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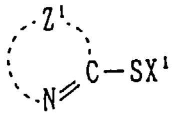
(54) A method for development processing of silver halide photographic materials

(57) A method for continuously developing an exposed silver halide photographic material containing a hydrazine derivative by an automatic processor, wherein the development is carried out by using a developer being substantially free from a dihydroxybenzene compound and containing an ascorbic acid and/or a derivative thereof as a developing agent, an aminophenol derivative as an auxiliary developing agent which exhibits a superadditive property and at least 0.5 mol/liter of a carbonate as a buffer, and wherein the developer is replenished with a developing replenisher having a pH at least 0.2 higher than that of the starting developing solution. In a preferred embodiment, the developing replenisher contains a silver stain inhibitor represented by the following general formula (1):



(1)

The symbols in the above general formula (1) are defined in the specification.

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Description

FIELD OF THE INVENTION

The present invention relates to a method for developing a silver halide photographic material (hereinafter referred to as a photographic material) which is used in the field of photomechanical processes, provides ultrahigh contrast and has reduced changes in photographic properties due to processing. Further, the present invention relates to a method for decreasing silver stain (also called silver sludge) adhered or precipitated to a photographic material, a development tank or roller of an automatic processor, and thus for facilitating routine maintenance of equipment and machinery.

BACKGROUND OF THE INVENTION

In general, in development of photographic materials, the use of automatic processors has increased from the viewpoints of rapidity, easiness and handling. In many cases, hydroquinones have been used as a developing agent in a developer in terms of cost and stability of photographic properties. However, hydroquinones are unfavorable in respect to safety, because of its allergic property. For such a reason, developers using ascorbic acid in place of hydroquinones are described, for example, in JP-A-6-19069 (the term "JP-A" as used therein means an "unexamined published Japanese patent application"), JP-A-7-114153, JP-A-7-175176 and EP-A-573700.

On the other hand, photographic processing waste liquid can not be discharged into sewerages as it is, and it is necessary to recover the waste liquid and to subject it to burning treatment. It has been therefore desired to reduce the replenishment rate of processing solutions when the photographic materials are processed by use of the automatic processors. However, a decrease in the replenishment rate of the developers raises the problems of deterioration of the stability of the photographic properties and adhesion of silver eluted from the photographic materials to the photographic materials to be processed, thereby staining images. This is called silver stain or silver sludge, and contaminates the automatic processors themselves. Accordingly, periodic cleaning and maintenance of the automatic processors are required.

Further, the developer using ascorbic acid or a derivative thereof is readily oxidized by air, and when oxidized, it produces an acid to lower the pH of the developer. The pH reduction of the developer deteriorates the activity of a nucleating agent to induce a reduction in contrast and D_{max}, resulting in instability of the photographic properties. It is therefore difficult to decrease a replenishment rate of a developer using ascorbic acid or a derivative thereof.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method for processing a photographic material with an ascorbic acid developer not using hydroquinones, which process causes less change in photographic properties and reduced silver stain which contaminates an automatic processor and a photographic material.

Other objects and effects of the present invention will be apparent from the following description.

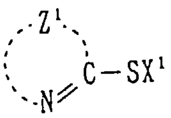
The above-described object has been achieved by providing a method for continuously developing an exposed silver halide photographic material containing a hydrazine derivative by an automatic processor,

wherein the development is carried out by using a developer being substantially free from a dihydroxybenzene compound but containing an ascorbic acid and/or a derivative thereof as a developing agent, an aminophenol derivative as an auxiliary developing agent which exhibits a superadditive property and at least 0.5 mol/liter of a carbonate as a buffer, and

wherein the developer is replenished with a developing replenisher having a pH at least 0.2 higher than that of the starting developing solution.

DETAILED DESCRIPTION OF THE INVENTION

The developing replenisher for use in the present invention preferably contains a compound represented by the following general formula (1):


(1)

wherein Z^1 represents a non-metallic atom group necessary to form a 5- or 6-membered nitrogen-containing aromatic heterocyclic ring together with the N and C atoms in general formula (1) and has R^1 and $(SX^2)_n$ as substituent groups, wherein R^1 represents a hydrogen atom, a halogen atom or a substituent group connected to the ring by a carbon atom, an oxygen atom, a nitrogen atom or a sulfur atom, X^1 and X^2 each represents a hydrogen atom or a cation, n is an integer of 0, 1 or 2, and two radicals each formed by eliminating any one hydrogen atom from Z^1 may combine to form a bis form structure.

General formula (1) is described in detail below.

Z^1 represents a non-metallic atom group necessary to form a 5- or 6-membered nitrogen-containing aromatic heterocyclic ring together with the N and C atoms in general formula (1). The 5-membered nitrogen-containing aromatic heterocyclic ring comprising Z^1, N and C is formed by combination of an element selected from carbon, oxygen and sulfur, in addition to nitrogen, and may be condensed with a hydrocarbon ring or a hetero-cyclic ring. Examples of such rings include pyrazole, imidazole, oxazole, thiazole, triazole, thiadiazole, oxa-diazole, indazole, benzimidazole, benzoxazole, benzothiazole, pyrazolotriazole and pyrrolotriazole. The 5-membered nitrogen-containing aromatic heterocyclic ring is preferably triazole, thiadiazole, oxadiazole, benzimidazole, benz-oxazole, benzothiazole, pyrazolotriazole or pyrrolotriazole, more preferably triazole, thiadiazole, oxadiazole or benz-imidazole, and most preferably triazole.

The 6-membered nitrogen-containing aromatic heterocyclic ring comprising Z^1, N and C is a monocyclic ring or a condensed ring formed by condensation with a carbon ring or a heterocyclic ring. Examples of such rings include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, phthalazine, quinoxaline, quinazoline, cinnoline, phenanthridine, phenanthroline, naphthyridine, pteridine, purine, triazolopyrimidine, imidazolopyridine, triazolopyridine, imidazolotriazine and triazolotriazine. The 6-membered nitrogen-containing aromatic heterocyclic ring is preferably pyrazine, pyrimidine, pyridazine, triazine, phthalazine, quinoxaline, quinazoline, naphthyridine, pteridine, purine, triazolopyrimidine, imidazolopyridine, triazolopyridine, imidazolotriazine or triazolotriazine, more preferably pyrimidine, pyridazine, triazine, pteridine, purine, triazolopyrimidine, imidazolotriazine or triazolotriazine, and most preferably pyrimidine, triazine or purine.

R^1 represents a hydrogen atom, a halogen atom or a substituent group connected to the ring by a carbon atom, an oxygen atom, a nitrogen atom or a sulfur atom. Examples of the substituent group connected by a carbon atom include alkyl, alkenyl, alkynyl, aryl, carbamoyl, alkoxycarbonyl, aryloxy-carbonyl, acyl, carboxyl, cyano and heterocyclic groups. Examples of those connected by an oxygen atom include hydroxyl, alkoxyl, aryloxy, heterocyclic oxy, acyloxy, carbamoyloxy and sulfonyloxy groups. Examples of those connected by a nitrogen atom include acylamino, amino, alkylamino, arylamino, heterocyclic amino, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, sulfonamido, imido and heterocyclic groups. Examples of those connected by a sulfur atom include alkylthio, arylthio, heterocyclic thio, sulfamoyl, alkoxysulfonyl, aryloxysulfonyl, sulfonyl, sulfo and sulfinyl groups. These groups may be further substituted by the group described as R^1. Z^1 may have a plurality of R^1 groups, and two R^1 groups may combine to form a ring if necessary.

R^1 is described in more detail. The halogen atom is, for example, a fluorine atom, a chlorine atom or a bromine atom. The alkyl group is a straight chain, branched chain or cyclic alkyl group having from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms, such as methyl, ethyl, isopropyl, t-butyl, benzyl and cyclopentyl. The alkenyl group is a group having from 2 to 10 carbon atoms, and examples of such groups include vinyl, 1-propenyl, 1-hexenyl and styryl. The alkynyl group is a group having from 2 to 10 carbon atoms, and examples of such groups include ethynyl, 1-butynyl and phenylethynyl. The aryl group is a group having from 6 to 10 carbon atoms, such as phenyl, naphthyl and p-methoxyphenyl.

The carbamoyl group is a group having from 1 to 8 carbon atoms, such as carbamoyl, N-ethylcarbamoyl and N-phenyl-carbamoyl. The alkoxycarbonyl group is a group having from 2 to 8 carbon atoms, such as methoxycarbonyl and benzyloxycarbonyl. The aryloxycarbonyl group is a group having from 7 to 12 carbon atoms, such as phenoxycarbonyl. The acyl group is a group having from 1 to 8 carbon atoms, such as acetyl and benzoyl. The heterocyclic group connected to the ring by a carbon atom is a 5- or 6-membered saturated or unsaturated heterocyclic ring having from 1 to 5 carbon atoms and containing at least one oxygen atom, nitrogen atom or sulfur atom. The number and the kind of the hetero atom constituting the ring may be one or more, and examples of such groups include 2-furyl, 2-thienyl, 2-pyridyl and 2-imidazolyl.

The alkoxyl group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as methoxy, 2-methoxyethoxy and 2-methanesulfonylethoxy. The aryloxy group is a group having from 6 to 12 carbon atoms, such as phenoxy, p-methoxyphenoxy and m-(3-hydroxy-propionamido)phenoxy. The heterocyclic oxy group is a 5- or 6-membered saturated or unsaturated heterocyclic oxy group having from 1 to 5 carbon atoms and containing at least one oxygen atom, nitrogen atom or sulfur atom. The number and the kind of the hetero atom constituting the ring may be one or more, and examples of such groups include 1-phenyltetrazolyl-5-oxy, 2-tetrahydropyranyloxy and 2-pyridyloxy. The acyloxy group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as acetoxy, benzoyloxy and 4-hydroxybutanoyloxy. The carbamoyloxy group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as N,N-dimethyl-carbamoyloxy, N-butylcarbamoyloxy and N-phenylcarbamoyloxy. The sulfonyloxy group is a group having from 1 to 8 carbon atoms, such as methanesulfonyloxy and benzenesulfonyloxy.

The acylamino group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as acetylamino and benzoylamino. The alkylamino group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as N,N-dimethylamino, N-(2-hydroxyethyl)amino and N-(3-dimethylamino-propyl)amino. The arylamino group is a group having from 6 to 10 carbon atoms, such as anilino and N-methylanilino. The heterocyclic amino group is a 5- or 6-membered saturated or unsaturated heterocyclic amino group having from 1 to 5 carbon atoms and containing at least one oxygen atom, nitrogen atom or sulfur atom. The number and the kind of the hetero atom constituting the ring may be one or more, and examples of such groups include 2-oxazolylamino, 2-tetra-hydrosopyranylamino and 4-pyridylamino. The ureido group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as ureido, methylureido, N,N-diethylureido and 2-methanesulfonamidoethylureido.

The sulfamoylamino group is a group having from 0 to 10 carbon atoms, preferably from 0 to 5 carbon atoms, such as methylsulfamoylamino and 2-methoxyethylsulfamoylamino. The alkoxycarbonylamino group is a group having from 2 to 10 carbon atoms, preferably from 2 to 6 carbon atoms, such as methoxycarbonylamino. The aryloxycarbonylamino group is a group having from 7 to 12 carbon atoms, such as phenoxycarbonylamino and 2,6-dimethoxyphenoxycarbonylamino. The sulfonamido group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as methanesulfonamido and p-toluenesulfonamido. The imido group is a group having from 4 to 10 carbon atoms, such as N-succinimido and N-phthalimido. The heterocyclic group connected to the ring by a nitrogen atom is a 5- or 6-membered heterocyclic ring comprising a nitrogen atom and at least one of a carbon atom, an oxygen atom and a sulfur atom. Examples of such groups include pyrrolidino, morpholino and imidazolino.

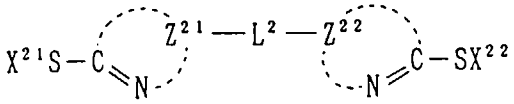
The alkylthio group is a group having from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms, such as methylthio and 2-carboxyethylthio. The arylthio group is a group having from 6 to 12 carbon atoms, such as phenylthio and 2-carboxyphenylthio. The heterocyclic thio group is a 5-or 6-membered saturated or unsaturated heterocyclic thio group having from 1 to 5 carbon atoms and containing at least one of an oxygen atom, a nitrogen atom and a sulfur atom. The number and the kind of the hetero atom constituting the ring may be one or more, and examples of such groups include 2-benzothiazolylthio and 2-pyridylthio.

The sulfamoyl group is a group having from 0 to 10 carbon atoms, preferably from 0 to 6 carbon atoms, such as sulfamoyl, methylsulfamoyl and phenylsulfamoyl. The alkoxysulfonyl group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as methoxysulfonyl. The aryloxysulfonyl group is a group having from 6 to 12 carbon atoms, preferably from 6 to 10 carbon atoms, such as phenoxysulfonyl. The sulfonyl group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as methanesulfonyl and benzenesulfonyl. The sulfinyl group is a group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, such as methanesulfinyl and benzenesulfinyl.

R^1 is preferably a hydrogen atom, an alkyl group, an aryl group, a carbamoyl group, an acyl group, a cyano group, an alkoxyl group, an aryloxy group, an amino group, an acylamino group, an ureido group, a sulfamoylamino group, a sulfonamido group, an alkylthio group, an arylthio group, a sulfamoyl group or a sulfonyl group, more preferably a hydrogen atom, an alkyl group, an alkoxyl group, an aryloxy group, an amino group, an acylamino group, an ureido group or an alkylthio group, and most preferably a hydrogen atom, an alkyl group, an alkoxyl group, an amino group or an alkylthio group.

X^1 and X^2 each represents a hydrogen atom or an cation. The cation is, for example, sodium, potassium, lithium, calcium, ammonium, tetrabutylammonium or triethylammonium. Preferred examples of X^1 and X^2 include a hydrogen atom, sodium, potassium and ammonium. n is preferably 1 or 2.

The compound having a bis form structure formed by connecting two radicals which may be the same or different and each is formed by eliminating any one hydrogen atom from general formula (1) is preferably a compound represented by the following general formula (2):



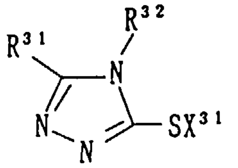
(2)

wherein Z^{21} and Z^{22} each represents a group represented by Z^1 of general formula (1) in which one hydrogen atom is eliminated therefrom, and X^{21} and X^{22} have the same meaning as defined for X^1. Preferred examples thereof are the same as with the above respective group of general formula (1). L^2 is a divalent connecting group (an alkylene group, an alkenylene group, an alkynylene group, an arylene group, a divalent heterocyclic group or the above described group connected through either alone or a combination of two or more of -O-, -S-, -NH-, -CO- and $-SO_2-$.

