (II) compound, either one of R^3 and R^4 preferably represents a hydrogen atom.

The organic heterocyclic group represented by Q or the divalent group represented by L may have a substituent. When the substituent has a carbon atom, it preferably has not more than 10 carbon atoms. This substituent or a substituent represented by R^1, R^2, R^3 and R^4 includes those as shown below.

(Examples of the substituent are as follows:)

a nitro, nitroso, cyano, carboxy, sulfo, mercapto or hydroxy group, a halogen atom (a fluorine, chlorine or iodine atom);

an alkyl group or aralkyl group, which may have a substituent, including a methyl, trifluoromethyl, benzyl, chloromethyl, dimethylaminomethyl, ethoxycarbonyl methyl, aminomethyl, acetylmethyl, ethyl, carboxyethyl, n-propyl, t-butyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, n-octyl, n-decyl and n-undecyl group;

an alkenyl group, which may have a substituent, including a vinyl, 2-chlorovinyl, 1-methylvinyl, 2-cyanovinyl, allyl and cyclohexene-1-yl group;

an alkinyl group, which may have a substituent, including an ethinyl, 1-propinyl and 2-ethoxycarbonylethinyl group;

an aryl group, which may have a substituent, including a phenyl, naphthyl, 3-hydroxyphenyl, 3-chlorophenyl, 4-acetylaminophenyl, 2-methanesulfonyl-4-nitrophenyl, 3-nitrophenyl, 4-methoxyphenyl, 4-methylsulfonylphenyl, and 2,4-dimethylphenyl group;

a heterocyclic ring group, which may have a substituent, including a 1-imidazolyl, 2-furyl, 2-pyridyl, 5-nitro-2-pyridyl, 3-pyridyl, 3,5-dicyano-2-pyridyl, 5-tetrazolyl, 5-phenyl-1-tetrazolyl, 2-benzothiazolyl, 2-benzoimidazolyl, 2-benzoxazolyl, 2-oxazoline-2-yl, and morpholino group;

An acyl group, which may have a substituent, including an acetyl, propionyl, iso-butyroyl, 2,2-dimethylpropionyl, benzoyl, 3,4-dichlorobenzoyl, 3-acetylamino-4-methoxybenzoyl and 4-methylbenzoyl group;

a sulfonyl group, which may have a substituent, including a methylsulfonyl, ethylsulfonyl, chloromethylsulfonyl, propylsulfonyl, butylsulfonyl, n-octylsulfonyl, phenylsulfonyl, and 4-toluenesulfonyl group;

an amino group, which may have a substituent, including an amino, methylamino, dimethylamino, ethylamino, ethyl-3-carboxypropylamino, ethyl-2-sulfoethylamino, phenylamino, methylphenylamino, and methyloctylamino group;

an alkoxy group, which may have a substituent, including a methoxy, ethoxy, n-propyloxy, and cyclohexylmethoxyoxy group;

an aryloxy or heteroaryloxy group, which may have a substituent, including a phenoxy, naphtyloxy, 4-acetylaminophenoxy, and pyrimidine-2-yloxy group;

an alkylthio group, which may have a substituent, including a methylthio, ethylthio, n-butylthio, n-octylthio, t-octylthio, ethoxycarbonylmethylthio, benzylthio, and 2-hydroxyethylthio group;

an arylthio or heteroarylthio group, which may have a substituent, including a phenylthio, 4-chlorophenylthio, 2-n-butoxy-5-t-octylphenylthio, 4-nitrophenylthio, 2-nitrophenylthio, 4-acetylaminophenylthio, 1-phenyl-5-tetrazolylthio, and 5-methylsulfonylbenzothiazole-2-yl group;

an ammonio group, which may have a substituent, including an ammonio, trimethylammonio, penyldimethylammonio, and dimethylbenzylammonio group;

a carbamoyl group, which may have a substituent, including a carbamoyl, methylcarbamoyl, dimethylcarbamoyl, bis-(2-metoxyethyl) carbamoyl, and cyclohexylcarbamoyl group;

a sulfamoyl group, which may have a substituent, including a sulfamoyl, methylsulfamoyl, dimethylsulfamoyl, bis-(2-metoxyethyl) sulfamoyl, and di-n-butylsulfamoyl group;

an acylamino group, which may have a substituent, including an acetylamino, 2-carboxybenzoylamino, 3-nitrobenzoylamino, 3-diethylaminopropanoylamino, and acryloylamino group;

an acyloxy group, which may have a substituent, including an acetoxy, benzoyloxy, 2-butenoyloxy, and 2-methylpropanoyloxy group;

a sulfonylamino group, which may have a substituent, including a methanesulfonylamino, phenylsulfonylamino, and 2-methoxy-5-n-methylphenyl-sulfonylamino group;

an alkoxycarbonylamino group, which may have a substituent, including a methoxycarbonylamino, 2-methoxyethoxycarbonylamino, iso-butoxycarbonylamino, benzyloxycarbonylamino, t-butoxycarbonylamino, and 2-cyanoethoxycarbonyamino group;

an aryloxycarbonylamino group, which may have a substituent, including a phenoxycarbonylamino, and 2,4-nitrophenoxycarbonylamino group;

an alkoxycarbonyloxy group, which may have a substituent, including a methoxycarbonyloxy, t-butoxycarbonyloxy, 2-phenylsulfonylethoxycarbonyloxy, and benzyloxycarbonyloxy group;

an aryloxycarbonyloxy group, which may have a substituent, including a phenoxycarbonyloxy, 3-cyanophenoxycarbonyloxy, 4-acetoxyphenoxycarbonyloxy, and 4-t-butoxycarbonylamino-phenoxycarbonyloxy group;

an aminocarbonylamino group, which may have a substituent, including a methylaminocarbonylamino, morpholinocarbonylamino, N-ethyl-N-phenylaminocarbonylamino, and 4-methylsulfonylaminocarbonylamino group;

an aminocarbonyloxy group, which may have a substituent, including a dimethylaminocarbonyloxy, pyrrolidinocarbonyloxy, and 4-dipropylaminocarbonyloxy group;

an aminosulfonylamino group, which may have a substituent, including a diethylaminosulfonylamino, di-N-butylaminosulfonylamino, and phenylaminosulfonylamino group;

a sulfonyloxy group, which may have a substituent, including a phenylsulfonyloxy, methylsulfonyloxy, chloromethylsulfonyloxy, and 4-chlorophenylsulfonyloxy group; and

an alkoxycarbonyl or aryloxycarbonyl group, which may have a substituent, including a methoxycarbonyl, ethoxycarbonyl, phenoxycarbonyl, and 2-methoxyethoxycarbonyl group.

The exemplified compounds of formula (I) or (II) will be shown below, but the invention are not limited thereto.

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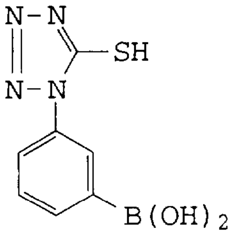

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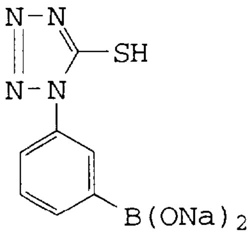

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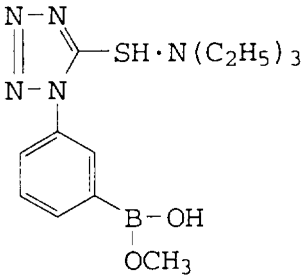

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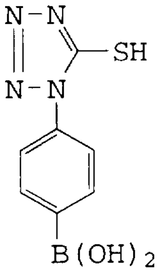

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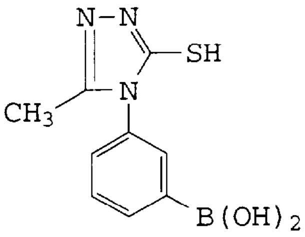

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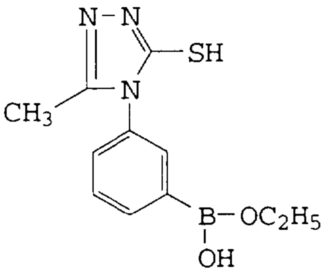

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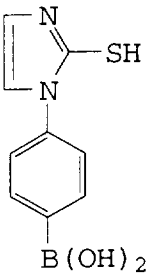

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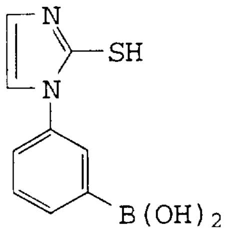

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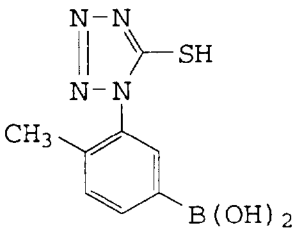

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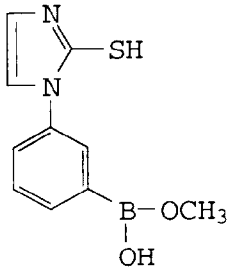

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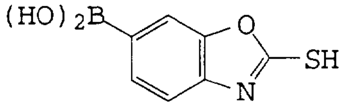

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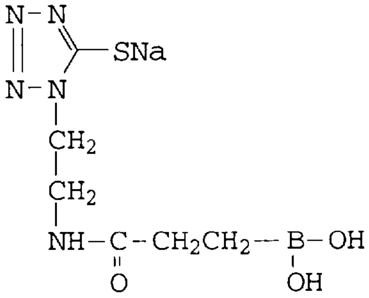

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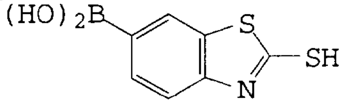

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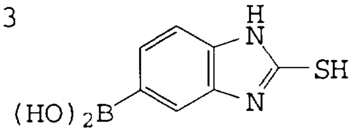

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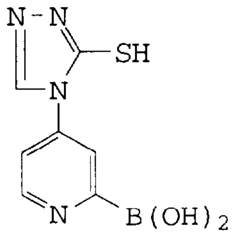

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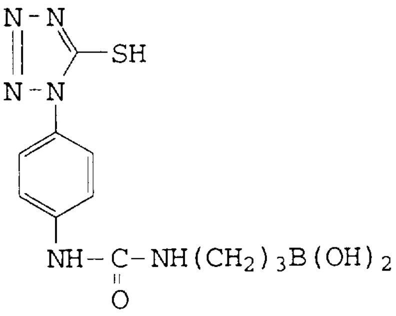

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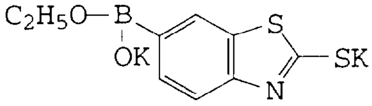

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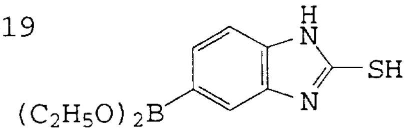

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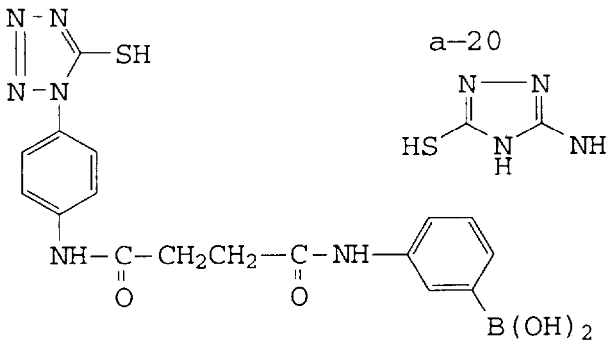

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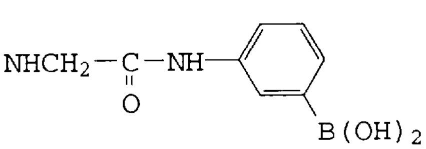

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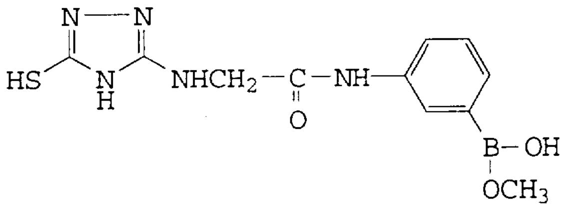

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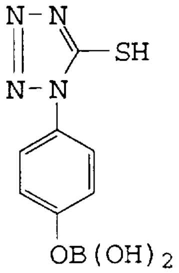

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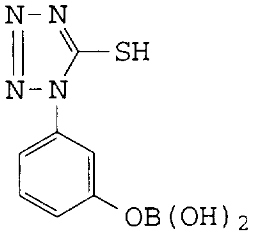

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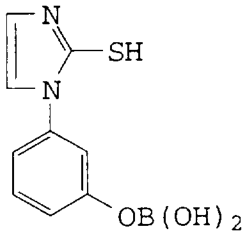

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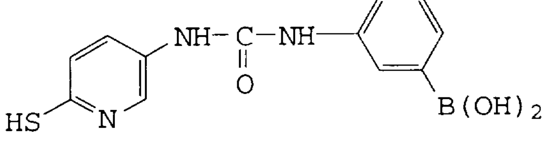