The alkylene group represented by L^2 is, for example, ethylene, trimethylene, pentamethylene, propylene, 2-butene-1,4-yl, 2-butine-1,4-yl or p-xylylene. The alkenylene group is, for example, ethene-1,2-yl. The alkynylene group is, for example, ethine-1,2-yl. The arylene group is, for example, phenylene. The divalent heterocyclic group is, for example, furan-1,4-diyl. L^2 is preferably an alkylene group, an -NH-(alkylene)-NH- group, an -O-(alkylene)-O- group, an

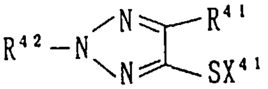
-S-(alkylene)-S-group, an -NH-(alkylene)-CONH-(alkylene)-NH-group or an -NH-(alkylene)-O-(alkylene)-NH- group, and more preferably an -NH-(alkylene)-NH- group or an -O-(alkylene)-O-group.

Of the compounds of the present invention represented by general formula (1), compounds represented by the following general formulas (3) to (10):



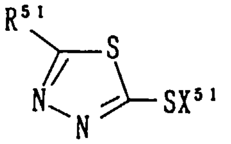
(3)

wherein R^{31} and X^{31} have the same meanings as defined for R^1 and X^1, respectively. R^{31} is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a hydroxyl group, an amino group which may be substituted, a mercapto group or an alkylthio group, more preferably a hydrogen atom, an alkyl group, a hydroxyl group, an amino group which may be substituted or a mercapto group, and most preferably a hydrogen atom, an alkyl group or a mercapto group. R^{32} is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a hydroxyl group or an amino group which may be substituted. R^{32} is preferably a hydrogen atom, an alkyl group, a hydroxyl group or an amino group which may be substituted, and more preferably a hydrogen atom or an alkyl group.



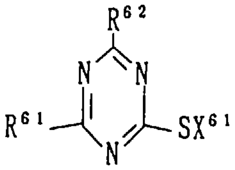
(4)

wherein R^{41}, R^{42} and X^{41} have the same meanings as defined for R^{31}, R^{32} and X^{31} of general formula (3), respectively, and preferred examples thereof are also the same as those defined for the above respective group of general formula (3).



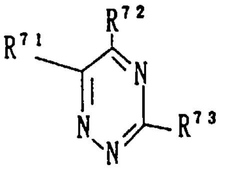
(5)

wherein R^{51} and X^{51} have the same meanings as defined for R^{31} and X^{31} of general formula (3), respectively. R^{51} is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a hydroxyl group, an amino group which may be substituted, a mercapto group or an alkylthio group, more preferably an alkyl group, an amino group which may be substituted, a mercapto group or an alkylthio group, and most preferably a mercapto group or an alkylthio group.



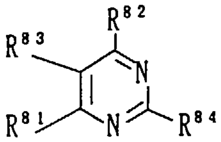
(6)

wherein R^{61}, R^{62} and X^{61} have the same meanings as defined for R^{31}, R^{32} and X^{31} of general formula (3), respectively. R^{61} is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a hydroxyl group, an amino group which may be substituted, a mercapto group or an alkylthio group, more preferably a hydroxyl group, an alkoxyl group, an amino group which may be substituted, a mercapto group or an alkylthio group, and most preferably a hydroxyl group, an amino group which may be substituted or mercapto group. R^{62} is preferably a mercapto group.



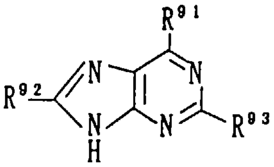
(7)

wherein R^{71}, R^{72} and R^{73} have the same meanings as defined for R^{61}, R^{62} and R^{62} of general formula (6), respectively, and preferred examples thereof are also the same as those defined for the above respective group of general formula (6), with the proviso that at least one of those is a mercapto group. It is more preferred that R^{73} is a mercapto group.



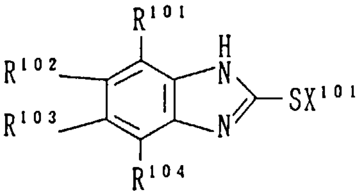
(8)

wherein R^{81}, R^{82}, R^{83} and R^{84} have the same meanings as defined for R^{61}, R^{62}, R^{61} and R^{62} of general formula (6), respectively, and preferred examples thereof are the same as those defined for the above respective group of general formula (6), with the proviso that at least one of those is a mercapto group. R^{83} is most preferably an amino group which may be substituted or a hydrogen atom. It is more preferred that R^{84} is a mercapto group.



(9)

wherein R^{91}, R^{92} and R^{93} each has the same meaning as defined for R^{61} of general formula (6), and preferred examples thereof are also the same as those defined for the above respective group of general formula (6), with the proviso that at least one of those is a mercapto group. It is more preferred that R^{92} or R^{93} is a mercapto group.

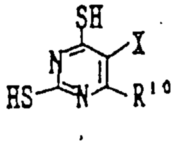


(10)

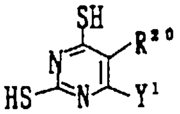
wherein R^{101} to R^{104} and X^{101} have the same meanings as defined for R^1 and X^1 of general formula (1), respectively. R^{101} to R^{104} are each preferably a hydrogen atom, a sulfo group, a carboxyl group, a hydroxyl group or a sulfamoyl group, and more preferably a hydrogen atom or a sulfo group. It is most preferred that R^{103} is a sulfo group.

Of the compounds represented by general formulas (3) to (10), the compounds represented by general formulas (3) and (5) to (9) are more preferred, and the compounds represented by general formulas (3), (6) and (8) are most preferred.

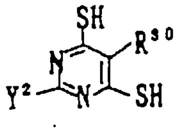
Furthermore, pyrimidine compounds represented by general formula (8) are particularly preferred. Of the pyrimidine compounds, preferred are those having two or three mercapto groups. Moreover, of such pyrimidine compounds having two or three mercapto groups, particularly preferred are those represented by the following general formula (I), (II) and (III).



(I)



(II)



(III)

In the above general formula (I), R^{10} represents a mercapto group, a hydrogen atom or an arbitrary substituent group; X represents a water-soluble group or a substituent substituted by a water-soluble group. In general formula (II), Y^1 represents a water-soluble group or a group substituted by a water-soluble group; and R^{20} represents a hydrogen atom or an arbitrary substituent group. In general formula (III), Y^2 represents a water-soluble group or a group substituted by a water-soluble group; and R^{30} represents a hydrogen atom or an arbitrary group. In the above, R^{10} in general formula (I) and Y^1 in general formula (II) each is not a hydroxyl group.

The pyrimidine compounds represented by general formula (I), (II) and (III) are described in more detail below.

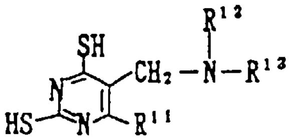
R^{10} in general formula (I) represents a mercapto group, a hydrogen atom or an arbitrary substituent group, provided that it is not a hydroxyl group.

Examples of the arbitrary group include those group by which Z^1 in general formula (1) may be substituted. R^{10} is preferably a mercapto group, a hydrogen atom or a substituent having from 0 to 15 carbon atoms selected from hydroxyl, amino, alkyl, aryl, alkoxy, aryloxy, acylamino, sulfonamido, alkylthio, arylthio, alkylamino and arylamino.

X in general formula (I) represents a water-soluble group or a substituent substituted by a water-soluble group. The water-soluble group is a salt of a carboxylic or sulfonic acid, a salt such as ammonio group, or a group containing a dissociative group which is partially or wholly dissociated in an alkaline developer. Examples thereof include a sulfo group (and salts thereof), a carboxyl group (and salts thereof), a hydroxyl group, a mercapto group, an amino group, an ammonio group, a sulfonamido group, an acylsulfamoyl group, a sulfonylsulfamoyl group, an active methine group, and groups containing one of these groups. In the present invention, the "active methine group" means a methyl group substituted by two electron attractive groups, and examples thereof include dicyanometyl, α-cyano-α-ethoxycarbonylmethyl and α-acetyl-α-ethoxycarbonylmethyl.

The substituent represented by X in general formula (I) is the above described water-soluble group or a substituent substituted by the above described water-soluble group. Examples of the substituent, which is substituted by water-soluble group, include an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, an (alkyl, aryl or heterocyclic) amino group, an acylamino group, a sulfonamido group, a ureido group, a thioureido group, an imido group, a sulfamoylamino group, an (alkyl, aryl or heterocyclic) thio group, an (alkyl or aryl) sulfonyl group, a sulfamoyl group and an amino group. Preferred of these are an alkyl group having from 1 to 10 carbon atoms (particularly, a methyl group substituted by an amino group), an aryl group, an aryloxy group, an (alkyl, aryl or heterocyclic) amino group, an (alkyl, aryl or heterocyclic) thio group.

Of the pyrimidine compounds represented by general formula (I), more preferred compounds are represented by the following general formula (I-A):



(I-A)

wherein R^{11} has the same meaning as R^{10} in general formula (I), and also has the same preferred examples; R^{12} and R^{13} may be the same or different and each represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group, provided that at least one of R^{12} and R^{13} has at least one water-soluble group, wherein the water-soluble group has the same meaning as that of X in general formula (I), and preferred examples thereof include sulfo (and salts thereof), carboxyl (and salts thereof), hydroxyl and amino.

R^{12} and R^{13} each is preferably an alkyl group or an aryl group. When R^{12} or R^{13} represents an alkyl group, the alkyl group is preferably a substituted or unsubstituted alkyl group having from 1 to 4 carbon atoms, and the substituent is preferably a water-soluble group, particularly, a sulfo group (or a salt thereof), a carboxyl group (or a salt thereof), a hydroxyl group or an amino group. When R^{12} or R^{13} represents an aryl group, the aryl group is preferably a substituted or unsubstituted phenyl group having from 6 to 10 carbon atoms, and the substituent is preferably a water-soluble group, particularly, a sulfo group (or a salt thereof), a carboxyl group (or a salt thereof), a hydroxyl group or an amino group.

When R^{12} and R^{13} represents an alkyl group or an aryl group, these group may combine with each other to form a cyclic structure. Further, an unsaturated heterocyclic ring may be formed by the cyclization.

Y^1 in general formula (II) represents a water-soluble group or a substituent substituted by a water-soluble group, and has the same meaning as that of X in general formula (I), provided that it is not a hydroxyl group. R^{20} represents a hydrogen atom or an arbitrary substituent. Examples of the substituent, which is substituted by a water-soluble group, represented by Y^1 include an alkyl group, an aryl group, a heterocyclic group (including nitrogen-containing heterocyclic groups substituted at the site of the nitrogen), an amino group, an (alkyl, aryl or heterocyclic) amino group, an (alkyl, aryl or heterocyclic) thio group, an alkoxy group and an aryloxy group. The water-soluble group has the same meaning as that of X in general formula (I), and preferred examples thereof include sulfo (and salts thereof), carboxyl (and salts thereof), hydroxyl and amino.

Y^1 in general formula (II) is preferably an active methine group having from 3 to 8 carbon atoms, an alkyl or aryl group substituted by a water-soluble group having from 1 to 15 carbon atoms, an alkyl- or aryl- amino group substituted by a water-soluble group having from 1 to 10 carbon atoms, an alkyl- or aryl- thio group substituted by a water-soluble group having from 1 to 10 carbon atoms, an alkoxy or aryloxy group substituted by a water-soluble group having from 1 to 10 carbon atoms, wherein the water-soluble group is particularly preferably a sulfo group (or a salt thereof), a carboxyl group (or a salt thereof), a hydroxyl group or an amino group.

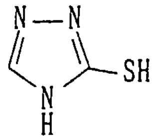
Y^1 is particularly preferably an (alkyl, aryl or heterocyclic) amino group having from 1 to 10 carbon atoms and substituted by a hydroxyl group, a sulfo group (or a salt thereof) or a carboxyl group (or a salt thereof). Such particularly preferred groups are represented by an $-N(R^{01})(R^{02})$ group, wherein R^{01} and R^{02} have the same meaning as that of R^{12} and R^{13} in general formula (1-A), respectively, and each also has the same preferred examples.

R^{20} represents a hydrogen atom or an arbitrary substituent. Examples of the arbitrary group include those group by which the nitrogen-containing aromatic heterocyclic ring formed by Z^1 in general formula (1) may be substituted. R^{20} is preferably a hydrogen atom or a substituent having from 0 to 15 carbon atoms selected from hydroxyl, amino, alkyl, aryl, alkoxy, aryloxy, acylamino, sulfonamido, alkylthio, arylthio, alkylamino, arylamino and hydroxylamino. R^{20} is most preferably a hydrogen atom.

In general formula (III), Y^2 represents a water-soluble group or a substituent substituted by a water-soluble group; and R^{30} represents a hydrogen atom or an arbitrary substituent. Y^2 and R^{30} have the same meaning as that in Y^1 and R^{20}, respectively, and each also has the same preferred examples.

Specific examples of the compounds represented by general formula (1) for use in the present invention are shown below, but are not limited thereto.

(1)



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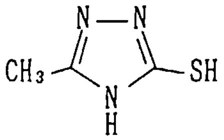

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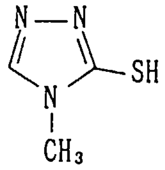

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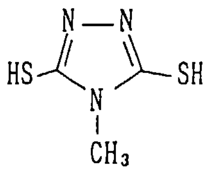

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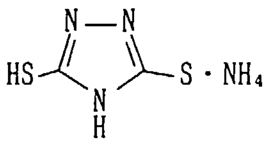

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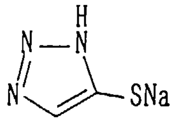

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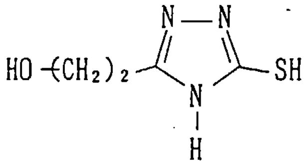

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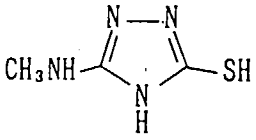

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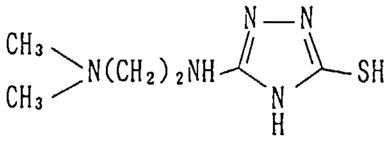

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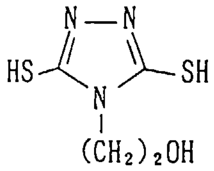

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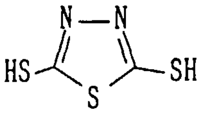

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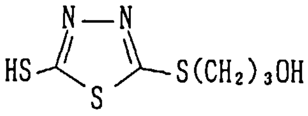

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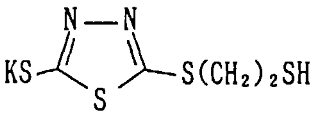

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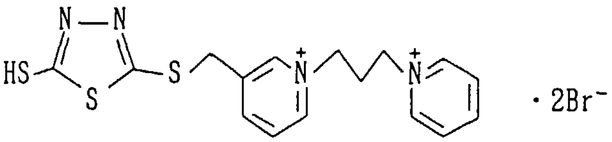

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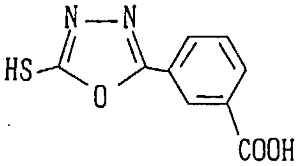

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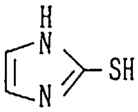

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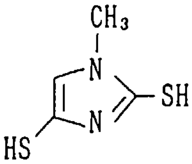

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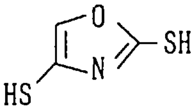

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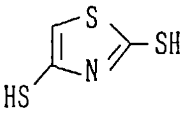

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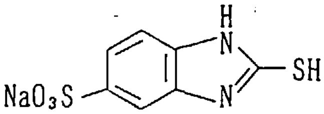

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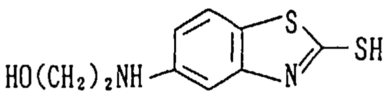

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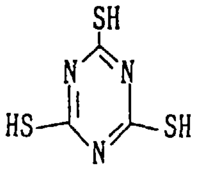

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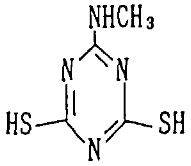

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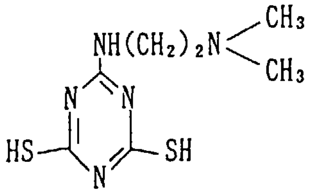

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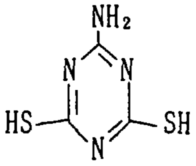

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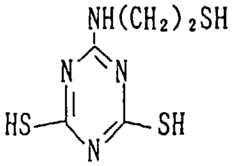

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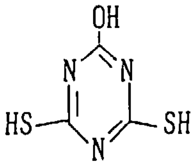

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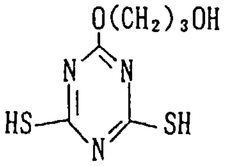

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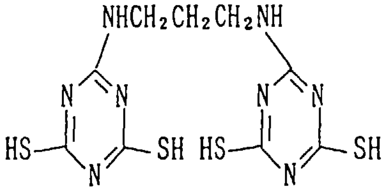

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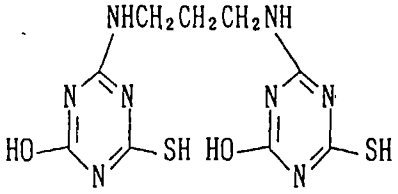

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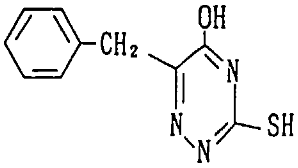

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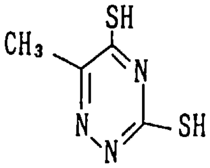

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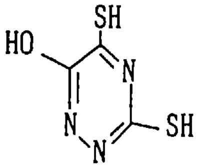

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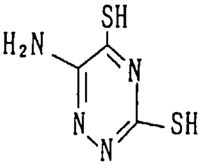

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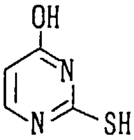

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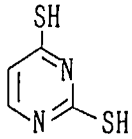

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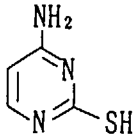

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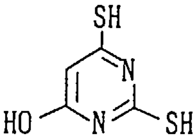

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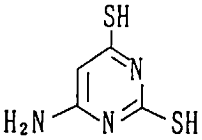

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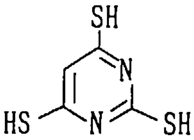

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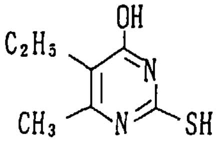

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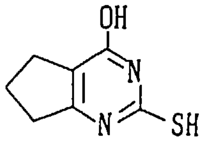

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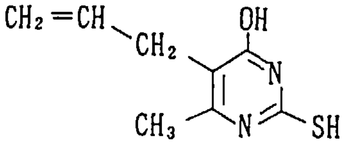

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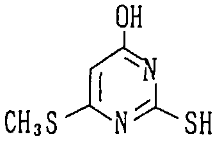

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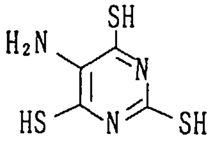

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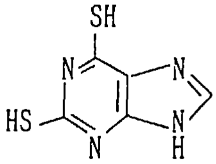

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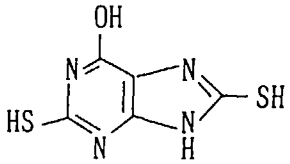

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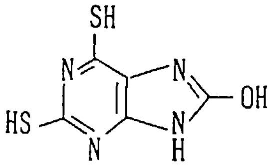

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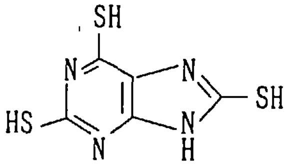

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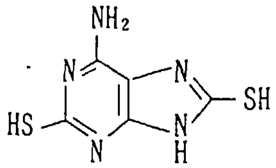

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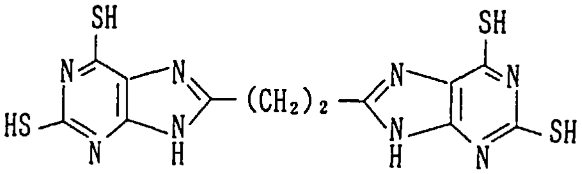

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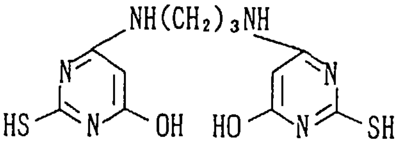

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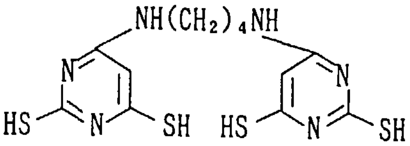

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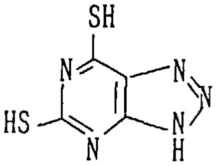

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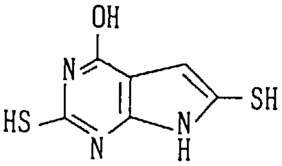

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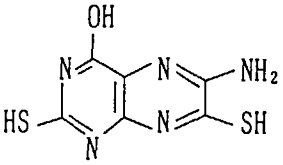

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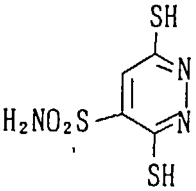

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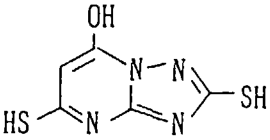

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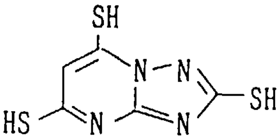

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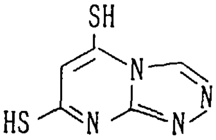

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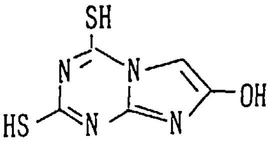

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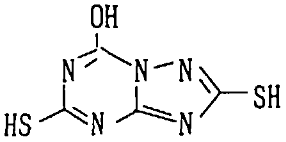

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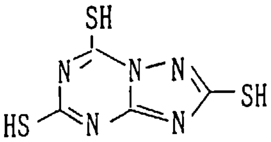

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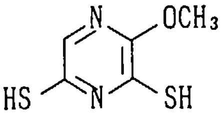

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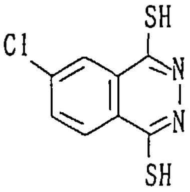

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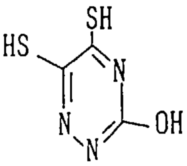

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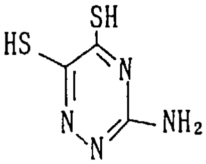

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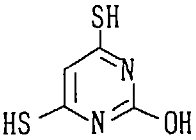

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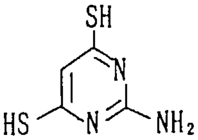

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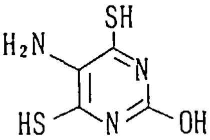

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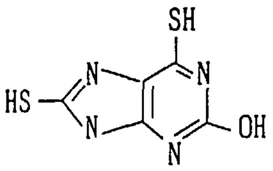
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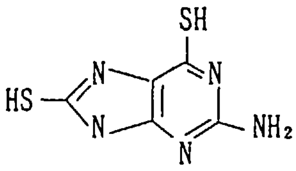
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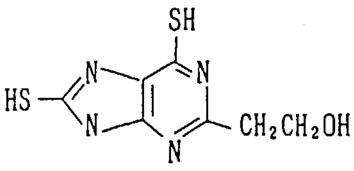
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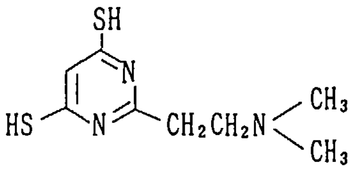
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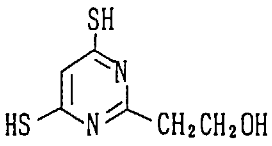
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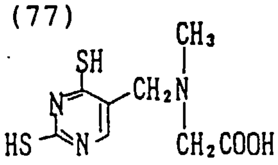

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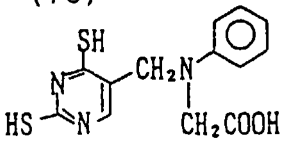

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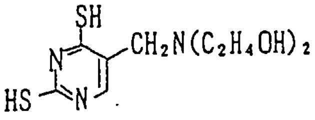

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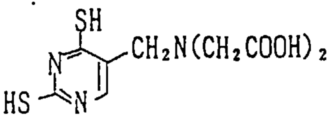

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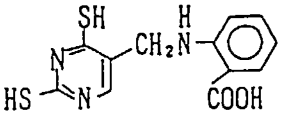

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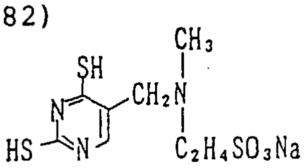

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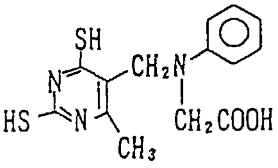

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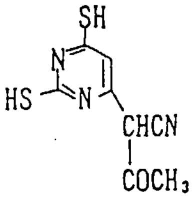

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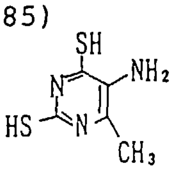

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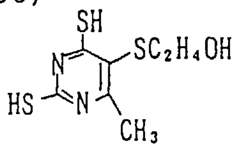

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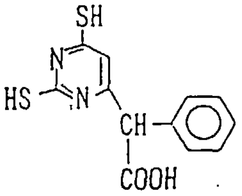

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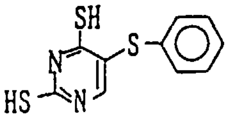

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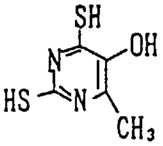

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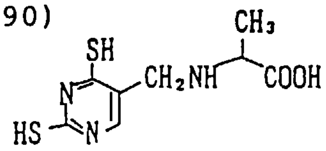

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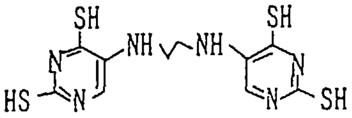

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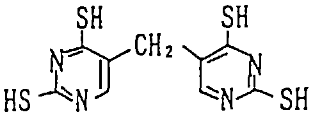

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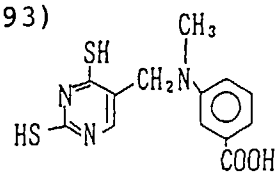

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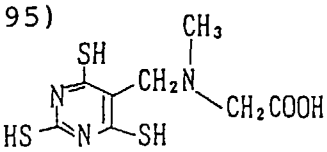

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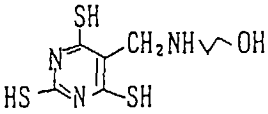

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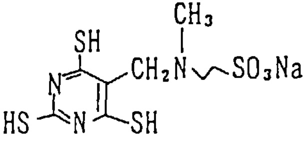

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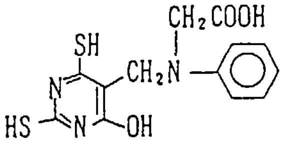

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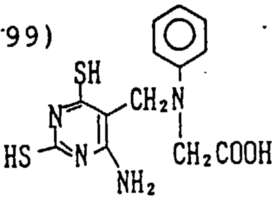

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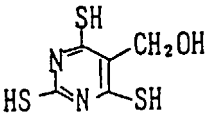

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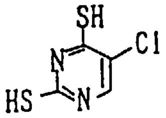

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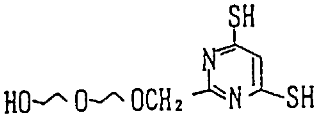

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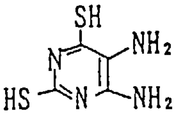

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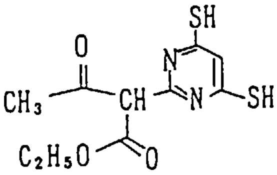

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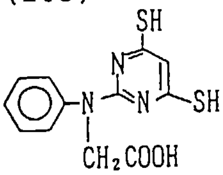

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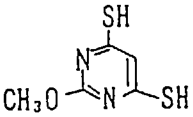

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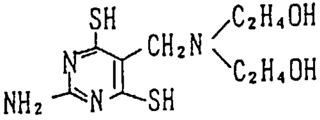

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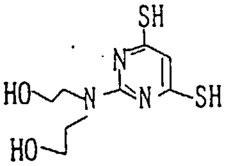

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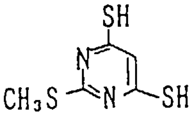

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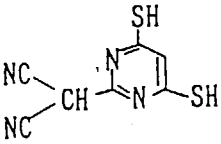

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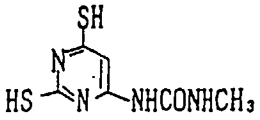

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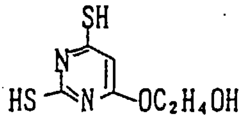

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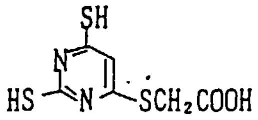

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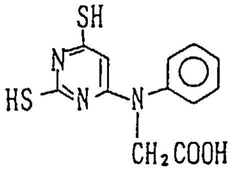

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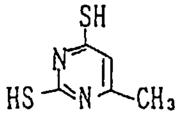

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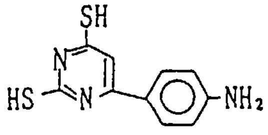

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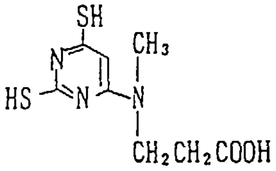

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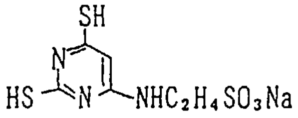

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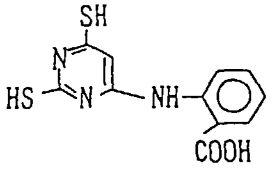

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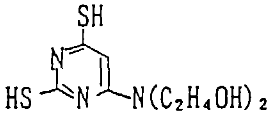

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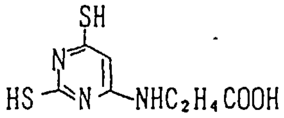

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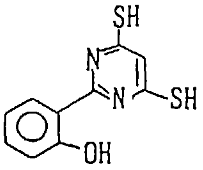
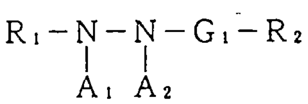


The compounds represented by general formula (1) for use in the present invention are described in the following patents, and in patents and references cited therein: JP-A-4-301837, JP-A-5-61159, JP-A-6-230525, JP-A-58-169147, JP-A-62-56959, U.S. Patent 3,212,892, JP-A-3-53244, JP-A-3-282457, JP-A-5-61159, JP-A-5-303179, JP-A-4-362942, JP-B-46-11630 (the term "JP-B" as used herein means an "examined Japanese patent publication") JP-A-6-175302 and JP-A-6-258783.