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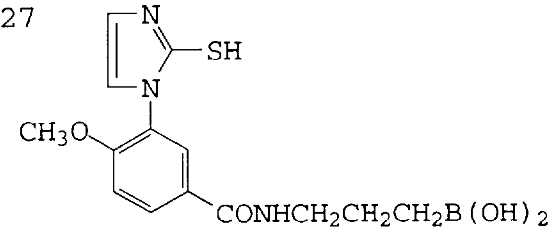

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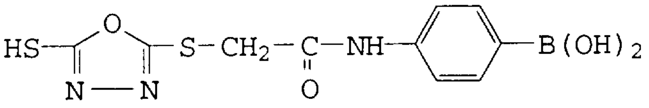

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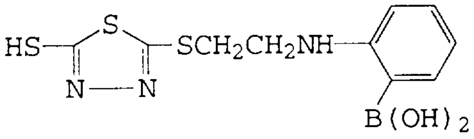

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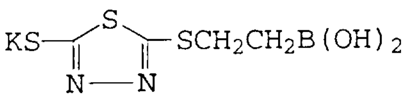

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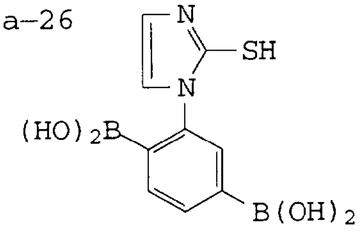

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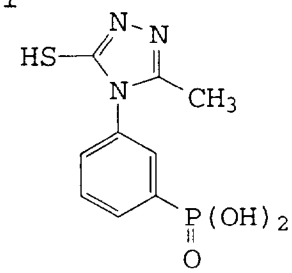

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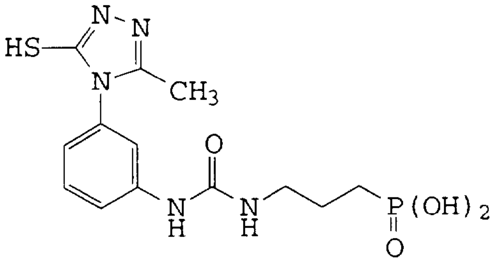

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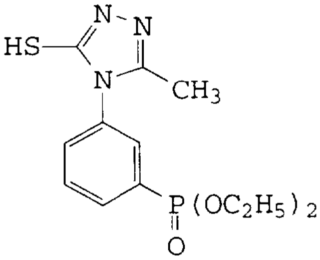

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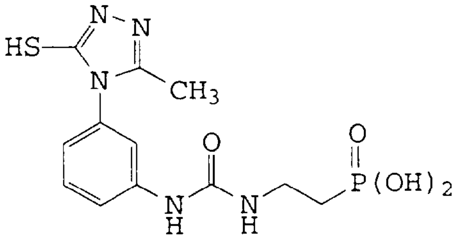

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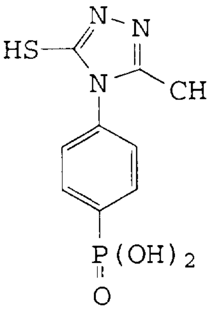

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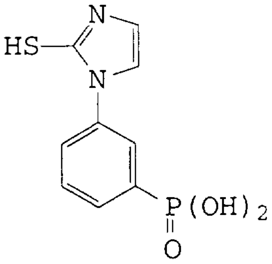

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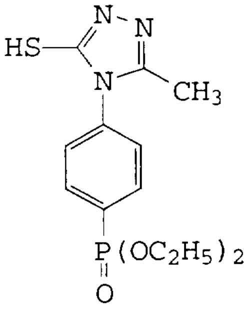

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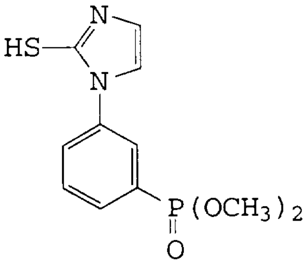

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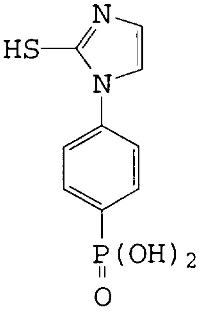

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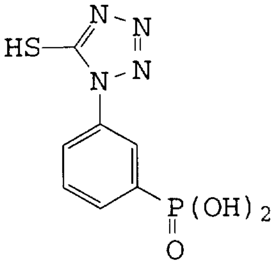

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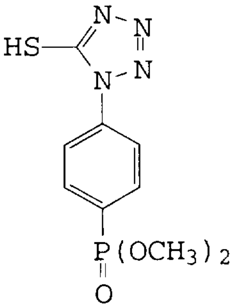

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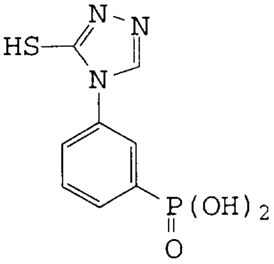

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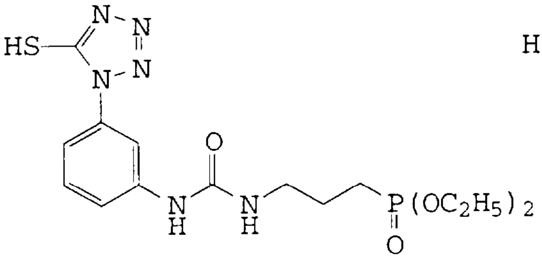

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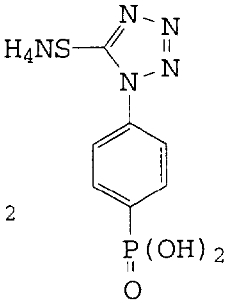

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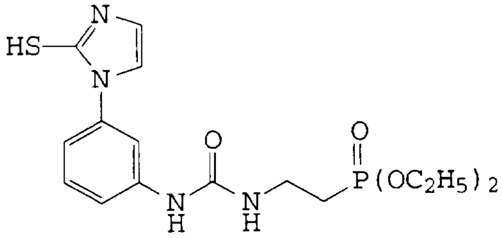

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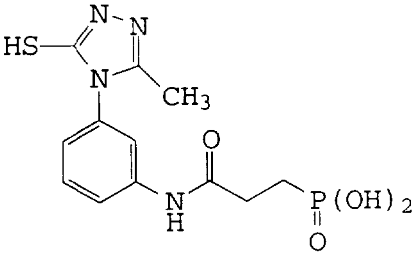

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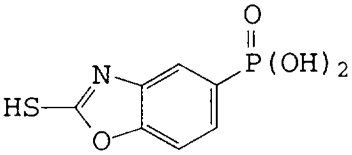

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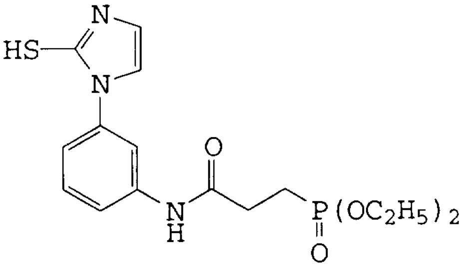

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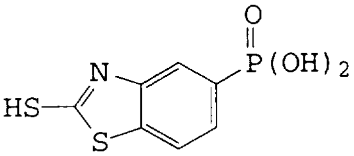

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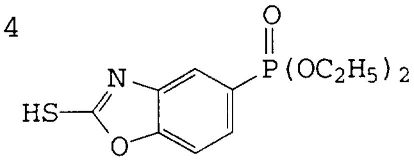

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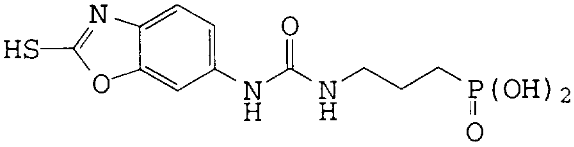

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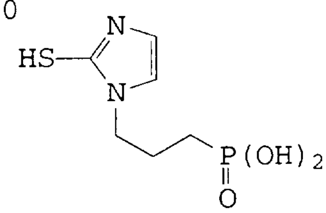

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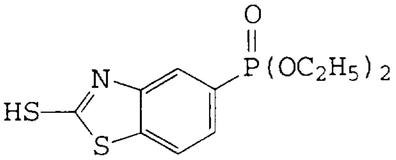

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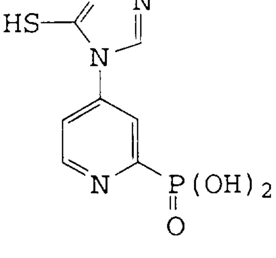

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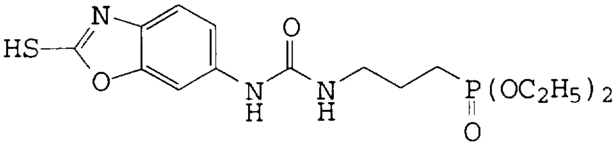

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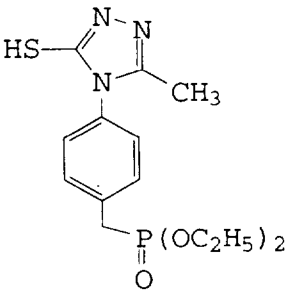

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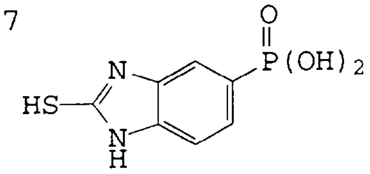

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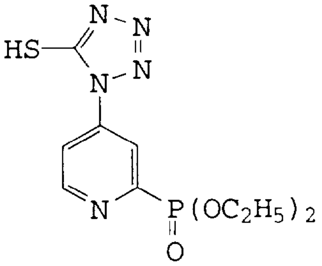

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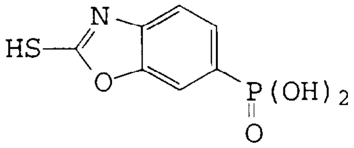

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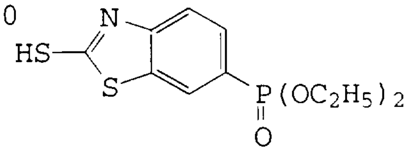

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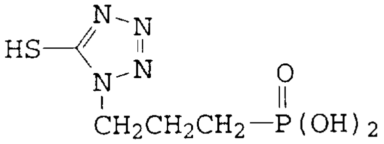

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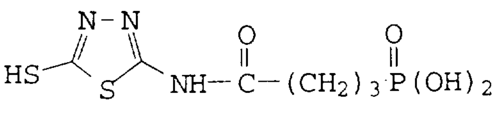

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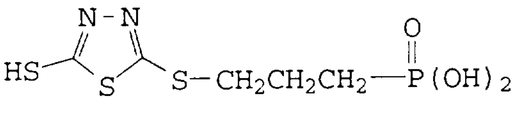

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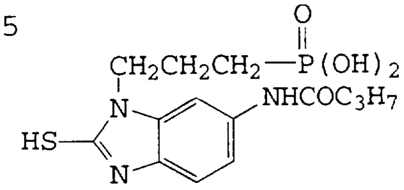

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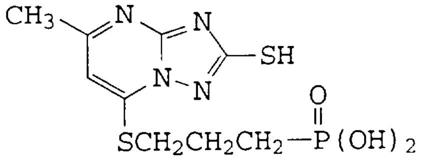

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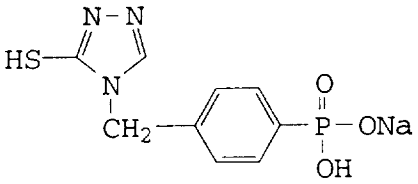

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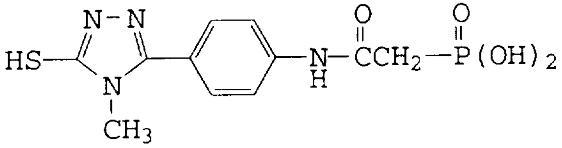

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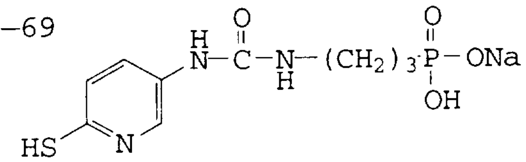

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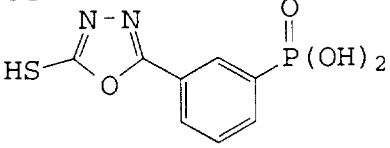

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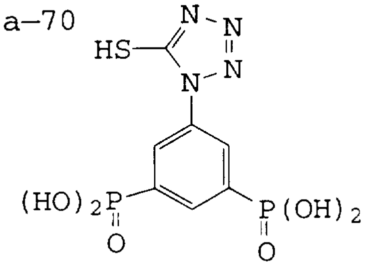


The compound represented by formula (I) or (II) can generally be synthesized according to methods described in US patent Nos.2,585,388 and 3,295,976, Japanese Patent O.P.I. Publication No. 3-145638/1991 and Japanese Patent Application No. 7-81931/1995 to the presnt inventors filed March 14, 1996.