When the compound represented by general formula (1) for use in the present invention is added to the developer, the addition amount thereof is preferably from 0.01 mmol to 10 mmol per liter of developer, and particularly preferably from 0.1 mmol to 5 mmol per liter.

Then, the hydrazine derivative for use in the present invention are described below.



$$R_1-\underset{A_1}{\underset{|}{N}}-\underset{A_2}{\underset{|}{N}}-G_1-R_2 \qquad (11)$$

wherein R_1 represents an aliphatic group, an aromatic group or a heterocyclic group; R_2 represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxyl group, an aryloxy group, an amino group or a hydrazino group; G_1 represents a -CO- group, an $-SO_2-$ group, an -SO- group, a $-P(=O)(R_3)-$ group, a -CO-CO- group, a thiocarbonyl group or an iminomethylene group; and A_1 and A_2 both represent hydrogen atoms, or one of them represents a hydrogen atom and the other represents a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group or a substituted or unsubstituted acyl group. R_3 is selected from the groups defined for R_2, and may be different from R_2.

In general formula (11), the aliphatic group represented by R_1 is preferably a substituted or unsubstituted, straight chain, branched chain or cyclic alkyl, alkenyl or alkynyl group having from 1 to 30 carbon atoms.

In general formula (11), the aromatic group represented by R_1 is a monocyclic or dicyclic aryl group, such as a benzene ring or a naphthalene ring. The heterocyclic group represented by R_1 is a monocyclic or dicyclic, aromatic or nonaromatic heterocyclic ring, and may be cyclocondensed with an aryl group to form a heteroaryl group. Examples thereof include pyridine, pyrimidine, imidazole, pyrazole, quinoline, isoquinoline, benzimidazole, thiazole and benzothiazole rings.

R_1 is preferably an aryl group. R_1 may be substituted, and typical examples of the substituent include alkyl (including active methine), alkenyl, alkynyl, aryl, groups containing heterocyclic rings, groups containing quaternized nitrogen atom-containing heterocyclic rings (for example, pyridinio), hydroxyl, alkoxyl (including groups containing ethyleneoxy or propyleneoxy repeating units), aryloxy, acyloxy, acyl, alkoxycarbonyl, aryloxycarbonyl, carbamoyl, urethane, carboxyl, imido, amino, carbonamido, sulfonamido, ureido, thioureido, sulfamoylamino, semicabazido, thiosemicabazido, groups containing hydrazino, groups containing quaternary ammonio, (alkyl, aryl or heterocyclic)thio, (alkyl or aryl)sulfonyl, (alkyl or aryl)sulfinyl, sulfo, sulfamoyl, acylsulfamoyl, (alkyl or aryl)sulfonylureido, (alkyl or aryl)sulfonylcarbamoyl, halogen atoms, cyano, nitro, phosphoric acid amido, groups having phosphoric ester structure, groups having acylurea structure, groups containing selenium or tellurium atoms and groups having tertiary or quaternary sulfonium structure. Preferred examples of the substituent groups include straight chain, branched or cyclic alkyl (preferably having from 1 to 20 carbon atoms), aralkyl (preferably having from 1 to 20 carbon atoms), alkoxyl (preferably having from 1 to 20 carbon atoms), substituted amino (preferably, substituted amino having from 1 to 20 carbon atoms), acylamino (preferably having from 2 to 30 carbon atoms), sulfonamido (preferably having from 1 to 30 carbon atoms), ureido (preferably having from 1 to 30 carbon atoms), carbamoyl (preferably having from 1 to 30 carbon atoms) and phosphoric acid amido (preferably having 1 to 30 carbon atoms).

In general formula (11), the alkyl group represented by R_2 is preferably an alkyl group having from 1 to 10 carbon atoms, and the aryl group is preferably a monocyclic or bicyclic aryl group, for example, a group containing a benzene ring.

The heterocyclic group is a 5- or 6-membered ring compound containing at least one of nitrogen, oxygen and sulfur atoms. Examples thereof include imidazolyl, pyrazolyl, triazolyl, tetrazolyl, pyridyl, pyridinio, quinolinio and quinolinyl groups. Pyridyl and pyridinio groups are particularly preferred.

The alkoxyl group is preferably an alkoxyl group having from 1 to 8 carbon atoms, and the aryloxy group is preferably a monocyclic group. The amino group is preferably an unsubstituted amino group or an alkyl-, aryl- or heterocyclic-amino group having from 1 to 10 carbon atoms.

R_2 may be substituted, and preferred substituent groups are the same as those exemplified as the substituent on R_1.

Of the groups represented by R_2, when G_1 is a -CO-group, a preferred example is a hydrogen atom, an alkyl group (for example, methyl, trifluoromethyl, difluoromethyl, 2-carboxytetrafluoroethyl, pyridiniomethyl, 3-hydroxypropyl, 3-methanesulfonamidopropyl or phenylsulfonylmethyl), an aralkyl group (for example, o-hydroxybenzyl) or an aryl group (for example, phenyl, 3,5-dichlorophenyl, o-methanesulfonamidophenyl, o-carbamoylphenyl, 4-cyanophenyl or 2-hydroxymethylphenyl). In particular, a hydrogen atom and an alkyl group are preferred.

When G_1 is an $-SO_2-$ group, R_2 is preferably an alkyl group (for example, methyl), an aralkyl group (for example, o-hydroxybenzyl), an aryl group (for example, phenyl) or a substituted amino group (for example, dimethylamino).

When G_1 is a -COCO- group, R_2 is preferably an alkoxyl group, an aryloxy group or an amino group. In particular, a substituted amino group (for example, 2,2,6,6-tetramethylpiperidine-4-ylamino, propylamino, anilino, o-hydroxyanilino, 5-benzotriazolylamino or N-benzyl-3-pyridinioamino) is preferred.

Further, R_2 may be a group which cleaves the G_1-R_2 moiety from the residual molecule to induce the cyclization reaction to form a cyclic structure containing atoms of the $-G_1-R_2$ moiety, and examples thereof include groups described in JP-A-63-29751.

A_1 and A_2 are hydrogen atoms, alkyl or arylsulfonyl groups having 20 or less carbon atoms (preferably phenylsulfonyl or phenylsulfonyl substituted so as to give a sum of Hammett substituent constants of -0.5 or more), or acyl groups having 20 or less carbon atoms (preferably, benzoyl or benzoyl substituted so as to give a sum of Hammett substituent constants of -0.5 or more, or straight chain, branched or cyclic, unsubstituted or substituted aliphatic acyl (examples of substituent groups include halogen, ether, sulfonamido, carbonamido, hydroxyl, carboxyl and sulfonic acid)).

A_1 and A_2 are most preferably hydrogen atoms.

The substituent groups on R_1 and R_2 of general formula (11) may be further substituted, and preferred examples thereof include the groups exemplified as a substituent group on R_1. The substituent groups may be further substituted in multiple, such as substitution of the substituent group, substitution of the substituent group on the substituent group, substitution of the substituent group on the substituent groups on the substituent groups, etc., and preferred examples thereof also include the groups exemplified as the substituent group on R_1.

R_1 or R_2 of general formula (11) may be a group in which a ballast group or a polymer commonly used in an inert photographic additive such as a coupler is incorporated. The ballast group is a group having 8 or more carbon atoms which are relatively inactive to photographic characteristics. For example, the ballast group can be selected from alkyl, aralkyl, alkoxyl, phenyl, alkylphenyl, phenoxy, alkylphenoxy, etc. Examples of the polymer include, for example, polymers described in JP-A-1-100530.

R_1 or R_2 of general formula (11) may be a group in which an adsorbent group for adsorbing a silver halide is incorporated. Such adsorbent groups include groups such as alkylthio, arylthio, thiourea, thioamido, mercapto heterocyclic and triazole groups described in U.S. Patents 4,385,108 and 4,459,347, JP-A-59-195233, JP-A-59-200231, JP-A-59-201045, JP-A-59-201046, JP-A-59-201047, JP-A-59-201048, JP-A-59-201049, JP-A-61-170733, JP-A-61-270744, JP-A-62-948, JP-A-63-234244, JP-A-63-234245 and JP-A-63-234246. These adsorbent groups to the silver halides may be precursors thereof. Such precursors include groups described in JP-A-2-285344.

R_1 or R_2 of general formula (11) may contain a plurality of hydrazino groups as substituent groups. In this case, the compound represented by general formula (11) is an oligomer in terms of hydrazino groups, and specific examples thereof include compounds described in JP-A-64-86134, JP-A-4-16938 and JP-A-5-197091.

The hydrazine derivatives particularly preferred in the present invention are described below.

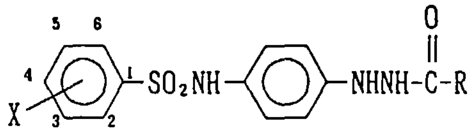
R_1 is particularly preferably a substituted phenyl group, and the phenyl group is preferably substituted by a ballast group, an adsorbent group to a silver halide, a group containing an quaternary ammonio group, a group containing repeating units of ethyleneoxy groups, an alkyl, aryl or heterocyclic thio group, a group dissociatable in an alkaline developer (such as carboxyl, sulfo or acylsulfamoyl), or a hydrazino group which can form an oligomer, via a sulfonamido group, an acylamino group, an ureido group or a carbamoyl group.

R_1 is most preferably a phenyl group substituted by a benzenesulfonamido group, and the benzenesulfonamido group preferably has any of the substituent groups described above as a substituent on the phenyl group.

G_1 is preferably a -CO- group or a -COCO- group, and particularly preferably a -CO- group. It is particularly preferred that when G_1 is a -CO- group, R_2 is a hydrogen atom, a substituted alkyl group or a substituted aryl group (an electron attractive group or an o-hydroxymethyl group is preferred as a substituent group), and that when G_1 is a -COCO- group, R_2 is a substituted amino group.

Specific examples of the compounds represented by general formula (11) are shown below, but the present invention is not limited thereto.

Table 1



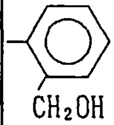
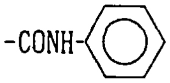
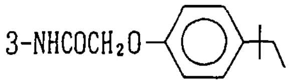
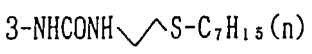
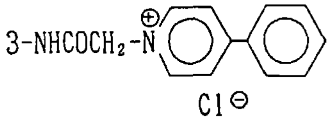
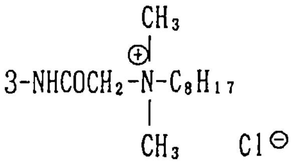
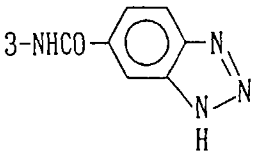
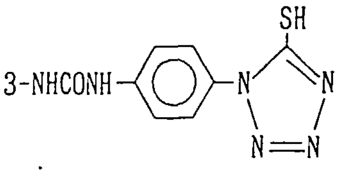
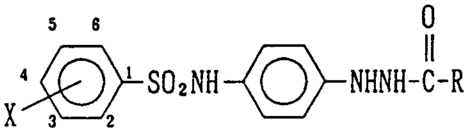
	R= X=	-H	$-C_2F_4-COOH$ (or $-C_2F_4COO^{\ominus}K^{\oplus}$)		
1		1 a	1 b	1 c	1 d
2		2 a	2 b	2 c	2 d
3		3 a	3 b	3 c	3 d
4	 $3\text{-}NHCOCH_2\text{-}N^{\oplus}(CH_3)_2\text{-}C_8H_{17}\ Cl^{\ominus}$	4 a	4 b	4 c	4 d
5		5 a	5 b	5 c	5 d
6		6 a	6 b	6 c	6 d
7	$2\text{-}CH_3$ $4\text{-}CH_3$ $3\text{-}SC_2H_4\text{-}(OC_2H_4)_4\text{-}OC_8H_{17}$	7 a	7 b	7 c	7 d

Table 2



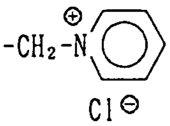
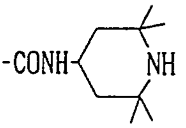
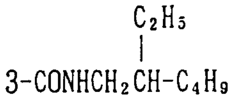
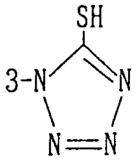
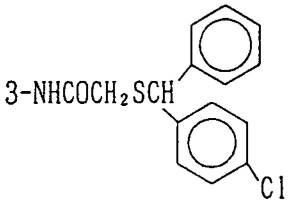
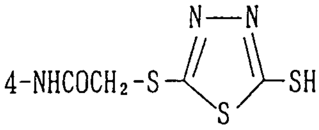
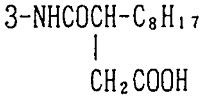
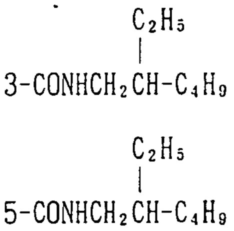
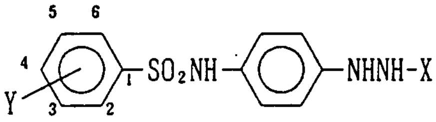
	X= \ R=	-H	$-CF_2H$		
8	 $\text{3-CONHCH}_2\text{CH(C}_2\text{H}_5\text{)-C}_4\text{H}_9$	8 a	8 e	8 f	8 g
9	$\text{6-OCH}_3\text{-3-C}_5\text{H}_{11}\text{(t)}$	9 a	9 e	9 f	9 g
10		10 a	10 e	10 f	10 g
11		11 a	11 e	11 f	11 g
12		12 a	12 e	12 f	12 g
13	 $\text{3-NHCOCH(CH}_2\text{COOH)-C}_8\text{H}_{17}$	13 a	13 e	13 f	13 g
14	 $\text{3-CONHCH}_2\text{CH(C}_2\text{H}_5\text{)-C}_4\text{H}_9$ $\text{5-CONHCH}_2\text{CH(C}_2\text{H}_5\text{)-C}_4\text{H}_9$	14 a	14 e	14 f	14 g

Table 3



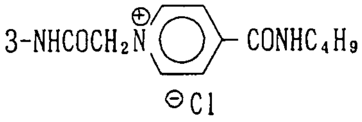
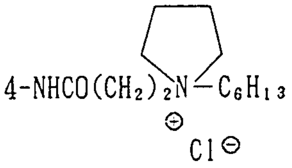
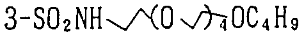
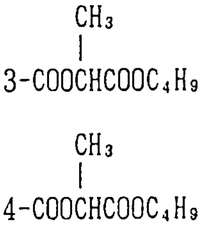
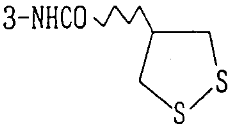
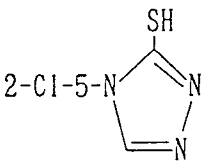
	X= Y=	-CHO	$-COCF_3$	$-SO_2CH_3$	$-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$
15		15a	15h	15i	15j
16		16a	16h	16i	16j
17		17a	17h	17i	17j
18	 $3\text{-}COO\underset{}{\overset{CH_3}{\overset{\vert}{C}}}HCOOC_4H_9$ $4\text{-}COO\overset{CH_3}{\overset{\vert}{C}}HCOOC_4H_9$	18a	18h	18i	18j
19		19a	19h	19i	19j
20	$3\text{-}NHSO_2NH\text{-}C_8H_{17}$	20a	20h	20i	20j
21		21a	21h	21i	21j

Table 4

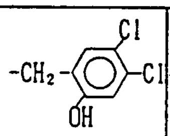
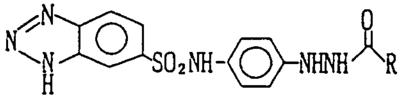
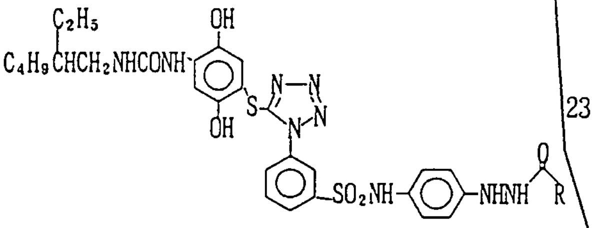
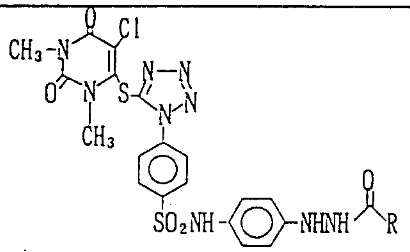
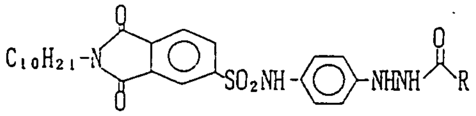
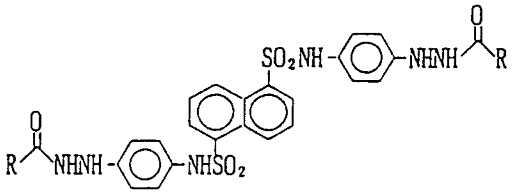
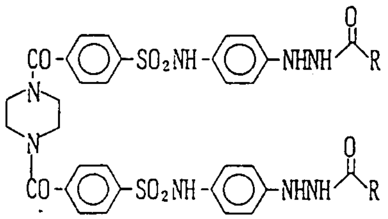
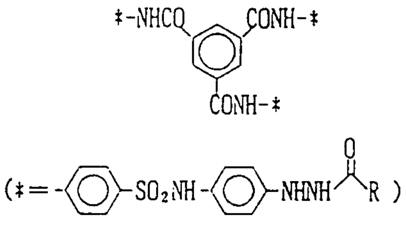
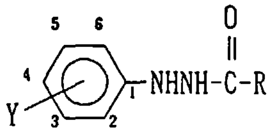
	R=	-H	-CF$_2$H		-CONHC$_3$H$_7$
22		22 a	22 e	22 k	22 l
23		23 a	23 e	23 k	23 l
24		24 a	24 e	24 k	24 l
25		25 a	25 e	25 k	25 l
26		26 a	26 e	26 k	26 l
27		27 a	27 e	27 k	27 l
28		28 a	28 e	28 k	28 l

Table 5



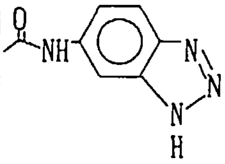
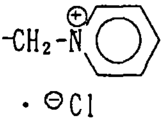
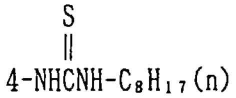
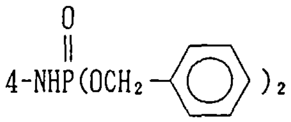
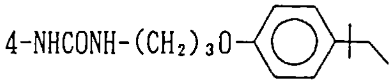
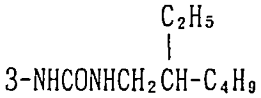
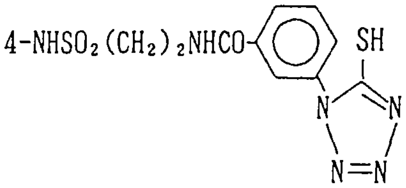
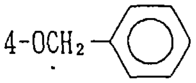
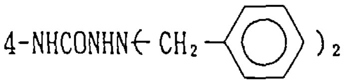
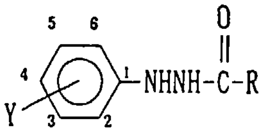
	R= / Y=	-H	$-CH_2OCH_3$		
29	 $4\text{-NH}\overset{S}{\overset{\|}{C}}\text{NH-}C_8H_{17}(n)$	29 a	29m	29 n	29 f
30		30 a	30m	30 n	30 f
31		31 a	31m	31 n	31 f
32	4-OH  $3\text{-NHCONHCH}_2\overset{C_2H_5}{\overset{\|}{C}}H\text{-}C_4H_9$	32 a	32m	32 n	32 f
33		33 a	33m	33 n	33 f
34		34 a	34m	34 n	34 f
35		35 a	35m	35 n	35 f

Table 6



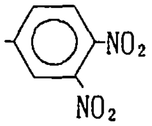
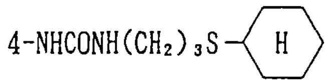
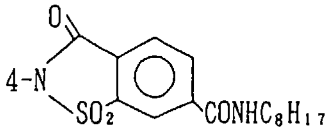
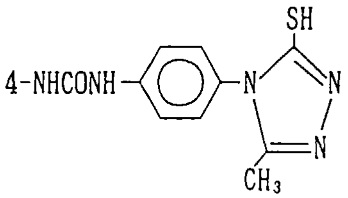
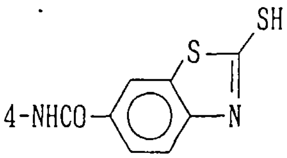
	Y= R=	-H	$-C_3F_6-COOH$	$-CONHCH_3$	
36	$2-NHSO_2CH_3-$ 	36a	36o	36p	36q
37	$2-OCH_3-$ $4-NHSO_2C_{12}H_{25}$	37a	37o	37p	37q
38	$3-NHCOC_{11}H_{23}-$ $4-NHSO_2CF_3$	38a	38o	38p	38q
39		39a	39o	39p	39q
40	$4-OCO(CH_2)_2COOC_6H_{13}$	40a	40o	40p	40q
41		41a	41o	41p	41q
42		42a	42o	42p	42q

Table 7

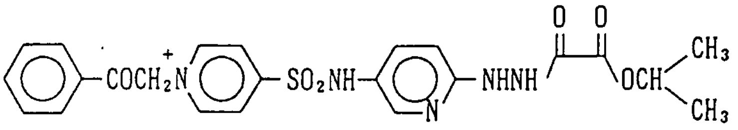
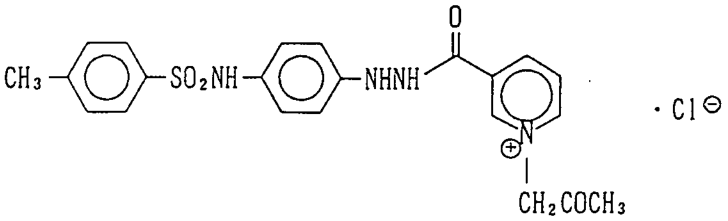
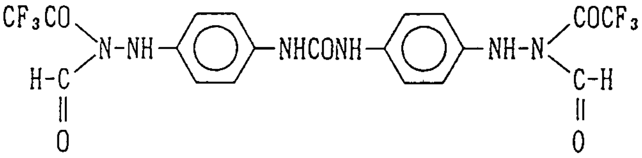
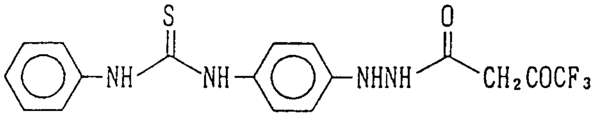
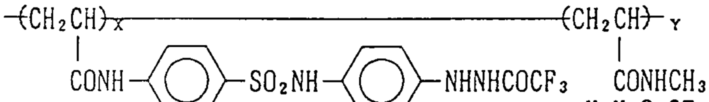
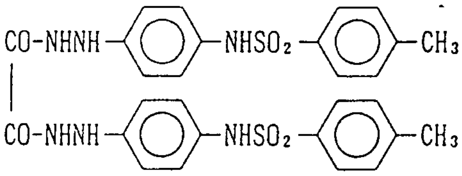
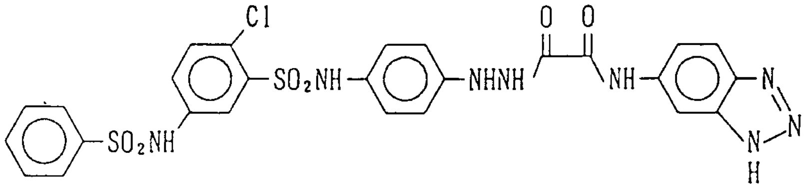
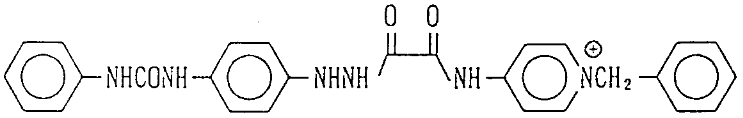
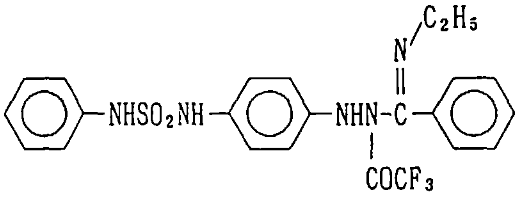
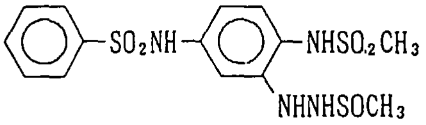
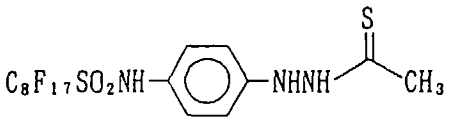
43	
44	
45	
46	
47	 X:Y=3:97 average molecular weight ≒ 100,000
48	
49	
50	

Table 8

51	
52	
53	

In addition to the above-described hydrazine derivatives, the following hydrazine derivatives can also be preferably used in the present invention. The hydrazine derivatives for use in the present invention can also be synthesized by various methods described in the following patents.

Compounds represented by Chemical Formula 1) described in JP-B-6-77138, and specifically, compounds described on pages 3 and 4 thereof; compounds represented by general formula (1) described in JP-B-6-93082, and specifically, compounds (1) to (38) described on pages 8 to 18 thereof; compounds represented by general formulas (4), (5) and (6) described in JP-A-6-230497, and specifically, compounds 4-1 to 4-10 described on pages 25 and 26 thereof, compounds 5-1 to 5-42 described on pages 28 to 36 and compounds 6-1 to 6-7 described on pages 39 and 40; compounds represented by general formulas (1) and (2) described in JP-A-6-289520, and specifically, compounds 1-1) to 1-17) and 2-1) described on pages 5 to 7 thereof; compounds represented by Chemical Formulas 2 and 3 described in JP-A-6-313936, and specifically, compounds described on pages 6 to 19 thereof; compounds represented by Chemical Formula 1 described in JP-A-6-313951, and specifically, compounds described on pages 3 to 5 thereof; compounds represented by general formula (I) described in JP-A-7-5610, and specifically, compounds I-1 to I-38 described on pages 5 to 10 thereof; compounds represented by general formula (II) described in JP-A-7-77783, and specifically, compounds II-1 to II-102 described on pages 10 to 27 thereof; and compounds represented by general formulas (H) and (Ha) described in JP-A-7-104426, and specifically, compounds H-1 to H-44 described on pages 8 to 15 thereof.

In the present invention, the hydrazine nucleating agent can be used by dissolving it in an appropriate water-miscible organic solvent, for example, alcohols (such as methanol, ethanol, propanol and fluorinated alcohol), ketones (such as acetone and methyl ethyl ketone), dimethylformamide, dimethyl sulfoxide and methyl cellosolve.

Alternatively, by the emulsifying dispersion methods already well known, the hydrazine nucleating agent can also be dissolved using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate and diethyl phthalate or an auxiliary solvent such as ethyl acetate and cyclohexanone to mechanically prepare emulsified dispersions for use of it. Further alternatively, the hydrazine derivatives can also be used by dispersing the powder thereof in water with a ball mill, a colloid mill or ultrasonic waves.

In the present invention, the hydrazine nucleating agent may be added to any of the silver halide emulsion layer and other hydrophilic colloidal layers provided on the silver halide emulsion layer side of the support. However, the hydrazine nucleating agent is preferably added to the silver halide emulsion layer or hydrophilic colloidal layers adjacent thereto.

In the present invention, the amount of the nucleating agent added is preferably $1X10^{-6}$ to $1X10^{-2}$ mol per mol of silver halide, more preferably $1X10^{-5}$ to $5X10^{-3}$ mol, and most preferably $2X10^{-5}$ to $5X10^{-3}$ mol.

Nucleating accelerators for use in the present invention include amine derivatives, onium salts, disulfide derivatives and hydroxymethyl derivatives. Examples thereof are enumerated below.