The example of the synthetic method will be shown below.

Synthesys of Exemplified compound a-1

In a solution containing 0.2g (5mmol) of sodium hydroxide and 3 ml of water were dissolved 72g (5mmol) of 3-aminophenylboronic acid, and cooled with ice. The resulting solution was added with 0.38ml (5mmol) of thiophosgen at not more than 5°C and stirred. After 10 minutes, yellow precipitate was filtered out, and the precipitate is added to a solution in which 1.3g of sodium azide is dissolved in 3ml water and refluxed for 5 hours. The resulting solution was cooled, and filtered out to obtain filtrate. The filtrate was acidified with concentrated hydrochloric acid to produce white precipitate. The precipitate was filtered out to obtain 0.53g of 3-(5-mercaptotetrazol-1-yl)phenylboronic acid. The product was recrystallized from a mixture solvent of water and ethanol to obtain 0.14g of colorless needle crystal. Melting point : more than 270°C, Anion FAB-MS (matrix-glycerin) m/e 193(M+Gly-2H_2O)

The other exemplified compounds are synthesized in the same manner as above.

The compound represented by formula (I) or (II) is contained in a light sensitive silver halide emulsion layer containing selenium or tellurium sensitized light sensitive silver halide grains, reduction sensitized light sensitive silver halide grains or silver halide grains having an aspect ratio of not less than 2 or in another hydrophilic colloid layer having a water permeable relation with said emulsion layer. The term "water permeable" herein referred to means that water permeates each layer in an alkaline condition during development. That is, "another hydrophilic colloid layer having a water permeable relation with said emulsion layer" herein referred to means another hydrophilic colloid layer on the silver halide emulsion layer side. For example, said another layer includes another silver halide emulsion layer directly or indirectly contacting said silver halide emulsion layer or an intermediate layer, a color mixture preventing layer, an anti-halation layer, a filter layer or a surface protection layer on said silver halide emulsion layer side, but not a backing layer on the support opposite said silver halide emulsion layer. The content in the silver halide photographic emulsion layer of the compound represented by formula (I) or (II) is preferably 1×10^{-6} to 1×10^{-1} mol/mole of silver halide, and more preferably 5×10^{-6} to 1×10^{-2} mol/mole of silver halide. The content in said another hydrophilic colloid layer of the compound represented by formula (I) or (II) is preferably 2×10^{-5} to 0.2 g/m^2, more preferably 1×10^{-4} to 0.1 g/m^2 and especially preferably 2×10^{-4} to 0.05 g/m^2. The compound represented by formula (I) or (II) is preferably added to a silver halide emulsion layer or its adjacent layer.

As a method of adding the compound represented by formula (I) or (II) to a silver halide photographic emulsion, any conventional method of adding an additive to the silver halide photographic emulsion may be acceptable. For example, the compound is dissolved in methanol, ethanol, methylcellosolve, acetone, water or a mixed solutions thereof, and added in the form of a mixture. In addition, the compound may be added as a dispersed solution prepared by means of a solid dispersion, an emulsifying dispersion, a supersonic dispersion and an oil-protected dispersion.

The compound represented by formula (I) or (II) may be added at any step of the silver halide emulsion production. It may also be added at any step during or after a photographic emulsion is manufactured or immediately before coating. In the present invention, the addition step is preferably between the end of the silver halide grain forming step and the completion of the coating solution preparation step.

The silver halide emulsion used a silver halide photographic light sensitive material of the invention is characterized in that the emulsion is sensitized by a selenium or tellurium compound.

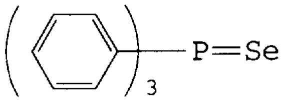
The selenium sensitizer used in the invention includes a conventional selenium compound which has been disclosed in patent publications. The example of the selenium sensitizer and its usage are disclosed in the following patent publications: US Patent Nos. 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320,069, 3,408,196, 3,408,197, 3,442,653, 3,420,670 and 3,591,385, Japanese Patent Publication Nos. 52-34491/1977, 52-34492/1977, 53-295/1978 and 57-22090/1982, Japanese Patent O.P.I. Publication Nos. 59-180536/1984, 59-185330/1984, 59-181337/1984, 59-187338/1984, 59-192241/1984, 60-150046/1985, 60-151637/1985, 61-246738/1986, 3-4221/1991, 3-24537/1991, 3-111838/1991, 3-116132/1991, 3-148648/1991, 3-237450/1991, 4-16838/1992, 4-25832/1992, 4-25832/1992, 4-32831/1992, 4-96059/1992, 4-109240/1992, 4-140738/1992, 4-147250/1992, 4-149437/1992, 4-184331/1992, 4-190225/1992, 4-191729/1992, 4-195035/1992, 4-271341/1992, 4-344636/1992, 5-11385/1993, 5-40324/1993, 5-224332/1993, 5-224333/1993, 6-40324/1994, 6-43576/1994, 6-75328/1994, 6-110149/1994, 6-175258/1994, 6-175259/1994, 6-180478/1194, 6-208184/1994, 6-208186/1994, 6-265118/1994 and 6-281642/1994.

The technique regarding selenium sensitization is also disclosed in E.H. Spencer et al., Journal of Photographic Science, 31, 158-169 (1983).

The useful selenium sensitizer includes colloidal selenium metal, isoselenocyanates (for example, allyl isoselenocyanate), selenoureas (for example, N,N-dimethylselenourea, N,N,N'-triethylselenourea, N,N,N'-trimethyl-N'-heptafluoroselenourea, N,N,N'-trimethyl-N'-heptafluoropropylcarbonylselenourea, N,N,N'-trimethyl-N'-4-nitrophenylcarbonylselenourea), selenoketones (for example, selenoacetone, selenoacetophenone), selenoamides (for example, selenoacetoamide, N,N-dimethylselenobenzamide), selenophosphates (for example, tri-p-triselenophosphate), selenides (for example, diethylselenide, diethyldiselenide, triphenylphosphinselenide). The especially preferable selenium sensitizer is selenoureas, selenophosphates or selenides.

The examples of the selenium compound (selenium sensitizer, which is used during chemical ripening of the silver halide emulsion of the invention, will be shown below.

b-1



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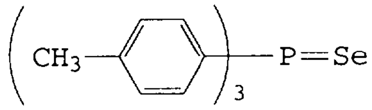
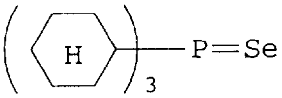


b-3

$(nC_4H_9)_3P=Se$

b-4



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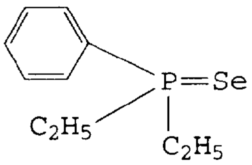

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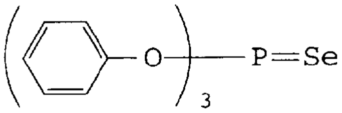

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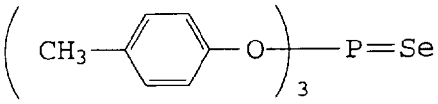

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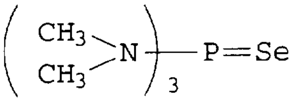

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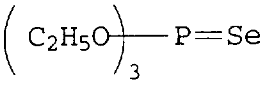

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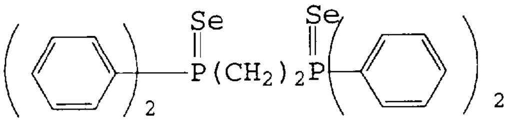

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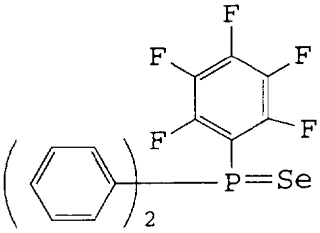

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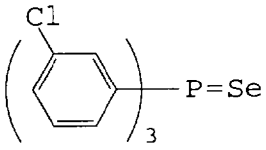

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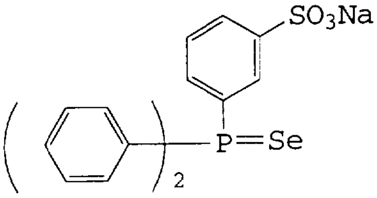

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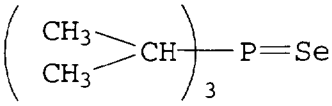

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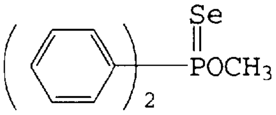

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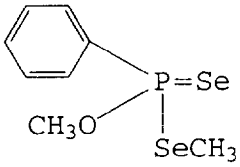

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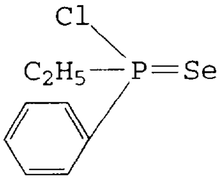

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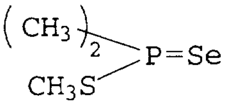

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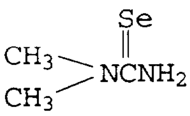

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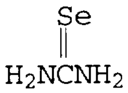
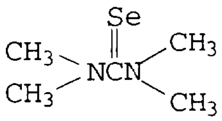


$H_2N\overset{\overset{Se}{\|}}{C}NH_2$

b-21



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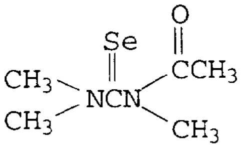

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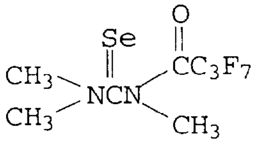

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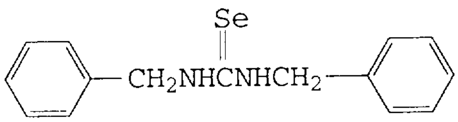

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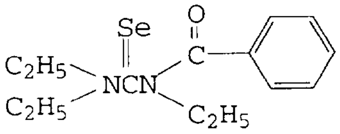

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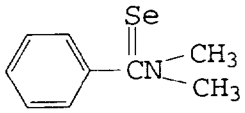

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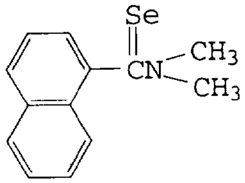

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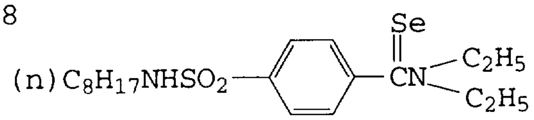

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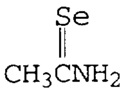
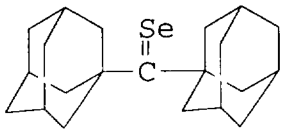


$CH_3C(=Se)NH_2$

b-30



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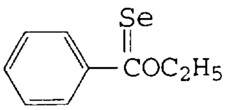

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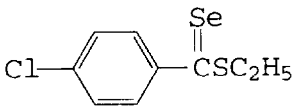

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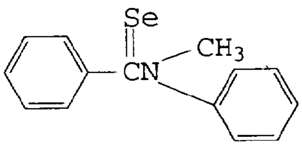

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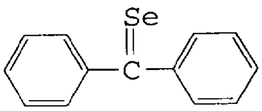

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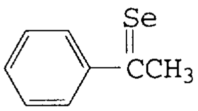

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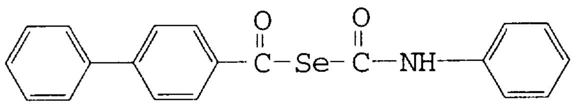

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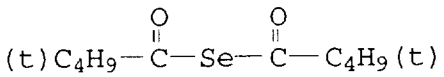


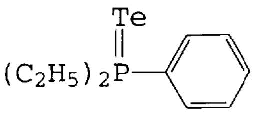
$$(t)C_4H_9-\overset{O}{\overset{\|}{C}}-Se-\overset{O}{\overset{\|}{C}}-C_4H_9(t)$$

The tellurium sensitizer and the selenium sensitization used in the chemical sensitization of the invention are disclosed in US Patent Nos. 1,623,499, 3,320,069, 3,772,031, 3,531,289 and 3,655,394, British Patent No. 235,211, 1,121,496, 1,295,462 and 1,396, 696, Canada Patent No. 800,958, Japanese Patent O.P.I. Publication Nos. 4-204640/1992, 4-271341/1992, 4-333043/1992, 5-303157/1993, 6-27573/1993, 6-175259/1994, 6-180478/1994, 6-208184/1994 and 6-208186/1994. The technique, which is disclosed in Journal of Chemical Society Chemical Communication, p. 635 (1980), P. 645 (1979), and P. 1102 (1980), and in Journal of Chemical Society Perkin Transaction, p. 12191 (1980), can be also used.

The useful tellurium sensitizer includes telluroureas (for example, N,N-dimethyltellurourea, tetramethyltellurourea, N-carboxyethyl-N,N'-dimethyltellurourea), phosphintellurides (tributylphosphintelluride, tricyclohexylphosphintelluride, triisopropylphosphintelluride), telluroamides (for example, telluroacetoamide, N,N-dimethyltellurobenzamide), telluroketones, telluroesters, and isotellurocyanates. The especially preferable selenium sensitizer is selenoureas, selenophosphates or selenides.

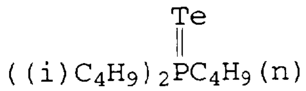
The examples of the tellurium compound (tellurium sensitizer, which is used during chemical ripening of the silver halide emulsion of the invention, will be shown below.

C–1



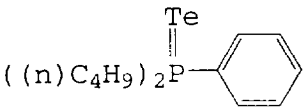
C–2 $((i)C_4H_9)_3P{=}Te$

C–3



$((i)C_4H_9)_2\overset{\overset{\displaystyle Te}{\|}}{P}C_4H_9(n)$

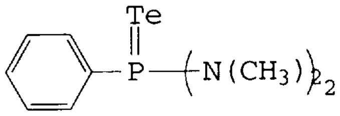
C–4



C–5 $((t)C_4H_9)_3P{=}Te$

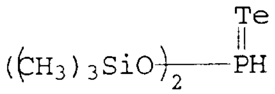
C–9 $((n)C_4H_9O)_3P{=}Te$

C–10



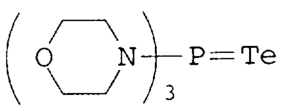
C–11 $((CH_3)_2N)_3P{=}Te$

C–12

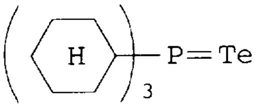


$((CH_3)_3SiO)_2\overset{\overset{\displaystyle Te}{\|}}{P}H$

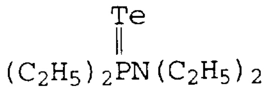
C–13



C-6

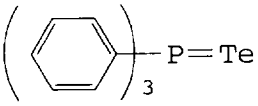


C-14

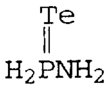


$(C_2H_5)_2\overset{\overset{Te}{\|}}{P}N(C_2H_5)_2$

C-7

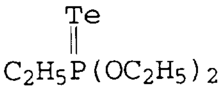


C-15



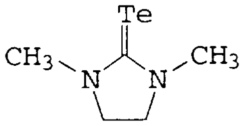
$H_2\overset{\overset{Te}{\|}}{P}NH_2$

C-8

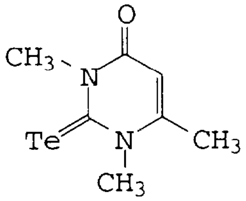


$C_2H_5\overset{\overset{Te}{\|}}{P}(OC_2H_5)_2$

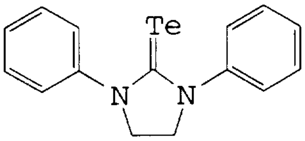
C-16



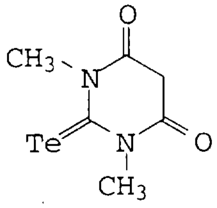
C-21



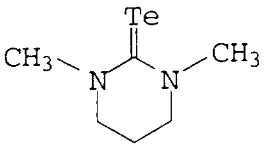
C-17



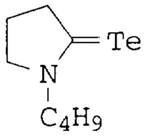
C-22



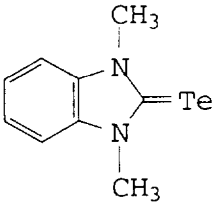
C-18



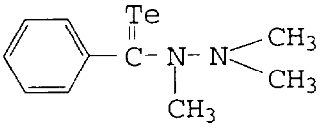
C-23



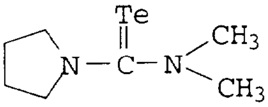
C–19



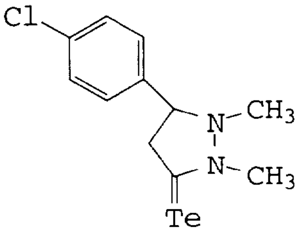
C–24



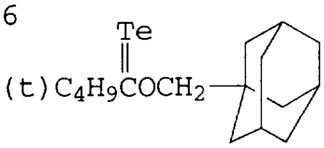
C–20



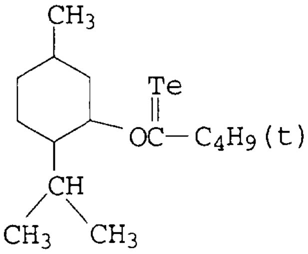
C–25



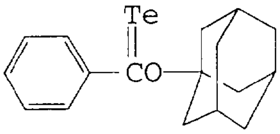
C–26



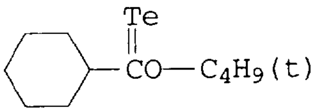
C–27



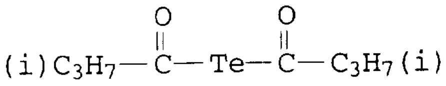
C–28



C-29



C-30



$$(i)C_3H_7-\overset{\overset{O}{\|}}{C}-Te-\overset{\overset{O}{\|}}{C}-C_3H_7(i)$$

The addition amount of the selenium or tellurium compound depends upon kinds of additives used, kinds of a silver halide emulsion used or chemical ripening conditions, but is in the range of 1 x 10^{-8} to 1 x 10^{-3} mol per mol of silver halide, and preferably in the range of 5 x 10^{-8} to 1 x 10^{-4} mol per mol of silver halide.

The selenium or tellurium compound is added, at chemical ripening stage, with a solution in which the selenium or tellurium compound is dissolved in water or an organic solvent such as methanol, ethanol or ethyl acetate or its mixture solvent depending on nature of the selenium or tellurium compound, a gelatin solution containing the selenium or tellurium compound or a dispersion solution containing an organic solvent soluble polymer and the selenium or tellurium compound.

The pAg (logarithms of reciprocal of silver ion concentration) at the chemical ripening is preferably 6.0 to 10.0, and more preferably 6.5 to 9.5. The pH at the chemical ripening is preferably 4 to 9, and more preferably 4.0 to 6.5. The temperature at the chemical ripening is preferably 40 to 90°C, and more 45 to 85°C.

At the chmical ripening of the silver halide emulsion used in the invention, other chemical sensitizers can be used in combination, and especially sulfur sensitizers are preferably used in combination.

The sulfur semsitizers include sulfur sensitizers disclosed in US Patent Nos. 1,574,944, 2,419,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955, West German Patent Publication No. 1,422,869, Japanese Patent O.P.I. Publication Nos. 55-45016/1980, 56-24937/1981 and 5-165135/1993. The preferable examples include thiourea derivatives such as 1,3-diphenylthiourea, triethylthiourea and 1-ethyl-3-(2-thiazolyl)thiourea, rhodanine derivatives, dithiacarbamic acids, polysulfide organic compounds and sulfur. The addition amount of the sulfur semsitizers depends upon kinds of additives used, kinds of a silver halide emulsion used or chemical ripening conditions, but is preferably in the range of 1 x 10^{-4} to 1 x 10^{-9} mol per mol of silver halide, and more preferably in the range of 1 x 10^{-5} to 1 x 10^{-8} mol per mol of silver halide.

In the invention gold sensitizers are preferably used in combination, and the examples include chloroauric acid, gold thiosulfate, gold thiocyanate and gold complexes with thioureas, rhodanines or other various compounds. The additon amount of the gold semsitizers depends upon kinds of additives used, kinds of a silver halide emulsion used or chemical ripening conditions, but is preferably in the range of 1 x 10^{-4} to 1 x 10^{-9} mol per mol of silver halide, and more preferably in the range of 1 x 10^{-5} to 1 x 10^{-8} mol per mol of silver halide.

In the invention sulfur and gold sensitizers is preferably used in combination, and the mol ratio of selenium sulfur and gold sensitizers may be any, but the used amount of sulfur sensitizers is preferably not less than that of selenium sensitizers (by mole).

Other chemical sensitizers used include salts of a noble metal such as platinum, palladium or rhodium disclosed in US Patent Nos. 2,448,060, 2,566,245 and 2,566,263.

The chemical sensitizing can be also carried out in the presence of a thiocyanate such as ammonium thiocyanate or potassium thiocyanate or a tetra-substituted thiourea such as tetramethyl thiourea, which is a silver halide solvent.

In the invention a formula (I) or (II) compound is preferably used with reduction sensitizing, which is one of the embodiments of the invention. The reduction sensitising nucleus can be produced in inner portions or surfaces of silver halide grains under suitable reduction conditions. The reduction sensitising is preferably carried out during growth of silver halide grains described later. The reduction sensitizing during the silver halide grain growth includes a method of carrying out reduction sensitizing while the grain growth is suspended and then growing the reduction sensitized grains as well as a method of carrying out reduction sesitizing during the grain growth. Typically, the reduction sensitizing is carried out by adding a reducing agent and/or a water-soluble silver salt to the silver halide emulsion.

The preferable reducing agent includes thiourea dioxide, ascorbic acid and their derivatives. The other preferable reducing agent includes polyamines such as hydrazines or diethylenetriamines, dimethylamine boranes and sulfites. The addition amount of the reducing agent is preferably varied depending upon kinds of reducing agent, a silver halide grain size, a composition or crystal habit of silver halide, or conditions such as pH or pAg of a silver halide emulsion. For example, the addition amount of thiourea dioxide is preferably in the range of 0.01 to 2 mg per mol of silver halide, and the addition amount of ascorbic acid is preferably in the range of 0.2 to 50 g per mol of silver halide. The reduction sensitizing is preferably carried out for 10-200 minutes at 40-80° C, at pH 5-11 and at pAg 1-10.

The water-soluble silver salt is preferably silver nitrate. The silver ripening, which is one kind of reduction sensitizations, is carried out by adding the water-soluble silver salt. The pAg during the silver ripening is preferably 1 to 6, and the temperature, time, and pH is preferably in the range described above.

It is preferable that the reducing agent added during grain formation is deactivated by adding, at a specific period, an oxidizing agent such as hydrogen peroxide (an aqueous hydrogen peroxide solution) or its adducts, peroxo acid salts, ozone, I_2 or thiosulfonic acid, whereby action of the reducing agent is restrained or prevented. The oxidizing agent is added at any time from silver halide grain formation to addition of the gold sensitizer (additon of chemical senstizers when no gold sensitizing is carried out) at the chemical sensitizing process.

A halogen composition of the silver halide emulsions used in the present invention is arbitrary and may be such as silver bromide, silver bromoiodide, silver chloride, silver bromochloride, silver bromoiodochloride or silver iodochloride. These composition can be prepared by methods described in Shimmy et Physique Photographic written by P. Graphkidess (published by Paul Montel, 1967), Photographic Emulsion Chemistry written by G. F. Duffin (published by The Focsal Press, 1966), Making and Coating Photographic Emulsion written by V. L. Jerikman and others (published by The Focal Press, 1964), Japanese Patent O.P.I. Publication Nos. 39027/1976, 48521/1979, 142329/1980, 13928/1983 and 138538/1985 and Japan Photographic Academy 1983 Annual Congress Summary, page 88. Namely, any of an acid method, a neutral method and an ammonia method may be used. In addition, as a method to react soluble silver salt and soluble halogen salt, any of a one-side mixing method, a double ject method a mixing method thereof wherein grains are formed in presence of excessive silver ions (a reverse mixing method) and a method to supply soluble silver salt and soluble halogen salt to fine seed crystals for growing may be used.

The silver halide grain distribution in a silver halide emulsion may be narrow or broad, but the emulsion is preferably monodisperse, in which the grain size is uniform.

Typically, grain size distribution broadness, which is defined by relative standard deviation represented by the following equation, is preferably not more than 25%, and more preferably not more than 20%.

Grain size standard deviation/average grain size x 100
= grain size distribution broadness (%)

The average grain size used in the silver halide grains used in the invention is not specifically limited, but a side length, when the grain volume is represented in terms of a cubic, is 0.05 to 2.0 μm, and preferably 0.1 to 1.2 μm.

The silver halide grains in the silver halide emulsion used in the invention may be in the uniform form of cubic, octahedral or tetradecahedral, in the irregular form such as twinned crystal as tabular grains, or in the form of a mixture thereof. The silver halide grains preferably comprises tabular grains.

The twinned crystal is a silver halide crystal having one or more twin planes in the crystal. The classification of the twin crystal is detailed in Klein and Moizer, Photographische Korrespondenz 99, page 99 and 100, page 57. The twinned crystal grain used in the invention has mainly an even number of parallel twin planes, which may or may not be parallel with each other, and has especially preferably two twin planes.