Compounds described in JP-A-7-77783, page 48, lines 2 to 37, and specifically, compounds A-1) to A-73) described on pages 49 to 58; compounds represented by Chemical Formulas 21, 22 and 23 described in JP-A-7-84331, and specifically, compounds described on pages 6 to 8 thereof; and compounds represented by general formulas [Na] and [Nb] described in JP-A-7-104426, and specifically, compounds Na-1 to Na-22 and Nb-1 to Nb-12 described on pages 16 to 20 thereof.

In the present invention, the nucleating accelerator can be used by dissolving them in an appropriate water-miscible organic solvent, for example, alcohols (such as methanol, ethanol, propanol and fluorinated alcohol), ketones (such as acetone and methyl ethyl ketone), dimethylformamide, dimethyl sulfoxide and methyl cellosolve.

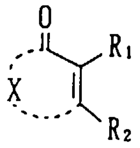
Further, by the emulsifying dispersion methods already well known, the nucleating accelerator can also be dissolved using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate and diethyl phthalate or an auxiliary solvent such as ethyl acetate and cyclohexanone to mechanically prepare emulsified dispersions for use of it. Alternatively, the nucleating accelerator can also be used by dispersing the powder thereof in water with a ball mill, a colloid mill or ultrasonic waves.

In the present invention, the nucleating accelerator may be added to any of the silver halide emulsion layer and other hydrophilic colloidal layers on the silver halide emulsion layer side of the support. However, the nucleating accelerator is preferably added to the silver halide emulsion layer or hydrophilic colloidal layers adjacent thereto.

In the present invention, the amount of the nucleating accelerator added is preferably $1X10^{-6}$ to $2X10^{-2}$ mol per mol of silver halide, more preferably $1X10^{-5}$ to $2X10^{-2}$ mol, and most preferably $2X10^{-5}$ to $1X10^{-2}$ mol.

The developer for use in the present invention are described below, but the present invention is not limited to the following description and specific examples.

The ascorbic acid derivative for use in the present invention as a developing agent is preferably compounds represented by the following general formula (12):

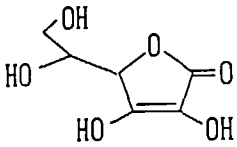


(12)

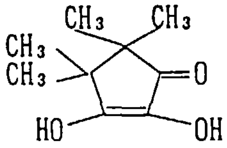
wherein R_1 and R_2 each represents a hydroxyl group, an amino group, an acylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, an alkoxycarbonylamino group, a mercapto group or an alkylthio group; and X comprises a carbon atom, an oxygen atom or a nitrogen atom, and forms a 5- or 6-membered ring together with the two vinyl carbon atoms at which R_1 and R_2 are substituted and the carbonyl carbon atom in general formula (12). General formula (12) is described in detail below. In the general formula, R_1 and R_2 each represents a hydroxyl group, an amino group (including amino groups having an alkyl group with 1 to 10 carbon atoms as a substituent group, for example, methyl, ethyl, n-butyl or hydroxyethyl), an acylamino group (such as acetylamino or benzoylamino), an alkylsulfonylamino group (such as methanesulfonylamino), an arylsulfonylamino group (such as benzenesulfonylamino or p-toluenesulfonylamino), an alkoxycarbonylamino group (such as methoxycarbonylamino), a mercapto group or an alkylthio group (such as methylthio or ethylthio). Preferred examples of R_1 and R_2 include hydroxyl, amino, alkylsulfonylamino and arylsulfonylamino groups. X comprises a carbon atom, an oxygen atom or a nitrogen atom, and forms a 5- or 6-membered ring together with the two vinyl carbon atoms at which R_1 and R_2 are substituted and the carbonyl carbon atom. Specifically, X comprises, for example, a combination of -O-, $-C(R_3)(R_4)-$, $-C(R_5)=$, -C(=O)-, $-N(R_6)-$ and -N=, wherein R_3, R_4, R_5 and R_6 each represents a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms which may be substituted (substituent groups include hydroxyl, carboxyl and sulfo groups), an aryl group having from 6 to 15 carbon atoms which may be substituted (substituent groups include halogen atoms, and alkyl, hydroxyl, carboxyl and sulfo groups) a hydroxyl group or a carboxyl group. Further, the 5- or 6-membered ring may comprises a saturated or unsaturated condensed ring. Examples of the 5- and 6-membered ring include dihydrofuranone, dihydropyrone, pyranone, cyclopentenone, cyclohexenone, pyrrolinone, pyrazolinone, pyridone, azacyclohexenone and uracil rings. Preferred examples thereof include dihydrofuranone, cyclopentenone, cyclohexenone, pyrazolinone, azacyclohexenone and uracil rings.

Examples of the compounds are shown below.

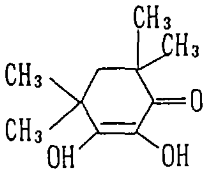
A－1



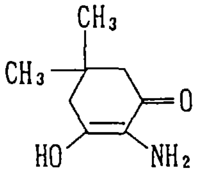
A－2



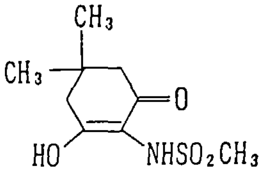
A－3



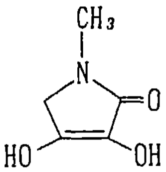
A－4



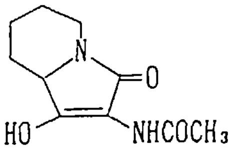
A－5



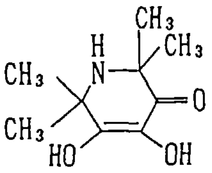
A－6



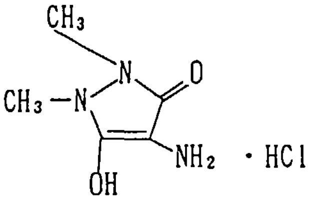
A－7



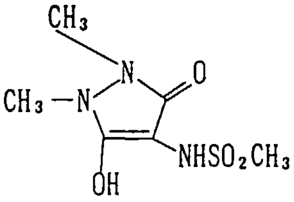
A－8



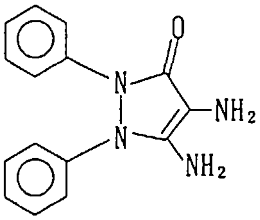
A－9



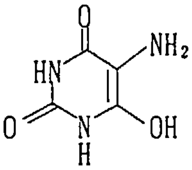
A－10



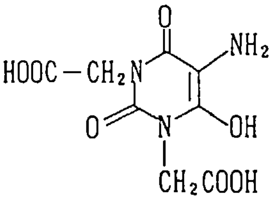
A－11



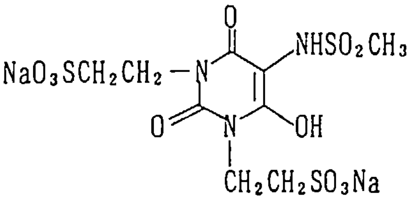
A－12



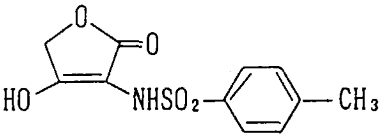
A－13



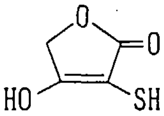
A－14



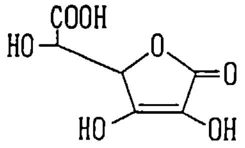
A－15



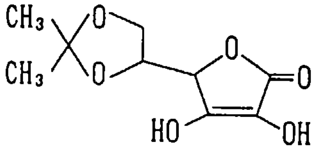
A－16



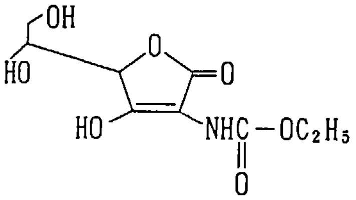
A-17



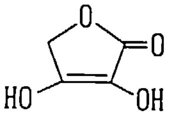
A-18



A-19



A-20



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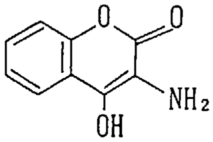

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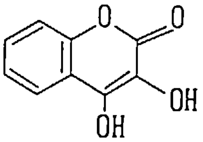

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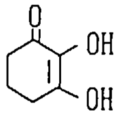
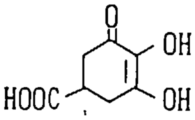


A-24



As the ascorbic acid derivatives for use in the developer in the present invention, the endiol type, enaminol type, the endiamin type, the thiol-enol type and the enamin-thiol type are generally known. Examples of these compounds are described in U.S. Patent 2,688,549 and JP-A-62-237443. Synthesis methods of these ascorbic acid derivatives are also well known, and are described, for example, in Tsugio Nomura and Hirohisa Ohmura, Chemistry of Reductons, Uchida Rohkakuho Shinsha (1969). The ascorbic acid derivatives for use in the present invention can also be used in the form of alkali metal salts such as lithium salts, sodium salts and potassium salts.

p-Aminophenol developing agents for use in the present invention include N-methyl-p-aminophenol, p-aminophenol, N-(β-hydroxyphenyl)-p-aminophenol and N-(4-hydroxyphenyl)-glycine, and N-methyl-p-aminophenol is preferred among others.

Although 3-pyrazolidone or derivatives thereof are generally used as auxiliary developing agents, the use of 3-pyrazolidone or the derivatives thereof is unfavorable in the present invention. 3-Pyrazolidone and the derivatives thereof inhibit nucleating development induced by hydrazine compounds to cause reductions in sensitivity and contrast. It is therefore preferred not to use 3-pyrazolidone and the derivatives thereof.

The ascorbic acid derivative developing agent is preferably used in an amount of 0.01 mol/liter to 0.5 mol/liter, and more preferably in an amount of 0.05 mol/liter to 0.3 mol/liter. In a combination of the ascorbic acid derivative and a p-aminophenol compound, it is preferred to use the ascorbic acid derivative in an amount of 0.01 mol/liter to 0.5 mol/liter and the p-aminophenol compound in an amount of 0.005 mol/liter to 0.2 mol/liter.

The developer for use in processing the photographic materials in the present invention can contain commonly used additives (for example, developing agents, alkali agents, pH buffers, preservatives and chelating agents). Specific examples thereof are shown below, but the present invention is not limited thereto.

The buffer for use in the developer for developing the photographic materials in the present invention includes carbonates, boric acid described in JP-A-62-286259, saccharides (for example, saccharose) described in JP-A-60-93433, oximes (for example, acetoxime), phenols (for example, 5-sulfosalicylic acid) and tertiary phosphates (for example, sodium salts and potassium salts), and the carbonates and boric acid are preferably used. The buffers, particularly carbonates, are preferably used in an amount of 0.5 mol/liter or more, and particularly preferably in an amount of from 0.5 to 1.5 mol/liter.

The preservative for use in the present invention include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite and sodium formaldehydebisulfite.

The concentration of the sulfite is preferably from 0.01 mol/liter to 0.05 mol/liter. If the concentration of the sulfite is too high, the amount of silver eluted from the photographic material to the developer increases to unfavorably cause silver stain.

For the pH of the developer for use in the present invention, the pH of developing replenisher is at least 0.2 higher than that of the starting developing solution.

The ascorbic acid as the developing agent releases an acid by processing fatigue to largely lower the pH of the developer. For preventing this reduction in pH, it is preferred that the pH of a developing replenisher is established higher than that of the starting developing solution. However, too high a pH deteriorates the resistance to air oxidation of the replenisher itself.

Accordingly, the pH of the developing replenisher is preferably 9.0 to 10.5, and the pH of the starting developing solution is preferably 8.8 to 10.3. The difference in pH between the developing replenisher and the starting developing solution (the pH value of the developing replenisher - the pH value of the starting developing solution) is preferably established to 0.2 to 1.0, and more preferably to 0.3 to 0.7.

The replenishment rate of the developing replenisher 15 preferably not more than 300 ml per m^2 of the photographic material, and more preferably from 30 ml/m^2 to 250 ml/m^2. The developing replenisher may have the same composition as that of the starting developing solution, except for the pH, or may have a composition different therefrom.

In the above, the starting developing solution means a so-called fresh solution (a developer placed in a development tank of an automatic processor at first and not used in photographic processing). The developing replenisher and the starting developing solution for use in the present invention are each substantially free from a dihydroxybenzene compound, and each contains the ascorbic acid and/or the derivative thereof as a developing agent, and further contains the aminophenol derivative as an auxiliary developing agent exhibiting a superadditive property and at least 0.5 mol/liter of a carbonate as a buffer. The phrase "substantially free from" used herein means that even if the solutions contain a dihydroxybenzene compound, the content thereof is too small to contribute to the development. In other words, the replenisher and the starting solution may contain a dihydroxybenzene compound in an amount such that it does not affect the development. Such an amount is generally about not more than 0.02 mol/liter.

Additives for use in addition to the above include development inhibitors such as sodium bromide and potassium bromide; organic solvents such as ethylene glycol, diethylene glycol, triethylene glycol and dimethylformamide; and development accelerators such as alkanolamines (e.g., diethanolamine and triethanolamine) and imidazole or derivatives thereof. Heterocyclic mercapto compounds (such as sodium 3-(5-mercaptotetrazole-1-yl)benzenesulfonate and 1-phenyl-5-mercaptotetrazole) and compounds described in JP-A-62-212651 can also be added as uneven physical development inhibitors.

Further, mercapto compounds, indazole compounds, benzotriazole compounds and benzoimidazole compounds may be contained as antifoggants or black pepper inhibitors. Examples thereof include 5-nitroindazole, 5-p-nitrobenzoyl-aminoindazole, 1-methyl-5-nitroindazole, 6-nitroindazole, 3-methyl-5-nitroindazole, 5-nitrobenzindazole, 2-isopropyl-5-nitrobenzimidazole, 5-nitrobenzotriazole, sodium 4-((2-mercapto-1,3,4-thiadiazole-2-yl)thio)butanesulfonate, 5-amino-1,3,4-thiadiazole-2-thiol, methylbenzotriazole, 5-methylbenzotriazole and 2-mercaptobenzotriazole. The amount of these additives is usually from 0.01 to 10 mmol, and more preferably from 0.1 to 2 mmol per liter of the developer.

Further, in the developers for use in the present invention, various kinds of organic and inorganic chelating agents can be used alone or in combination.

Sodium tetrapolyphosphate and sodium hexametaphosphate can be used as the inorganic chelating agents.

On the other hand, organic carboxylic acids, aminopoly-carboxylic acids, organic phosphonic acids, aminophosphonic acids and organic phosphonocarboxylic acids can be mainly used as the organic chelating agents.