As another embodiment used in the invention, tabular silver halide grains have an average aspect ratio of not less than 3, preferably 3 to 10, and more preferably 4 to 8. The average aspect ratio is defined as an average of a ratio, grain diameter/grain thickness. The crystal walls of the tabular silver halide grains may be substantially composed of a {111} face or a {100} face. Further, the crystal walls of the tabular silver halide grains may be composed of a mixture of {111} and {100} faces, in which the grains have a {111} face of preferably not less than 50%, more preferably not less than 60 to 90%, especially preferably not less than 70 to 95%. As a face other than a {111} face, a {100} face is preferable. The face ratio is obtained by a method described in T. Tani, J. Imaging Sci., 29, 165 (1985) which employs the sensitizing dye adsorption difference between {111} and {100} faces.

The thickness distribution in the silver halide grains used in the invention is preferably narrow.

Typically, the grain thickness distribution broadness, which is defined by the following equation, is preferably not more than 25%, and more preferably not more than 20%.

Grain thickness standard deviation/average grain thickness x 100
= grain thickness distribution broadness (%)

The halogen content distribution of each of the tabular silver halide grains used in the invention is preferably narrow.

Typically, the halogen content distribution broadness, which is defined by the following equation, is preferably not more than 25%, and more preferably not more than 20%.

Halogen content standard deviation/ average halogen content x 100
= halogen content distribution broadness (%)

The tabular silver halide grains are preferably in the form of a hexagon. The hexagonal tabular silver halide grains (hereinafter referred to also as hexagonal tabular grains) mean grains in which the main plane ({111} face) is hexagonal and the maximum adjacent side ratio is 1.0 to 2.0. The maximum adjacent side ratio means a ratio of the longest side length to the shortest side length in the hexagon. As long as the maximum adjacent side ratio in the hexagonal tabular grains is 1.0 to 2.0, the corners are preferably roundish. The tabular grains are also preferably circular without the corners. When the corners are roundish, the side length is represented by a length of a line combining intersections at which the extended lines of the side and its adjacent sides intersect. Not less than a half of each side in the hexagonal tabular grains are substantially a straight line, and the adjacent side ratio is more preferably 1.0 to 1.5.

The dislocation of silver halide grains can be observed by a direct method using a transmittance electron microscope at low temperature which is described in J. F. Hamilton, Phot. Sci. Eng., 57 (1967) or T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213 (1972). The grains are taken out from a silver halide emulsion not to apply pressure, which produces dislocation, to the grains, and put on a mesh for electron microscope observation. The resulting grains are cooled to prevent damage (for example, print-out) by an electron beam and observed by a transmission method. As the grains are thicker, an electronic beam is more difficult to transmit. Therefore, the grains can be observed more sharply by the usage of a high voltage type electron microscope (200 KV or more for 0.25 μm thick grains). The dislocation position or its number of each grain can be obtained from grain photographs obtained according to such a method. When the distance between the grain center and the grain surface is designated as L, the dislocation position of silver halide grains is preferably between 0.58L to 1.0L, and more preferably between 0.80L to 0/98L. The dislocation is in a line direction toward the grain surface from the grain center, but often is in a zigzag direction. The grain center herein referred to is defined as a method described in Inoue et al., Nihon Shashin Gakkai Koenyoshishu, p. 46-48. The silver halide fine grains are dispersed and fixed in a methacrylate resin and cut into a thin slice by a microtome to obtain a section of the grains. The grain center is a center of the minimum circumcircle of the grain sections in the slice having the maximum sectional area and the section having 90% or more of the maximum sectional area.

In the invention the distance L between the surface and the center is defined as a distance between the circle center and an intersection at which the lines extended from the center and the circumference of the grains intersect.

Regarding the number of the dislocation of silver halide grains, the content of grains comprising one or more dislocation are preferably not less than 50% by number. It is preferable that the content of tabular grains comprising the dislocation line is higher.

The grain size of the tabular grains is the diameter of a circular image area equivalent to a projection image of the grains. The projection image area of the grains is obtained from the sum of this grain area.

The grain size and projection image area can be obtained by observing, through an electron microscope, silver halide grains which are spread out on a flat surface such that the grains form a single layer.

The grain size of the average projection image of the tabular silver halide grains is represented by the diameter of a circle equivalent to the projection image area of the grains. The grain size is preferably not less than 0.30 μm, more preferably 0.30 to 5 μm, and still more preferably 0.40 to 2 μm. The grain size can be obtained by photographing the grains at a 10,000-70,000 magnification ratio by an electron microscope, obtaining a print thereof and then measuring the grain area of the photographed grains on the print. The average grain size (Φ_i) can be obtained from the following equation:

$$\text{Average grain size } (\Phi_i)=(\Sigma n_i d_i)/n$$

(at least 1000 randomly sampled grains were measured), wherein n represents the number of grains measured; Φ_i represents a grain size; and n_i represents the frequency of grains having grain size of Φ_i. The thickness of the grains is obtained by observing the grains at an angle through an electron microscope. The thickness of the tabular grains in the invention is preferably 0.03 to 1.0 μm, and more preferably 0.05 to 0.05 μm.

The ratio of the silver halide grain thickness (b) to the longest twin plane distance (a) of the silver halide grain having two or more parallel twin planes, (b/a), is preferably not less than 5, and the content of silver halide grains having the b/a ratio of not less than 5 is preferably 50% by number.

The twin plane distance (a) can be obtained from the following:

The samples are observed through a transmission electron microscope, and the (a) of 100 tabular silver halide grains showing sectional planes substantially perpendicular to the main planes is measured, and the arithmetic average is calculated. The average of (a) is preferably not less than 0.008 μm, and more preferably 0.010 to 0.05 μm. Further, the twin plane distance (a) is in the above range and at the same time its deviation coefficient is not more than 35% and preferably not more than 30%.

Further, taking into consideration an aspect ratio and grain thickness, the tabular property of silver halide grains is preferably not less than 20. The tabular property is represented by the following formula:

$$A = ECD/b^2$$

wherein ECD represents the average projection grain diameter (μ) of tabular silver halide grains; and b is the thickness of the grains. The average projection grain diameter herein referred to means the number average of the diameter of a circle equivalent to the projection area of the tabular grains. The silver halide grains used in the invention may be those of the core/shell type, which have at least two layer structures substantially different in halide composition, or those of a uniform halide composition, but are preferably those of the core/shell type. In the latter case, the grain center may have a halide composition different than the core of the grain. In such a case, the halogen composition of seed grains may be any combination selected from silver bromide, silver iodobromide, silver chloroiodobromide, silver chlorobromide, silver chloride and silver bromide. The core/shell type silver halide grains can be prepared according to methods described in West German Patent No. 1,169,290, British Patent No. 1,027,146, Japanese Patent O.P.I. Publication No. 57-15423/1982 and Japanese Patent Publication No. 51-1417/1986.

The average silver iodide content, in the silver halide emulsion regarding the invention, is preferably not more than 20 mol%, and more preferably 0.1 to 10 mol%. Of the grains having a layer structure different in halide composition, grains having a high silver iodide content layer in an inner portion of the grains and having a low silver iodide content layer or a silver bromide layer on the surface of the grains are preferable. It is preferable that the silver iodide content of the inner portion (core), which has the maximum silver iodide content, is preferably not less than 2.5 mol%, and more preferably 5 mol%, the silver iodide content of the surface (shell) is 0 to 10 mol%, and preferably 0 to 8 mol%, and further, the silver iodide content of the core is higher than that of the shell by at least 3%. The silver iodide distribution is usually uniform, but may be non-uniform. For example, the silver iodide content may gradually increase from the center to the outer portion of the grains or may have its maximum or minimum concentration in the intermediate portion of the grains.

The grains in the invention may be a so-called halogen conversion type. The halogen conversion amount is preferably 0.2 to 2.0 mol% based on the silver amount. The conversion stage may be during or after physical ripening. The halogen conversion method is carried out by adding a halide solution or fine silver halide grains which can form a silver halide having a solubility product lower than silver halide present on the silver halide grain surface before the conversion. The grain size of the fine silver halide grains is preferably not more than 0.2 μm, and more preferably 0.02 to 0.1 μm.

The silver iodide content or average silver iodide content in the silver halide grains can be obtained by an EPMA (Electron Probe Micro Analyzer) method. According to this method, elemental analysis of the minute portions can be carried out by X-ray analysis due to electron excitation which exposes, to an electron beam, well dispersed silver halide grains not in contact with each other. The halogen composition of each silver halide grain is obtained from the strength of characteristic X-rays of silver or iodine irradiated from each silver halide grain. The silver iodide content of at least one hundred grains is obtained by an EPMA method, and the average silver iodide content can be obtained therefrom.

Further, at least one metal ion selected from a cadmium salt, a zinc salt, a lead salt, a thallium salt, iridium salt (an iridium complex), a rhodium salt (a rhodium complex) and an iron salt (an iron complex) can be added to silver halide grains during formation and/or growth of the grains to incorporate this metal in the inner portion and/or on the surface of the grains.

In the silver halide emulsion used in the invention undesirable soluble salts may or may not be removed after the silver halide grain growth. The removal of the soluble salts can be carried out by the method described in Research Disclosure (hereinafter referred to as RD) No. 17643, Item II.

In the invention, two or more kinds of silver halide emulsions, which are separately prepared, can be used in admixture.

A hydrophilic protective colloid used for preparing the silver halide photographic light-sensitive material of the present invention includes gelatin derivatives such as acetylated gelatin and phthalated gelatin, water-soluble cellulose derivatives and other synthetic or natural hydrophilic polymers, in addition to gelatin for conventional silver halide emulsions as described in Product Licensing Index, Volume 92 on page 108 "Vehicle".

To the silver halide photographic light-sensitive material of the present invention, conventional technologies and additives can be added as necessary. For example, in addition to light-sensitive silver halide emulsion layer, auxiliary layers such as protective layers, filter layers, anti-halation layers, cross-over light cutting layers and backing layers may be provided. In the above-mentioned layers, various chemical sensitizers, noble metal sensitizers, light-sensitive dyes, super sensitizers, couplers, high boiling solvents, bleaching accelerators, fixing accelerators, antistaining agents, formalin scavengers, color tone agents, hardeners, surfactants, viscosity raising agents, plasticizers, lubricants, UV absorbers, anti-irradiation dyes, filter light absorption dyes, anti-mildew agents, polymer latexes, heavy metals, antistatic agents and matting agents can be added by various method. In addition, anti-foggants and development inhibitors can also be added in addition to the organic compounds of the present invention.

The above-mentioned additives are described in detail in Research Disclosure (hereinafter, abbreviated as "RD") Volume 176, Item/17643 (December, 1978), RD Volume 184, Item/18431 (August, 1979), RD Volume 187, Item/18716 (November, 1979) and RD Volume 308, Item/308119 (December, 1989).

The kinds of compounds illustrated in the above-mentioned three RDs and their description points are described as follows:

	[RD-17643]		[RD-18716]	[RD-308119]	
	Page	Category	Page	Page	Category
Chemical sensitizer	23	III	648 upper right	996	III
Sensitizing dye	23	IV	648-649	996-998	IV
Desensitizing dye	23	IV		998	IV
Dye	25-26	VIII	649-650	1003	VIII

development accelerator	29	XXI	648 upper right		
Anti-foggant, Development inhibitor	24	IV	649 upper right	1006-1007	VI
Brightening agent	24	V		998	V
Hardener	26	X	651 left	1004-1005	X
Surfactant	26-27	XI	650 right	1005-1006	XI
Anti-static agent	27	XII	650 right	1006-1007	XIII
Plasticizer	27	XII	650 right	1006	XII
Lubricant	27	XII			
Matting agent	28	XVI	650 right	1008-1009	XVI
Binder	26	XXII		1003-1004	IX
Support	28	XVII		1009	XVII

As a support usable for the silver halide photographic light-sensitive material of the present invenion, those described in the above-mentioned RD-17643, on page 28, RD-308119, on page 1009 and Product Licensing Index, Volume 92, on page 108, Item "Support" are cited.

As a preferable support, polyester cellulose triacetate, cellulose nitrate, polyethylene terephthalate and polyethylene-2,6-naphthalate, polyolefine such as polyethylene, polystyrene, baryta paper, paper wherein polyethylene is laminated, glass and metal are cited.

In order to improve adhesion of the coating layer, the surface of the support may be provided with subbing processing such as corona discharge processing, UV ray irradiation and provision of a subbing polymer adhesive layer.

The silver halide photographic light-sensitive material of the present invention may be any silver halide photographic light-sensitive material as long as it includes the above-mentioned light-sensitive silver halide emulsion. For example, black-and-white silver halide photographic light-sensitive materials (such as a medical light-sensitive material, a graphic arts light-sensitive material, a microfilm light-sensitive material and a negative film light-sensitive material for amateur use), color photographic light-sensitive materials (such as a color negative light-sensitive material, a color reversal light-sensitive material and a color print light-sensitive material), diffusion transfer light-sensitive materials and thermal development light-sensitive materials may be used.

When the silver halide photographic light-sensitive material of the present invention is subjected to photographic processing, developing agents described in Product Licensing Index, Volume 92, on page 110, Item "Process", The Theory of the Photographic Process, fourth Edition, pp 291 to 334 and Journal of the American Chemical Society, Volume 73, on page 3100 (1951)can be preferable.