The organic carboxylic acids include, for example, acrylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, gluconic acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, nonanedicarboxylic acid, decanedicarboxylic acid, undecanedicarboxylic acid, maleic acid, itaconic acid, malic acid, citric acid and tartaric acid.

The aminopolycarboxylic acids include, for example, aspartic acid diacetic acid, iminodiacetic acid, nitrilotriacetic acid, nitrilotripropionic acid, ethylenediaminemonohydroxyethyltriacetic acid, ethylenediaminetetraacetic acid, glycolethertetraacetic acid, 1,2-diaminopropanetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, 1,3-diamino-2-propanoltetraacetic acid, glycoletherdiaminetetraacetic acid and compounds described in JP-A-52-25632, JP-A-55-67747, JP-A-57-102624 and JP-B-53-40900.

Examples of the organic phosphonic acids include hydroxyalkylidenediphosphonic acids described in U.S. Patents 3,214,454 and 3,794,591 and West German Patent Publication (OLS) 2,227,396, and compounds described in Research Disclosure, 181, Item 18170 (May, 1979).

The aminophosphonic acids include, for example, compounds described in Research Disclosure, 18170 described above, JP-A-57-208554, JP-A-54-61125, JP-A-55-29883 and JP-A-56-97347, as well as aminotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid and aminotri-methylenephosphonic acid.

Examples of the organic phosphonocarboxylic acids include compounds described in JP-A-52-102726, JP-A-53-42730, JP-A-54-121127, JP-A-55-4024, JP-A-55-4025, JP-A-55-126241, JP-A-55-65955, JP-A-55-65956 and Research Disclosure, 18170 described above.

These organic and/or inorganic chelating agents are not limited to the above-described agents, and may be used in the form of alkali metal salts or ammonium salts. The amount of these chelating agents added is preferably from $1X10^{-4}$ to $1X10^{-1}$ mol per liter of developer, and more preferably from $1X10^{-3}$ to $1X10^{-2}$ mol per liter of the developer.

As fixing agents of fixing processing agents in the present invention, ammonium thiosulfate, sodium thiosulfate and ammonium sodium thiosulfate can be used. The amount of the fixing agent used can be appropriately changed, but it is generally from about 0.7 to about 3.0 mol/liter.

The fixing solution for use in the present invention may contain water-soluble aluminum salts or water-soluble chromium salts acting as hardening agents, and water-soluble aluminum salts are preferred. Examples thereof include aluminum chloride, aluminum sulfate, potassium alum, ammonium aluminum sulfate, aluminum nitrate and aluminum lactate. It is preferred that these are contained in an amount of 0.01 to 0.15 mol/liter in terms of the aluminum ion concentration in working solutions.

When the fixing solution is preserved as a concentrated solution or solid agents, they may be composed of a plurality of parts with separating from the hardeners and the like as other parts, or may be composed of one part containing all components.

The fixing processing agents can contain preservatives (for example, 0.015 mol/liter or more, preferably from 0.02 mol/liter to 0.3 mol/liter of sulfites, bisulfites or metabisulfites), pH buffers (for example, from 0.1 mol/liter to 1 mol/liter, preferably from 0.2 mol/liter to 0.7 mol/liter of acetic acid, sodium acetate, sodium carbonate, sodium hydrogencarbonate, phosphoric acid, succinic acid or adipic acid) and compounds having aluminum-stabilizing ability or water-softening ability (for example, from 0.001 mol/liter to 0.5 mol/liter, preferably from 0.005 mol/liter to 0.3 mol/liter of gluconic acid, iminodiacetic acid, 5-sulfosalicylic acid, glucoheptanoic acid, malic acid, tartaric acid, citric acid, oxalic acid, maleic acid, glycolic acid, benzoic acid, salicylic acid, Tiron, ascorbic acid, glutaric acid, aspartic acid, glycine, cysteine, ethylenediaminetetraacetic acid, nitrilotriacetic acid, derivatives or salts thereof, saccharides or boric acid), if desired.

In addition, the fixing processing agent can contain compounds described in JP-A-62-78551, pH regulators (for example, sodium hydroxide, ammonium and sulfuric acid), surfactants, wetting agents and fixing accelerators. The surfactants include, for example, anionic surfactants such as sulfates and sulfonates, polyethylene surfactants and amphoteric surfactants as described in JP-A-57-6840, and known antifoaming agents can also be used. The wetting agents include alkanolamines and alkylene glycols. The fixing accelerators include alkyl- and allyl-substituted thiosulfonic acids and salts thereof as described in JP-A-6-308681, thiourea derivatives described in JP-B-45-35754, JP-B-58-122535 and JP-B-58-122536, alcohols having a triple bond in its molecule, thioether compounds described in U.S. Patent 4,126,459, mercapto compounds described in JP-A-64-4739, JP-A-1-4739, JP-A-1-159645 and JP-A-3-101728, mesoionic compounds described in JP-A-4-170539, and thiocyanates.

The pH of the fixing solution for use in the present invention is 4.0 or more, and preferably from 4.5 to 6.0.

The replenishment rate of the fixing solution is not more than 500 ml per m^2 of the photographic material, preferably not more than 390 ml/m^2, and more preferably from 30 ml/m^2 to 320 ml/m^2. The replenisher may have the same composition and/or concentration as that of the starting solution, or may have a composition and/or a concentration different therefrom.

The fixing solution can be regenerated by known regeneration methods of a fixing solution such as electrolytic silver recovery to use it. Regeneration devices include Reclaim R-60 manufactured by Fuji Hunt Electronics Technology Co. Ltd.

When the developing processing agent and the fixing processing agent for use in the present invention are preserved in the liquid form, they are preferably stored in wrapping up in packaging materials having a low oxygen permeability as described, for example, in JP-A-61-73147. Further, when these solutions are supplied as concentrated solutions, the concentrated solutions are diluted with water to give a predetermined concentration at the time of use, for example, at a rate of from 0.2 to 3 parts of water per part of the concentrated solution.

The developing processing agent and the fixing processing agent for use in the present invention provide results similar to those when used in the liquid form, also when used in the solid form, and solid processing agents are described below.

The solid processing agents for use in the present invention can be used in known forms (such as powdery, granular, massive, tablet, compactor, briquette, tabular, breaked, rod-like and paste-like forms).

In order to separate components which react with each other in contact, the components may be coated with water-soluble coating agents or coating films, or may be formed in a plurality of layers to separate the components which react with each other, or these methods may be used in combination.

Known compounds can be used for coating, and polyvinylpyrrolidone, polyethylene glycol, polystyrenesulfonic acid and vinyl compounds are preferred. In addition, gelatin, pectin, polyacrylic acid, polyvinyl alcohol, vinyl acetate copolymers, polyethylene oxide, sodium carboxymethyl cellulose, hydroxypropyl cellulose, methyl cellulose, ethyl cellulose, alginic acid, chitaric acid gum, gum arabic, tragacanth gum, carrageenan, methyl vinyl ether, maleic anhydride copolymers, polyoxyethylene alkyl ethers such as polyoxyethylene stearyl ether and polyoxyethylene ethyl ether, polyoxyethylene alkylphenol ethers such as polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether, and water-soluble binders described in EP-A-469877 are used alone or as a combination of two or more thereof. These can also be used as granulating auxiliaries.

In the case of the plural layer constitution, a component which does not react even in contact may be put between components which react with each other, to thereby form a plural-layered product, which may be processed to the tablet or briquette form, or components of known forms may be formed to similar constitution, which may be wrapped. These methods are described, for example, in JP-A-61-259921, JP-A-4-15641, JP-A-4-16841, JP-A-4-32837, JP-A-4-78848 and JP-A-5-93991.

The apparent density of the solid processing agent is preferably from 0.5 to 6.0 g/cm^3. In particular, it is preferably from 1.0 to 5.0 g/cm^3 for tablet forms, and from 0.5 to 1.5 g/cm^3 for the granules.

As methods for producing she solid processing agents for use in the present invention, any of known methods can be used. For example, methods described in JP-A-61-259921, JP-A-4-16841 and JP-A-4-78848 can be used as packaging methods. Further, methods described in JP-A-4-85533, JP-A-4-85534, JP-A-4-85535, JP-A-5-134362, JP-A-5-197070, JP-A-5-204098, JP-A-5-224361, JP-A-6-138604 and JP-A-6-138605 can be used as solidifying methods. More specifically, rolling granulation, extrusion granulation, compression granulation, pulverization granulation, stirring granulation, spray drying, dissolution coagulation, briquetting and roller compacting can be used.

The grain size and the form of granulated products suitable for the present invention vary depending on desired characteristics. However, considering the solubility generally desired for photographic processing agents and the amount of residual powders in packaging materials after solution preparation, or considering the resistance to destruction of the granulated products by vibration in transferring, the grain size (converted to the spherical size) of the granular products is from about 0.5 to about 50 mm, and preferably from about 1 to about 15 mm, and the form thereof is cylindrical, spherical, cubic or rectangular parallelepiped form, and preferably spherical or cylindrical.

Products processed by roller compacting may be pulverized, and further filtered to obtain a size of from about 2 mm to about 1 cm.

For the briquette and tablet products, although the grain size and the form similarly vary depending on desired characteristics, the grain size is preferably about 2 mm to about 5 cm, and the form is cylindrical, spherical, cubic or rectangular parallelepiped form, and preferably spherical or cylindrical. When improvements in solubility are desired, tabular products decreased in thickness, products further decreased in thickness of central portions thereof and hollow doughnut-shaped are also useful. Conversely, in order to carry out dissolution slowly, the size or the thickness may be increased, and can be arbitrarily adjusted. Further, in order to control the solubility, the surface conditions (such as smoothness and porousness) may be changed, furthermore, in order to give different solubilities to a plurality of products or match the solubility of materials different in solubility, it is also possible to use a plurality of forms. A multilayer granulated product may also be used in which a surface thereof is different from the inside thereof in composition.

As the packaging materials for the solid processing agents, materials having low oxygen permeability and low moisture permeability are preferred, and those in known forms such as bag-like, cylindrical and box-like forms can be used for the packaging materials. Collapsible forms as disclosed in JP-A-6-242585, JP-A-6-242586, JP-A-6-242587, JP-A-6-242588, JP-A-6-247432, JP-A-6-247448, JP-A-7-5664, JP-A-7-5666, JP-A-7-5667, JP-A-7-5668 and JP-A-7-5669 are also preferred to decrease the space for storing waste packaging materials. These packaging materials may be provided with screw caps, pull tops or aluminum seals at outlets for the processing agents, or heat sealed. However, other known means may be used, without limitation thereto. It is preferred in respect to environmental protection to recycle or reuse the waste packaging materials.

There is no particular limitation on methods for dissolving and replenishing the solid processing agents for use in the present invention, and known methods can be used. Examples of these methods include a method of dissolving a specified amount of the solid processing agent in a dissolving device having a stirring function and replenishing with the resulting solution; a method of dissolving the solid processing agent in a dissolving device having a dissolving section and a section for stocking a completed solution, and replenishing the solution from the stocking section; a method of supplying the solid processing agent to a circulating system of an automatic processor, dissolving it, and replenishing with the resulting solution as described in JP-A-5-119454, JP-A-6-19102 and JP-A-7-261357; and a method of supplying the processing agent to an automatic processor containing a dissolving tank to dissolve it, according to the processing of a photographic material. However, any of other known methods can be used. The package may be either manually opened to supply the processing agent, or automatically opened to automatically supply the processing agent with a dissolving device or an automatic processor having an opening mechanism. The latter is preferred from the view-point of working environment. Specifically, there are methods of breaking through, peeling off, cutting off and push-cutting the outlets of the packages, and methods described in JP-A-6-19102 and JP-A-6-95331.

The photographic materials which have been developed and fixed are then subjected to washing and stabilization processing (unless otherwise specified, "washing" as used hereinafter include "stabilization processing", and a solution used therefor is referred to as water or washing water). Water used for washing may be tap water, ion-exchanged water, distilled water or stabilized water. The replenishment rate thereof is generally from about 8 liters to about 17 liters per m^2 of the photographic material, but washing can also be conducted at a replenishment rate of less than the above range. In particular, washing at a replenishment rate of 3 liters or less (including 0, namely pool washing) not only makes water-saving processing possible, but also can make piping for installation of an automatic processor unnecessary. When washing is carried out with a small amount of water, it is more preferred to provide washing tanks of squeeze rolls and crossover rolls described in JP-A-63-18350 and JP-A-62-287252. In order to reduce environmental pollution load which raises a problem in washing with a small amount of water, and to prevent water scale, addition of various oxidizing agents (for example, ozone, hydrogen peroxide, sodium hypochlorite, active halogen, chlorine dioxide and sodium carbonate peroxyhydrate) and filtration through filters may be combined with each other.

As a method for decreasing the replenishment rate of washing water, a multi-stage countercurrent system (for example, two-stage, three-stage and the like) has been known, and the replenishment rate of washing water is preferably from 50 to 200 ml per m^2 of the photographic material. This effect is also similarly obtained by an independent multi-stage system (a method for replenishing a fresh solution to multi-stage washing tanks, separately, without use of countercurrent replenishment).

Further, water scale prevention means may be applied to a fixing stage in the method of the present invention. As the water scale prevention means, known means can be used, and there is no particular limitation thereon. Examples thereof include methods of adding antifungal agents (so-called water scale inhibitors), methods of passing electric currents, methods of irradiating ultraviolet rays, infrared rays or far infrared rays, methods of applying magnetic fields, methods of treating with ultrasonic waves, methods of applying heat and methods of making tanks empty at the time of nonuse. These water scale prevention means may be applied according to the processing of the photographic materials, or at certain intervals, regardless of the conditions of use, or only for periods in which the processing is not conducted, for example, at night. Further, washing water previously subjected to the water scale prevention means may be replenished. It is also preferred for prevention of generation of resistant bacteria to apply different water scale prevention means for every definite period.

There is no particular limitation on the antifungal agents, and known ones can be used. Examples thereof include chelating agents such as glutaraldehyde and aminopolycarboxylic acid, cationic surfactants and mercaptopyridine oxide (for example, 2-mercaptopyridine-N-oxide), as well as the above-described oxidizing agents. They may be used alone or in combination of two or more thereof.

As the methods for passing electric currents, methods described in JP-A-3-224685, JP-A-3-224687, JP-A-4-16280 and JP-A-4-18980 can be used.

In addition, for preventing water bubble unevenness or transfer of stains, known water-soluble surfactants or antifoaming agents may be added. In order to prevent contamination caused by dyes eluted from the photographic materials, dye adsorbents described in JP-A-63-163456 may be added to washing systems.