EXAMPLES

The invention will be detailed according to the following examples, but is not Example limited thereto.

Example 1

Preparation of twinned crystal seed emulsion (T-1)

The seed emulsion 2 was prepared according to descriptions of Japanese Patent O.P.I. Publication No. 5-34851/1993 and the following method, which comprised grains having two parallel twin planes.

(Solution A)

Ossein gelatin	80.0 g
Potassium bromide	47.4 g
$HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_{19.8}(CH_2CH_2O)_nH$ (m+n=9.77, 10% methanol solution)	0.48 ml
Water was added to make 8000.0 ml.	

(Solution B)

Sodium nitrate	1200.0 g
Water was added to make 1600.0 ml.	

(Solution C)

Ossein gelatin	32.2 g
Potassium bromide	790.0 g
Potassium iodide	70.34 g
Water was added to make 1600 ml.	

(Solution D)

Aqueous ammonia	470.0 ml

By the use of a mixing stirrer described in Japanese Patent Publication Nos. 62-160128/1987, Solutions B and C were added to Solution A with vigorous stirring in 7.7 minutes at 40°C by a double-jet method to form a nuclei. During the process, pBr was kept at 1.60.

Thereafter, the temperature of the resulting emulsion was lowered to 20°C in 35 minutes, and Solution D was added thereto and ripened for 20 minutes. During the ripening, the concentrations of potassium bromide and ammonia were kept at 0.03 mol/liter and 0.66 mol/liter, respectively.

After the ripening, the resulting emulsion was adjusted to pH 6.0, and desalted according to an ordinary method.

When this seed emulsion was observed by means of an electron microscope, they had silver halide grains having an average diameter of 0.225 µm in which two parallel twin plane grains was 75% based on the total grain number.

Preparation of Emulsion (EM-1)

Emulsion (Em-1) was prepared using the following five solutions.

(Solution A-1)

Ossein gelatin	66.5 g
Distilled water	3227.0 ml
$HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_{19.8}(CH_2CH_2O)_nH$	

(continued)

(m+n=9.77, 10% methanol solution)	2.50 ml
Seed emulsion (T-1)	98.5 g
Distilled water was added to make 3500.0 ml.	

(Solution B-1)

3.5N Sodium nitrate solution	4702.0 ml

(Solution C-1)

Potassium bromide	2499.0 g
Distilled water was added to make 6000 ml.	

(Solution D-1)

*Fine gain emulsion containing a 3 weight % gelatin solution and silver iodide grains having an average grain size of 0.05 µm

(*) Preparation of fine gain emulsion)

Two hundred milliliters of each of a 7.06 mol $AgNO_3$ solution and a 7.06 mol KI solution was added in 10 minutes to five hundred milliliters of a 6.0 weight % gelatin solution containing 0.06 mol of KI. During the fine grain formation, the temperature was 40°C. The resulting emulsion was 12.53 kg. After the grain formation the pH was adjusted to 6.0 using a sodium carbonate solution.

(Solution E-1)

Aqueous 1.75N KBr solution	a necessary amount

Solution A-1 was placed in a reaction vessel and solutions B-1 through D-1 were added with vigorous stirring according to Table 1 by a double-jet method. The seed grains were grown and a core/shell type silver halide emulsion was prepared.

Herein, the addition rates of solutions B-1, C-1 and D-1 and solutions B-1 and C-1 was varied as a function of time to meet a critical grain growing rate, and suitably controlled not to produce fine grains other than the seed grains and not to cause polydispersion due to Ostwald ripening.

During grain crystal growth, the temperature was kept at 75°C and pAg 8.8. In order to control pAg, E-1 was optionally added with solution E-1. The pH was not controlled, but kept at 5.0 to 6.0 during the grain growth. The added silver amount at the addition time of the solutions and the silver iodide content of silver halide grains during grain growth are also shown in Table 1.

After the grain growth, the resulting emulsion was subjected to desalting according to descriptions of Japanese Patent O.P.I. Publication No. 5-72658/1993. To the resulting emulsion were added 1.19 liter of a 20 weight % aqueous gelatin solution and dispersed at 50°C for 30 minutes. After the dispersion, the emulsion was adjusted to give pH of 5.80 and pBr of 3.55.

The resulting emulsion had tabular silver halide grains having an average grain size of 1.34 µm (diameter to circle according to projected area), an average aspect ratio of 2.6 and a grain size distribution broadness of 18%.

Table 1

Solutions to be added	Time to be added (minute)	Silver amount to be added (%)	Silver iodide content (mol%)
(1)B-1,C-1,D-1	0.00	0.0	10.0

Table 1 (continued)

Solutions to be added	Time to be added (minute)	Silver amount to be added (%)	Silver iodide content (mol%)
│	30.99	3.0	10.0
│	52.47	6.0	10.0
│	76.48	10.0	10.0
│	76.48	10.0	30.0
│	117.30	18.0	30.0
│	150.13	25.0	30.0
│	150.13	25.0	10.0
↓	176.09	31.0	10.0
(2)B-1,C-1	176.09	31.0	0.0
	209.51	50.0	0.0
	221.07	64.0	0.0
	230.68	80.0	0.0
	239.00	100.0	0.0

Preparation of Emulsion (EM-2)

Emulsion (EM-2) was prepared in the same manner as in Emulsion (EM-2), except that pAg in the reaction vessel during grain formation was adjusted to 9.3 and the addition rates of solutions (B-1), (C-1) and (D-1) were varied to be in accordance with critical formation rate of the grains.

The resulting emulsion had tabular silver halide grains having an average grain size of 1.51 µm (diameter to circle according to projected area), an average aspect ratio of 3.7 and a grain size distribution broadness of 21%.

Preparation of Emulsion (EM-3)

Emulsion (EM-2) was prepared in the same manner as in Emulsion (EM-2), except that pAg in the reaction vessel during grain formation was adjusted to 9.8 and the addition rates of solutions (B-1), (C-1) and (D-1) were varied to be in accordance with critical formation rate of the grains.

The resulting emulsion had tabular silver halide grains having an average grain size of 1.60 µm (diameter to circle according to projected area), an average aspect ratio of 4.4 and a grain size distribution broadness of 22%.

Preparation of Emulsion (EM-4)

Emulsion (EM-4) was prepared in the same manner as in Emulsion (EM-3), except that the following procedures were carried out: When 6% of the total silver addition amount after addition of solutions (B-1), (C-1) and (D-1) were added, pH of the resulting emulsion was adjusted to 8.0 with a 10% potassium hydroxide solution. After the grain growth, the emulsion was desalted, 1.19 liter of a 20% gelatin solution were added, dispersed at 50°C for 15 minutes, pAg was adjusted to 1.5 with a 3.5N potassium bromide solution at 50°C, the following solution H-0 was added with stirring in 30 seconds, was stirred for another 20 minutes, pH was adjusted to 5.80 and pBr was adjusted to 3.55.

Solution H-0

Fine grain emulsion comprising gelatin in an amount of 3 weight % and silver bromide grain (an average grain size of 0.04 µm) 0.212 mol in terms of silver

The pH change in the reaction vessel was as follows:

Added Amount of silver (%)	pH in the vessel
6.0	8.00
10.0	7.51
25.0	6.40
31.0	6.36
100.0	5.84

Preparation of Emulsion (EM-5)

Emulsion (EM-5) was prepared in the same manner as in Emulsion (EM-3), except that, when 6% of the total silver addition amount after addition of solutions (B-1), (C-1) and (D-1) were added, the following solution K-1 was added.

Solution K-1

A solution containing thiourea dioxide in an amount of 1 x 10^{-6} per mole of silver of Emulsion EM-5

Preparation of Emulsion (EM-6)

Emulsion (EM-6), which had the same halide composition as Emulsion (EM-1), was prepared according to methods described in Japanese Patent O.P.I. Publication Nos. 60-138538/1985.

The resulting emulsion (EM-6) had octahedron silver halide grains having an average grain size of 0.9 μm (corresponding to a side length of a cubic having the same volume as the grains) and a grain size distribution broadness of 17%.

Table 2 shows characteristics of EM-1 through EM-6.

Table 2

Emulsion No.	Average grain size (μm)	Average aspect ratio	Grain size distribution broadness (%)	Average silver iodide content (mol%)	Reduction sensitization
EM-1	1.34*	2.6	18	6.1	None
EM-2	1.51*	3.7	21	6.1	None
EM-3	1.60*	4.4	22	6.1	None
#EM-4	1.57*	4.2	21	6.0	pH8.0
EM-5	1.60*	4.4	23	6.1	Thiourea dioxide
EM-6	0.90**	-	17	6.1	None

* grain diameter in terms of circle corresponding to projected area

** a side length of a cubic having the same volume as the grains

Reduction sensitization was carried out by controlling pH and pAg.

Example 2

Sensitization of emulsion

To Emulsion (EM-3) prepared in Example 1 was added 9.5 x 10^{-5} mol/mole Ag of sensitizing dye S-1 described later, 9.5 x 10^{-5} mol/mole Ag of sensitizing dye S-2 described later, 9.5 x 10^{-5} mol/mole Ag of sensitizing dye S-3 described later, sodium thiosulfate (in an amount as shown in Table 3), selenium or tellurium sensitizer (in an amount as shown in Table 3), 3.2 x 10^{-6} mol/mole Ag of chloroauric acid and 8.0 x 10^{-4} mol/mole Ag of ammonium thiocyanate at 50°C, and ripened for a specific period, whereby optimum spectral and chemical sensitizations were carried out.

Thereafter, 600 mg/mole Ag of Stabilizer ST-1 described later, and Comparative anti-foggant AF-1 (in an amount as shown in Table 3) or inventive compound (in an amount as shown in Table 3) were added, and cooled to be allowed to stabilize.

Thus, sensitized emulsions SEM-3a through SEM-3n were prepared.

Table 3

Sensitized emulsion No.	Sodium thiosulfate (mol)	Selenium or tellurium sensitizer (mol)	AF-1 (mol)	Inventive compounds (mol)
SEM-3a	5.4×10^{-5}	-	2.5×10^{-4}	-
SEM-3b	5.4×10^{-5}	-	-	(a-1) 2.5×10^{-4}
SEM-3c	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-

Table 3 (continued)

Sensitized emulsion No.	Sodium thiosulfate (mol)	Selenium or tellurium sensitizer (mol)	AF-1 (mol)	Inventive compounds (mol)
SEM-3d	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}
SEM-3e	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-6) 2.5×10^{-4}
SEM-3f	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-12)2.5×10^{-4}
SEM-3g	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-14)2.5×10^{-4}
SEM-3h	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-43)2.5×10^{-4}
SEM-3i	4.3×10^{-5}	(b-19)1.1×10^{-5}	2.5×10^{-4}	-
SEM-3j	4.3×10^{-5}	(b-19)1.1×10^{-5}	-	(a-4) 2.5×10^{-4}
SEM-3k	4.3×10^{-5}	(b-19)1.1×10^{-5}	-	(a-41)2.5×10^{-4}
SEM-3l	4.3×10^{-5}	(c-4) 1.1×10^{-5}	2.5×10^{-4}	-
SEM-3m	4.3×10^{-5}	(c-4) 1.1×10^{-5}	-	(a-1) 2.5×10^{-4}
SEM-3n	4.3×10^{-5}	(c-4) 1.1×10^{-5}	-	(a-43)2.5×10^{-4}

The addition amount was based on 1 mol of silver halide.

(Preparation of a silver halide photographic light sensitive material)

A subbing layer was coated on one side of a triacetylcellulose film support, and the following composition layers were coated in order on the surface of the support opposite the subbing layer.

Rear side first layer

Aluminazol AS-100 (aluminum oxide) (produced by Nissan Chemical Co., Ltd.)	0.8 g

Rear side second layer

Diacetyl cellulose	100 mg
Stearic acid	10 mg
Silica fine particles (average particle size 0.2 μm)	50 mg

On the surface of a triacetyl cellulose film support provided with subbing, the following individual layers, whose composition is shown below, were formed so that color photographic light-sensitive materials (Sample Nos. 1 through 14) were prepared.

First layer: Anti-halation layer (HC)

Black colloidal silver	0.15 g
UV absorber (UV-1)	0.20 g
Dye (CC-1)	0.02 g
High boiling solvent (Oil-1)	0.20 g
High boiling solvent (Oil-2)	0.20 g
Gelatin	1.6 g

Second layer: Intermediate layer (IL-1)

Gelatin	1.3 g

Third layer: Silver halide light-sensitive layer

Sensitized emulsion (SEM-3a-3n, shown in Table 4)	1.8 g (in terms of silver)
Magenta coupler (M-1)	0.30 g
Magenta coupler (M-2)	0.13 g
Colored magenta coupler (CM-1)	0.04 g
DIR compound (D-1)	0.004 g
High boiling solvent (Oil-2)	0.35 g
Gelatin	1.0 g

Fourth layer: First protective layer (Pro-1)

Fine particle silver bromide emulsion (average grain size was 0.08 µm)	0.3 g
UV absorber (UV-1)	0.07 g
UV absorber (UV-2)	0.10 g
Additive 1 (HS-1)	0.2 g
Additive 2 (HS-2)	0.1 g
High boiling solvent (Oil-1)	0.07 g
High boiling solvent (Oil-3)	0.07 g
Gelatin	0.8 g

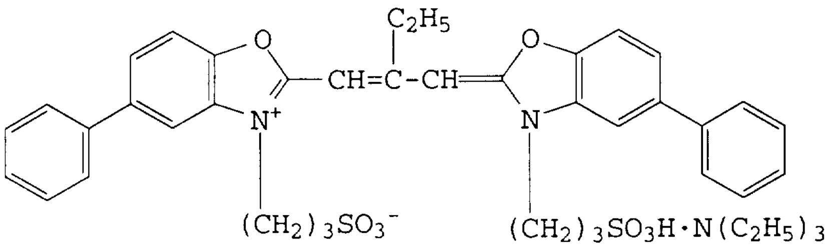
Fifth layer: Second protective layer (Pro-2)

Additive 3 (HS-3)	0.04 g
Additive 4 (HS-4)	0.01 g
Polymethylmethacrylate (average grain sizet was 3 µm)	0.02 g
Methylmethacrylate:ethylmethacrylate:methacrylic acid copolymer (3:3:4 in terms of weight ratio) (Average grain size was 3 µm)	0.13 g
Gelatin	0.5 g

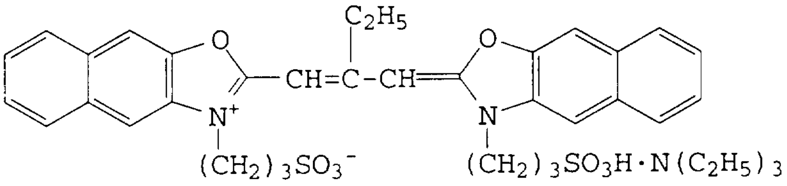
The above compositions was further added with surfactants SA-1, SA-2 and SA-3, a viscosity adjusting agent, hardeners H-1 and H-2, stabilizing agent ST-2 (an agent having a weight average molecular weight of 10,000 and a agent having a weight average molecular weight of 1,100,000, respectively) and antiseptic DI-1.

Oil-1 : Dioctylphthalate
Oil-2 : Tricresylphosphate
Oil-3 : Dibutylphthalate
SH-1 : Hydantoin
SH-2 : 4-Ureidohydantoin
SH-3 : Sodiumsulfo di(2,2,3,3,4,4,5,5,6,6,7,7-dodecylfluoroheptyl) succinate
SA-1 : Sodium tri-i-propylnaphthalene sulfonate
SA-2 : Sodiumsulfo di(2-ethylhexyl) succinate
SA-3 : Sodium benzene sulfonate
H-1 : Sodium 2,4-dichlore-6-hydroxy-s-triazine
H-2 : 1,2-bis(α-vinylsulfoylacetoamido)ethane

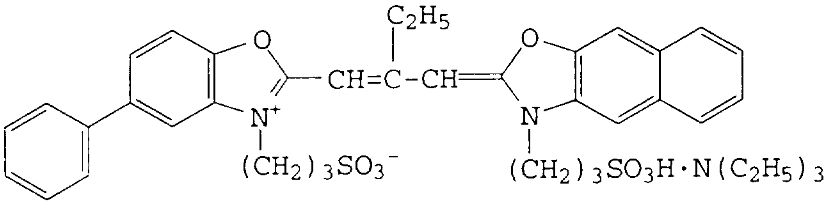
S-1



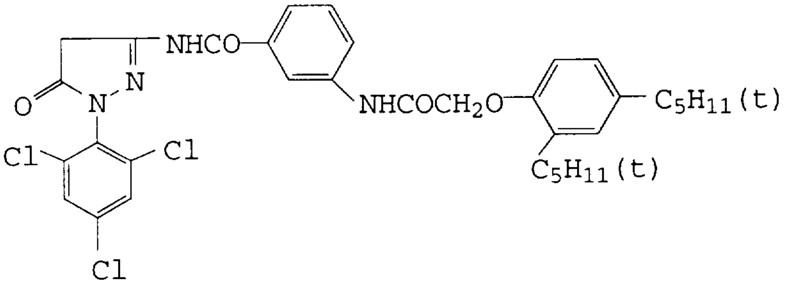
S-2



S-3



M-1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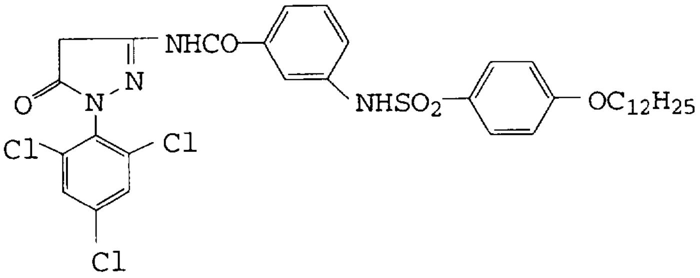
N
N
O
Cl
Cl
Cl
NHCOCH2O
C5H11(t)
C5H11(t)

M-2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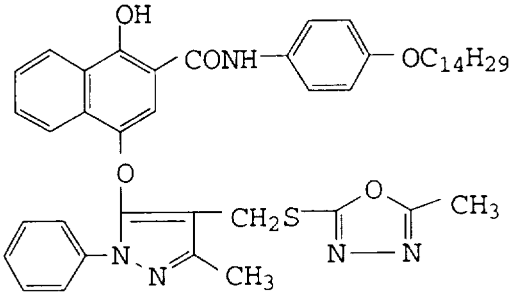
Cl
Cl
Cl
NHSO2
OC12H25

D-1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CONH
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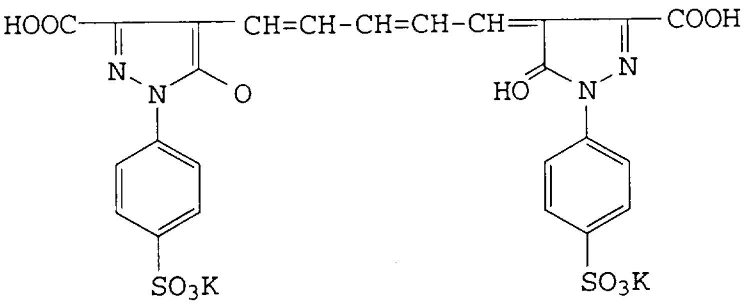
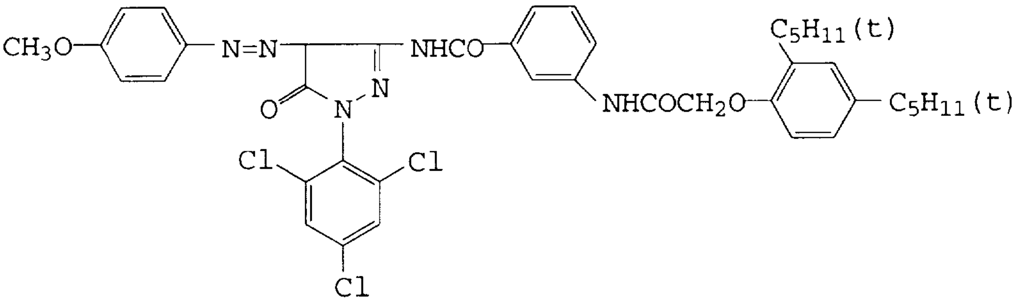
O
CH2S
O
CH3
N
N
N
N
CH3

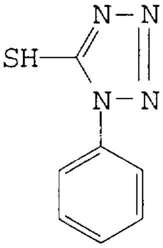
CC-1



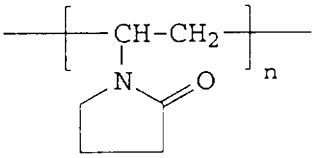
CM-1



AF-1

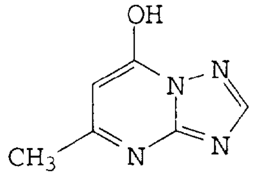


ST-2

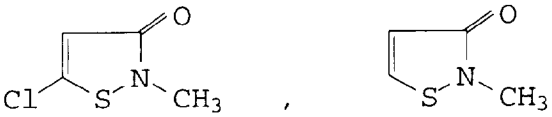


n: polymerization degree

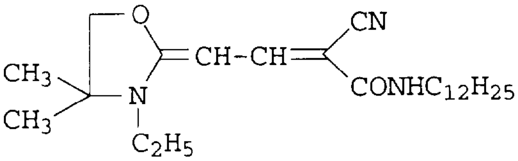
ST-1



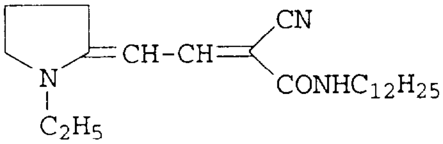
DI-1 (a mixure of the following components



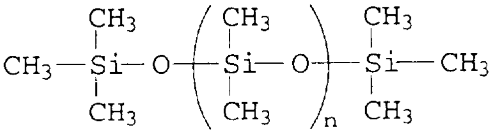
UV-1



UV-2



HS-4



Average weight molecular weigtht Mw = 3,000

(Evaluation of photographic properties)

The above obtained sample Nos. 1 through 14 were divided into two groups A and B. The A group samples were wedge exposed according to an ordinary method, and processed according to the following processing steps. The B group samples were stored at 55°C and at 80%RH for 7 days, and thereafter, the resulting samples were wedge exposed and processed in the same manner as in A group above. The optical density of the processed samples were measured by means of through an optical densitometer PDA-65 (produced by Konica Corporation).

The fog and sensitivity at green density of the resulting samples of groups A and B are shown in Table 4.

Sensitivity was represented by a reciprocal of exposure necessary to give a green density of fog plus 0.30, and sensitivity of the samples was represented by a relative sensitivity when sensitivity of sample No. 1 (A group) is 100. The results are shown in Table 4.

(Processing Steps)

Processing Step	Processing Time	Processing Temperature	Replenishing Amount*
Color developing	3 min. 15 sec.	38 ± 0.3°C	780 ml
Bleaching	45 sec.	38 ± 2.0°C	150 ml
Fixing	1 min. 30 sec.	38 ± 2.0°C	830 ml
Stabilizing	60 sec.	38 ± 5.0°C	830 ml
Drying	1 min.	38 ± 5.0°C	-

* Replenishing amount is an amount per m^2 of light sensitive material processed.

A color developing solution, a bleaching solution, a fixing solution and their respective replenishing solutions were prepared in the following manner.

Color developing solution and color developing replenishing solution

	Developing Solution	Replenishing Solution
Water	800 ml	800ml
Potassium carbonate	30 g	35 g
Sodium hydrogencarbonate	2.5 g	3.0 g
Potassium sulfite	3.0 g	5.0 g
Sodium bromide	1.3 g	0.4 g
Potassium iodide	1.2 mg	-
Hydroxylamine sulfate	2.5 g	3.1 g
Sodium chloride	0.6 g	-
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.5 g	6.3 g
Diethylene triamine pentaacetic acid	3.0 g	3.0 g
Potassium hydroxide	1.2 g	2.0 g

Water was added to make 1 liter, and the developing solution was regulated to pH 10.06 and the replenishing developing solution was regulated to pH 10.18 by the use of potassium hydroxide or a 20% surfuric acid solution. Bleaching solution and bleaching replenishing solution

	Bleachig Solution	Replenishing Solution
Water	700 ml	700 ml
Ferric (III) ammonium of 1,3-diaminopropane tetraacetic acid	125 g	175 g

Ethylenediamine tetraacetic acid	2 g	2 g
Sodium nitrate	40 g	50 g
Ammonium bromide	150 g	200 g
Glacial acetic acid	40 g	56 g

Water was added to make 1 liter, and the bleaching solution was regulated to pH 4.4 and the replenishing bleaching solution was regulated to pH 4.0 by the use of aqueous ammonia or glacial acetic acid.

Fixing solution and fixing replenishing solution

	Fixing Solution	Replenishing Solution
Water	800 ml	800 ml
Ammonium thiocyanate	120 g	150 g
Ammonium thiosulfate	150 g	180 g
Sodium sulfite	15 g	20 g
Ethylenediamine tetraacetic acid	2 g	2 g

The fixing solution was regulated to pH 6.5 and the replenishing solution to pH 4.4 by the use of aqueous ammonia or glacial acetic acid, and then, water was added to make 1 liter.

Stabilizing solution and stabilizing replenishing solution

Water	900 ml
Substance to which 10 mol of p-octylphenol ethyleneoxide was added	2.0 g
Dimethylol urea	0.5 g
Hexamethylene tetraamine	0.2 g
1,2-benzisothiazoline-3-on	0.1 g
Siloxane (L-77 produced by UCC)	0.1 g
Aqueous ammonia	0.5 ml

Water was added to make 1 liter, and pH was regulated to 8.5 by the use of aqueous ammonia or a 50% sulfuric acid solution.

Table 4

Sample No.	Sensitized emulsion	A group		B group		Remarks
		Fog	Sensitivity	Fog	Sensitivity	
1	SEM-3a	0.12	100	0.18	62	Comparative
2	SEM-3b	0.13	193	0.18	158	Invention
3	SEM-3c	0.20	162	0.29	94	Comparative
4	SEM-3d	0.18	334	0.24	308	Invention
5	SEM-3e	0.20	341	0.26	282	Invention
6	SEM-3f	0.19	337	0.27	301	Invention
7	SEM-3g	0.18	330	0.25	295	Invention
8	SEM-3h	0.20	345	0.26	306	Invention
9	SEM-3i	0.23	145	0.33	85	Comparative
10	SEM-3j	0.22	287	0.30	251	Invention
11	SEM-3k	0.24	270	0.32	233	Invention
12	SEM-3l	0.28	184	0.37	103	Comparative
13	SEM-3m	0.26	383	0.33	334	Invention
14	SEM-3n	0.28	359	0.34	310	Invention

As is apparent from Table 4, the compound of the invention in combination of selenium or tellurium sensitized emulsion gives high sensitivity with reduced fog, and minimizes deterioration of photographic properties such as fog increase and sensitivity lowering due to storage. Example 3

Sensitization of emulsion

Emulsion (EM-4) and (EM-5), which were prepared in Example 1, were subjected to optimum spectral and chemical sensitization and stabilized in the same manner as Emulsion (EM-3) in Example 2. Thus, Sensitized emulsion 4a through 4j, and 5a through 5e were obtained. The addition amount of sodium thiosulfate, selenium or tellurium sensitizer or anti-foggant AF-1 or inventive compound was shown in Table 5.

(Preparation of a silver halide photographic light sensitive material and evaluation of its photographic properties)

Light sensitive material sample Nos. 31 through 45 were prepared in the same manner as in Sample No. 1 of Example 2, except that sensitized emulsions as shown in Table 6 were used in the third layer. The above obtained samples were evaluated for photographic properties in the same manner as in Example 2. The results are shown in Table 6.

Table 5

Sensitize emulsion No.	Sodium thiosulfate (mol)	Selenium or tellurium sensitizer (mol)	AF-1 (mol)	Inventive compounds (mol)
SEM-4a	5.4×10^{-5}	-	2.5×10^{-4}	-
SEM-4b	5.4×10^{-5}	-	-	(a-1) 2.5×10^{-4}
SEM-4c	5.4×10^{-5}	-	-	(a-12)2.5×10^{-4}
SEM-4d	5.4×10^{-5}	-	-	(a-45)2.5×10^{-4}
SEM-4e	5.4×10^{-5}		-	(a-48)2.5×10^{-4}
SEM-4f	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-
SEM-4g	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}

Table 5 (continued)

Sensitize emulsion No.	Sodium thiosulfate (mol)	Selenium or tellurium sensitizer (mol)	AF-1 (mol)	Inventive compounds (mol)
SEM-4h	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-45)2.5×10^{-4}
SEM-4i	4.3×10^{-5}	(c-4) 1.1×10^{-5}	3.8×10^{-4}	
SEM-4j	4.3×10^{-5}	(c-4) 1.1×10^{-5}	-	(a-1) 3.8×10^{-4}
SEM-5a	5.4×10^{-5}	-	2.5×10^{-4}	-
SEM-5b	5.4×10^{-5}	-	-	(a-1) 2.5×10^{-4}
SEM-5c	5.4×10^{-5}	-	-	(a-45)2.5×10^{-4}
SEM-5d	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-
SEM-5e	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}

The addition amount was based on 1 mol of silver halide.

Table 6

Sample No.	Sensitized emulsion	A group		B group		Remarks
		Fog	Sensitivity	Fog	Sensitivity	
31	SEM-4a	0.17	129	0.26	78	Comparative
32	SEM-4b	0.17	205	0.25	174	Invention
33	SEM-4c	0.18	221	0.27	196	Invention
34	SEM-4d	0.18	214	0.26	179	Invention
35	SEM-4e	0.19	225	0.27	194	Invention
36	SEM-4f	0.23	175	0.35	102	Comparative
37	SEM-4g	0.21	372	0.31	328	Invention
38	SEM-4h	0.23	363	0.32	318	Invention
39	SEM-4i	0.26	193	0.39	111	Comparative
40	SEM-4j	0.24	398	0.32	351	Invention
41	SEM-5a	0.19	124	0.29	66	Comparative
42	SEM-5b	0.18	193	0.25	165	Invention
43	SEM-5c	0.20	199	0.26	168	Invention
44	SEM-5d	0.26	173	0.44	92	Comparative
45	SEM-5e	0.26	339	0.36	296	Invention

As is apparent from Table 6 and the results of sample Nos. 1 and 2 in Table 4, the compound of the invention in combination of reduction sensitiozed emulsion gives high sensitivity with reduced fog, and minimizes deterioration of photographic properties such as fog increase and sensitivity lowering due to storage.

Example 4

Sensitization of emulsion

Emulsion (EM-1), (EM-2) and (EM-6), which were prepared in Example 1, were subjected to optimum spectral and chemical sensitization and stabilized in the same manner as Emulsion (EM-3) in Example 2. Thus, Sensitized emulsion la through lc, 2a through 2c and 6a through 6e were obtained.

The addition amount of sensitizing dyes S-1, S-2 and S-3 was varied according to the suface area of the silver halide grains in the emulsion. The addition amount of sodium thiosulfate, selenium or tellurium sensitizer or anti-foggant

AF-1 or inventive compound was shown in Table 7.

Table 7

Sensitized emulsion No.	Sodium thiosulfate (mol)	Selenium or tellurium sensitizer (mol)	AF-1 (mol)	Inventive compounds (mol)
SEM-1a	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-
SEM-1b	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}
SEM-1c	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-43)2.5×10^{-4}
SEM-2a	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-
SEM-2b	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}
SEM-2c	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-43)2.5×10^{-4}
SEM-6a	3.6×10^{-5}	(b-1) 1.8×10^{-5}	2.5×10^{-4}	-
SEM-6b	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-1) 2.5×10^{-4}
SEM-6c	3.6×10^{-5}	(b-1) 1.8×10^{-5}	-	(a-43)2.5×10^{-4}
SEM-6d	5.4×10^{-5}	-	2.5×10^{-4}	-
SEM-6e	5.4×10^{-5}	-	-	(a-1) 2.5×10^{-4}

The addition amount was based on 1 mol of silver halide.

(Preparation of a silver halide photographic light sensitive material and evaluation of its photographic properties)

Light sensitive material sample Nos. 51 through 61 were prepared in the same manner as in Sample No. 1 of Example 2, except that sensitized emulsions as shown in Table 7 were used in the third layer. The above obtained samples were evaluated for photographic properties in the same manner as in Example 2. The results are shown in Table 8.

Table 8

Sample No.	Sensitized	A group		B group		Remarks
		Fog	Sensitivity	Fog	Sensitivity	
51	SEM-1a	0.21	121	0.31	70	Comparative
52	SEM-1b	0.19	281	0.24	250	Invention
53	SEM-1c	0.20	272	0.25	246	Invention
54	SEM-2a	0.20	134	0.31	72	Comparative
55	SEM-2b	0.19	305	0.25	277	Invention
56	SEM-2c	0.20	293	0.25	258	Invention
57	SEM-6a	0.21	107	0.30	59	Comparative
58	SEM-6b	0.20	243	0.24	202	Invention
59	SEM-6c	0.20	236	0.26	195	Invention
60	SEM-6d	0.21	74	0.30	35	Comparative
61	SEM-6e	0.20	66	0.28	31	Comparative

As is apparent from Table 8 and the results of sample Nos. 3 through 5 in Table 4, the compound of the invention in combination of tabular grains having a larger aspect ratio gives high sensitivity with reduced fog, and minimizes deterioration of photographic properties such as fog increase and sensitivity lowering due to storage.

Example 5

Sensitized emulsion SEM-4K was prepared in the same manner as sensitized emulsion SEM-4f in Example 3, except that anti-foggant AF-1 was not added. Light sensitive material sample Nos. 71 through 75 were prepared in the same manner as in Sample No. 36 of Example 3, except that sensitized emulsion SEM-4K was used instead of sensitized emulsion SEM-4f and inventive compound a-4 as shown in Table 9 was added.

Table 9

Sample	Layer in which a-4 was added	Addition amount of a-4 (mol/m^2)
71	First Layer	2.5×10^{-5}
72	Second Layer	2.5×10^{-5}
73	Third Layer	6.0×10^{-6}
74	Fourth Layer	2.5×10^{-5}
75	Fifth Layer	2.5×10^{-5}m

The above obtained samples were evaluated for photographic properties in the same manner as in Example 2. The results are shown in Table 10.

Table 10

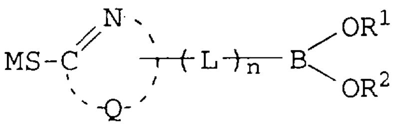
Sample No.	A group		B group	
	Fog	Sensitivity	Fog	Sensitivity
71	0.30	425	0.45	345
72	0.24	408	0.38	352
73	0.24	403	0.32	358
74	0.26	410	0.37	364
75	0.31	419	0.43	352

As is apparent from Table 10, the compound of the invention can give the effect of the invention, even if it is contained in any hydrophilic colloid layer of a silver halide photographic light sensitive material, and it is especially useful when it is contained in a silver halide emulsion layer or its adjacent layer.

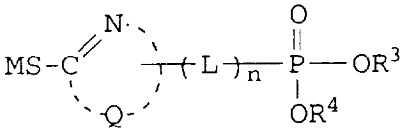
Claims

1. A silver halide photographic light sensitive material comprising a support and provided thereon, a light sensitive silver halide emulsion layer containing selenium, tellurium or reduction sensitized silver halide grains, wherein said light sensitive silver halide emulsion layer or another hydrophilic colloid layer on said silver halide emulsion layer side contains a compound represented by the following formula (I) or (II):

formula [I]



formula [II]



wherein M represents a hydrogen atom, a metal atom or a quaternary ammonium group; Q represents a non-metal atomic group necessary to form a single or condensed heterocyclic ring; L represents a divalent group selected from the group consisting of an alkylene group, an arylene group, an aromatic heterocyclic divalent group, -O-, -S-, -NH-, -C(=O)O-, -CONH- and -SO_2- and their mixture divalent group; n is an integer of 0 to 2; and R^1, R^2, R^3, and R^4 independently represent a hydrogen atom, a cation, a nitro, nitroso, cyano, carboxy, sulfo, mercapto or hydroxy group, a halogen atom, an alkyl group, an aralkyl group, an alkenyl group, an alkinyl group, an aryl group, a heterocyclic ring group, an acyl group, a sulfonyl group, an amino group, an alkoxy group, an aryloxy group, a heteroaryloxy group, an alkylthio group, an arylthio group, a heteroarylthio group, an ammonio group, a carbamoyl group, a sulfamoyl group, an acylamino group, an acyloxy group, a sulfonylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an aminocarbonylamino group, an aminocarbonyloxy group, an aminosulfonylamino group, a sulfonyloxy group, an alkoxycarbonyl or aryloxycarbonyl group, or R^1 and R^2 combine with each other to form a ring and R^3 and R^4 combine with each other to form a ring.

2. The silver halide photographic light sensitive material of claim 1, wherein said light sensitive silver halide emulsion layer contains said compound in an amount of 1×10^{-6} to 1×10^{-1} mol per mol of silver.

3. The silver halide photographic light sensitive material of claim 1, wherein said hydrophilic colloid layer contains said compound in an amount of 2×10^{-5} to 0.2 g per m^2.

4. The silver halide photographic light sensitive material of claim 1, wherein said silver halide emulsion layer contains silver halide grains having an average aspect ratio of not less than 2.

5. The silver halide photographic light sensitive material of claim 1, wherein in formulae (I) and (II), said Q includes an imidazole ring, a pyrazole ring, a triazole ring, a tetrazole ring, an oxazole ring, a thiazole ring, a selenazole ring, a tellurazole ring, an oxadiazole ring, a thiadizole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, a benzoimidazole ring, a benzooxazole ring, a benzothiazole ring and a tetrazaindene ring.

6. The silver halide photographic light sensitive material of claim 1, wherein in formulae (I) and (II), said L represents at least one selected from the group consisting of an alkylene group, an arylene group, an aromatic heterocyclic group, an ether group, a thioether group, an imino group, an ester group, an amido group and a sulfonyl group.

7. The silver halide photographic light sensitive material of claim 1, wherein at least one of said R^1 and R^2 in formula (I) represents a hydrogen atom; and at least one of said R^3 and R^4 in formula (II) represents a hydrogen atom.