An overflowed solution from the washing stage can also be partly or wholly mixed with a processing solution having fixing ability to use the mixed solution, as described in JP-A-60-235133. It is also preferred from the view point of natural environmental protection to reduce the concentration of silver contained in drainage by draining after decreases in biological oxygen demand (BOD), chemical oxygen demand (COD) and iodine consumption by biological treatments (for example, treatments with filters in which sulfur-oxidizing bacteria, activated sludge or microorganisms are carried on porous carriers such as activated carbon and ceramics) or by oxidation treatments by electric current passing or with oxidizing agents, or by precipitating silver by use of filters using polymers having affinity for silver or addition of compounds forming slightly soluble silver complexes of trimercaptotriazine, etc.

Further, the above-described washing processing may be followed by stabilization processing. As an example thereof, baths containing compounds described in JP-A-2-201357, JP-A-2-132435, JP-A-1-102553 and JP-A-46-44446 may be used as final baths for the photographic materials. Ammonium compounds, compounds of metals such as Bi and Al, fluorescent whitening agents, various chelating agents, membrane pH regulators, hardening agents, disinfectants, antifungal agents, alkanolamines or surfactants can also be added to these stabilizing baths, if necessary.

Additives such as the antifungal agents added to the washing and stabilizing baths and stabilizing agents can also be used as solid agents similarly with the above-described developing and fixing processing agents.

Waste liquids of the developer, the fixing solution, the washing water and the stabilizing solution for use in the present invention are preferably burned to dispose them. It is also possible to concentrate or solidify these waste liquids with a concentrating device as described in JP-B-7-83867 and U.S. Patent 5,439,560, followed by disposition.

When the replenishment rate is reduced, it is preferred to prevent evaporation and air oxidation of the solution by decreasing the opening area of the processing tank. Roller transfer type automatic processors are described in U.S. Patents 3,025,779 and 3,545,971, and briefly referred to as roller transfer type automatic processors in this specification. This automatic processor comprises the four stages of development, fixing, washing and drying. It is most preferred that the methods of the present invention also follow these four stages, although not excluding another stage (for example, a stop stage). Further, a rinsing bath may be provided between development and fixing, and/or between fixing and washing.

In the present invention, the development processing is preferably conducted for from 25 to 160 seconds at dry to dry. The developing and fixing time is 40 seconds or less, and preferably from 6 to 35 seconds, and the temperature of each solution is preferably from 25 to 50°C, and more preferably from 30 to 40°C. The temperature and the time of washing are preferably from 0 to 50°C and 40 seconds or less, respectively. According to the present invention, washing water may be squeezed off from the photographic material which have been developed, fixed and washed, namely, such a material may be passed between squeeze rolls, followed by drying. The drying is carried out at from about 40 to about 100°C, and the drying time can be appropriately varied according to the environmental conditions. Any of known drying methods can be used, and there is no particular limitation thereon. Examples thereof include hot air drying, heat roller drying described in JP-A-4-15534, JP-A-5-2256 and JP-A-5-289294, and drying by far infrared rays, and the plural methods may be used in combination.

The silver halide emulsion for use in the photographic material of the present invention can contain any silver halides used in ordinary silver halide emulsions, such as silver bromide, silver iodobromide, silver chloride, silver chlorobromide and silver chloroiodobromide. Silver chlorobromide containing 60 mol% or more of silver chloride is preferred for a negative type silver halide emulsion, and silver chlorobromide, silver bromide and silver iodobromide containing 60 mol% or more of silver bromide are preferred for a positive type silver halide emulsion. The silver halide grains may be obtained by any of the acidic method, the neutral method and the ammonia method. The silver halide grain may be either a grain having uniform silver halide composition distribution therein or a core/shell grain in which the inside of the grain is different from a surface of the grain in silver halide composition. The silver halide grain may be either a grain in which a latent image is mainly formed on a surface of the grain or a grain in which a latent image is mainly formed in the inside of the grain. Further, the grain may be a grain whose surface is previously fogged. The form of the silver halide grain according to the present invention may be any. One preferred example thereof is a cube having a {100} face as a crystal surface. Further, grains having octahedral, tetradecahedral or dodecahedral form produced by methods described U.S. Patents 4,183,756 and 4,225,666, JP-A-55-26589, JP-B-55-42737 and J. Photogr. Sci., 21-39 (1973) can also be used. Furthermore, grains having twin planes may be used. The silver halide grain for use in the present invention may be either grains having a single form, or mixed grains comprising those having various forms. In the present invention, monodisperse emulsions are preferred. Monodisperse silver halide grains in the monodisperse emulsions are preferably those in which the weight of silver halides contained within the grain size range of a mean grain size $\gamma \pm 10\%$ accounts for 60% or more of the total weight of silver halide grains.

There is no particular limitation on the halogen composition of the silver halide emulsion for use in the present invention. In order to achieve the objects of the present invention more effectively, silver chloride, silver chlorobromide and silver chloroiodobromide having a silver halide content of 50 mol% or more are preferred. The content of silver iodide is preferably less than 5 mol%, and more preferably less than 2 mol%.

In the present invention, photographic materials suitable for high illumination exposure such as scanner exposure and photographic materials for line camera work generally contain a rhodium compound in order to achieve high contrast and low fog.

As the rhodium compounds for use in the present invention, water-soluble rhodium compounds can be used. Examples thereof include rhodium (III) halide compounds or rhodium complex salts having a halogen, an amine, oxalato or the like as a ligand, for example, hexachlororhodium (III) complex salts, hexabromorhodium (III) complex salts, hexaaminerhodium (III) complex salts and trioxalatorhodium (III) complex salts. These rhodium compounds are dissolved in water or an appropriate solvent to use them. In order to stabilize the solution of the rhodium compound, a method generally frequently used, that is, the method of adding an aqueous solution of a hydrogen halide (for example, hydrochloric acid, hydrobromic acid or hydrofluoric acid) or an alkali halide (for example, KCl, NaCl, KBr or NaBr) can be used. Instead of use of the water-soluble rhodium, it is also possible to add and dissolve other silver halide grains previously doped with rhodium in preparing the silver halide.

The amount added is generally from $1X10^{-8}$ to $5X10^{-6}$ mol per mol of silver contained in the silver halide emulsion, and preferably from $5X10^{-8}$ to $1X10^{-6}$ mol.

Addition of these compounds can be appropriately conducted in preparing the silver halide emulsion grains and in each stage prior to coating of the emulsions. In particular, the compounds are preferably added in forming the emulsions to incorporate them into the silver halide grains.

The photographic emulsions for use in the present invention can be prepared by use of the methods described in P. Glafkides, Chimie et Physique Photographique (Paul Montel, 1967), G. F. Duffin, Photographic Emulsion Chemistry (The Focal Press, 1966) and V. L. Zelikman et al., Making and Coating Photographic Emulsion (The Focal Press, 1964).

A soluble silver salt and a soluble halogen salt may be reacted with each other by using any of the single jet process, the double jet process and a combination thereof. A process in which grains are formed in the presence of excess silver ions (so-called reverse mixing process) can also be used. As a type of double jet process, there can also be used a process for maintaining the pAg in a liquid phase constant, in which a silver halide is formed, namely the so-called controlled double jet process. Further, it is preferred that so-called solvents for silver halides such as ammonium, thioether and tetra-substituted thiourea are used to form grains. More preferably, tetra-substituted thiourea compounds are used, which are described in JP-A-53-82408 and JP-A-55-77737. Preferred examples of the thiourea compounds are tetramethylthiourea and 1,3-dimethyl-2-imidazolidinethione.

According to the controlled double jet process and the grain forming process using the solvent for silver halides, silver halide emulsions having a regular crystal form and a narrow grain size distribution can be readily prepared. These processes are useful means for preparing the silver halide emulsions for use in the present invention.

There is no particular limitation on the form of silver halide grains for use in the present invention, and tabular silver halide grains having a high aspect ratio described in Research Disclosure, 22534 (January, 1983), as well as cubic, octahedral and spherical grains, can be used.

Further, in order to homogenize the grain size, it is preferred that grains are allowed to grow rapidly within the range not exceeding the critical degree of saturation by the method of changing the addition rate of silver nitrate and alkali halides depending on the growth speed of grains as described in British Patent 1,535,016, JP-B-48-36890 and JP-B-52-16364, and the method of changing the concentration of aqueous solutions as described in British Patent 4,242,445 and JP-A-55-158124.

The emulsion for use in the present invention is preferably a monodisperse emulsion, and the coefficient of variation thereof is 20% or less, and particularly preferably 15% or less.

The mean grain size of the grains contained in the monodisperse silver halide emulsion is 0.5 μm or less, and particularly preferably from 0.1 μm to 0.4 μm.

The silver halide emulsion for use in the present invention is preferably subjected to chemical sensitization. As the chemical sensitization methods, known methods such as sulfur sensitization, selenium sensitization, tellurium sensitization and noble metal sensitization can be used alone or in combination. When they are used in combination, for example, sulfur sensitization and gold sensitization; sulfur sensitization, selenium sensitization and gold sensitization; and sulfur sensitization, tellurium sensitization and gold sensitization are preferred.

The sulfur sensitization for use in the present invention is usually conducted by adding a sulfur sensitizer and stirring an emulsion at a high temperature of 40°C or more for a definite period of time. As the sulfur sensitizers, known compounds can be used. Examples thereof include various sulfur compounds such as thiosulfates, thiourea compounds, thiazole compounds and rhodanine compounds, as well as sulfur compounds contained in gelatin. Preferred sulfur compounds are thiosulfates and thiourea compounds. Although the amount of the sulfur sensitizers added varies depending on various conditions such as the pH and the temperature in chemical ripening and the size of silver halide grains, it is preferably from 10^{-7} to 10^{-2} mol per mol of silver halide, and more preferably from 10^{-5} to 10^{-3} mol.

As the sulfur sensitizers, various sulfur compounds such as thiosulfates, thiourea compounds, thiazole compounds and rhodanine compounds, as well as sulfur compounds contained in gelatin, can be used. Preferred sulfur compounds are thiosulfates and thiourea compounds, and the pAg in the chemical sensitization is preferably 8.3 or less, and more preferably within the range of from 7.3 to 8.0.

Further, a method of using polyvinylpyrrolidone in combination with a thiosulfate as reported by Moisar, etc., Klein Gelationc. Proc. Symp., 2nd., 301-309 (1970) also gives a good result.

As selenium sensitizers for use in the present invention, known selenium compounds can be used. That is, the selenium sensitization is usually conducted by adding an unstable type and/or non-unstable type selenium compound and stirring an emulsion at a high temperature of 40°C or more, for a definite period of time. As the unstable type selenium compounds, compounds described in JP-B-44-15748, JP-B-43-13489, JP-A-4-109240 and JP-A-4-324855 can be used. In particular, compounds represented by general formulas (VIII) and (IX) in JP-A-4-324855 are preferably used.

Tellurium sensitizers for use in the present invention is a compound which produces silver telluride presumed to be a sensitizing nucleus in the surface or the inside of a silver halide grain. The forming rate of silver telluride in the silver halide emulsion can be tested by the method described in JP-A-5-313284.

Specifically, compounds can be used which are described in U.S. Patents 1,623,499, 3,320,069 and 3,772,031, British Patents 235,211, 1,121,496, 1,295,462 and 1,396,696, Canadian Patent 800,958, JP-A-4-204640, JP-A-4-271341, JP-A-4-333043 and JP-A-5-303157, J. Chem. Soc. Chem. Commnun., 635 (1980), ibid., 1102 (1979), ibid., 645 (1979), J. Chem. Soc. Perkin. Trans., 1, 2191 (1980), The Chemistry of Organic Selenium and Tellurium Compounds, vol.1, edited by S. Patai (1986) and ibid. vol. 2 (1987). In particular, compounds represented by general formulas (II), (III) and (IV) in JP-A-5-313284 are preferably used.

Although the amount of the selenium and tellurium sensitizers for use in the present invention varies depending on silver halide grains used, chemical ripening conditions, etc., it is generally from 10^{-8} to 10^{-2} mol per mol of silver halide, and preferably about from 10^{-7} to 10^{-3} mol. There is no particular limitation on the conditions of chemical sensitization in the present invention. However, the pH is generally from 5 to 8, the pAg is generally from 6 to 11 and preferably from 7 to 10, and the temperature is generally from 40 to 95°C and preferably from 45 to 85°C.

Noble metal sensitizers for use in the present invention include gold, platinum, palladium and iridium, and particularly, gold sensitization is preferred of these. Examples of gold sensitizers for use in the present invention include chloroauric acid, potassium chloroaurate, potassium aurithiocyanate and gold sulfide. They can be used in an amount of about 10^{-7} to 10^{-2} mol per mol of silver halide.

In the course of formation of the silver halide grains and physical ripening, cadmium salts, sulfites, lead salts and thallium salts may be allowed to coexist with the silver halide emulsion for use in the present invention.

In the present invention, the reduction sensitization can be used. As reduction sensitizers, stannous salts, amines, formamidinesulfinic acid and silane compounds can be used.

Thiosulfonic acid compounds may be added to the silver halide emulsion for use in the present invention by the method shown in EP-A-293,917.

The silver halide emulsion in the photographic material for use in the present invention may be used alone or in combination (for example, emulsions different in mean grain size, emulsions different in halogen composition, emulsions different in crystal habit, and emulsions different in the conditions of chemical sensitization).

In the present invention, silver halide emulsions particularly suitable for photographic materials for dot to dot work comprise silver halides containing 90 mol% or more, more preferably 95 mol% or more, of silver chloride, and silver chlorobromide or silver chloroiodobromide containing 0 to 10 mol% of silver bromide. An increase in the proportion of silver bromide or silver iodide unfavorably deteriorates safelight safety in an illuminated room or decreases γ.

Further, it is desirable that the silver halide emulsion for use in the photographic material for dot to dot work in the present invention contains a complex of a transition metal. The transition metal includes Rh, Ru, Re, Os, Ir and Cr.

The ligand thereof includes nitrosyl and thionitrosyl ligands, halide ligands (fluorides, chlorides, bromides and iodides), cyanide ligands, cyanate ligands, thiocyanate ligands, selenocyanate ligands, tellurocyanate ligands, azido ligands and aquo ligands. When the aquo ligands exist, one or two ligands are preferably occupied by the aquo ligands.

Specifically, when rhodium atoms are introduced, they are added as metal salts of any form such as single salts or complex salts in preparing the grains.

The rhodium salts include rhodium monochloride, rhodium dichloride, rhodium trichloride and ammonium hexachlororhodate, and preferably include water-soluble halogen complex compounds of trivalent rhodium, for example, hexachlororhodic (III) acid or salts thereof (such as ammonium salts, sodium salts and potassium salts).

These water-soluble rhodium salts are added in an amount ranging from 1.0×10^{-6} mol to 1.0×10^{-3} mol per mol of silver halide, preferably in an amount of from 1.0×10^{-5} mol to 1.0×10^{-3}, and particularly preferably in an amount of from 5.0×10^{-5} mol to 5.0×10^{-4} mol.

The following complexes of transition metals are also preferred.

1 $[Ru(NO)Cl_5]^{-2}$
2 $[Ru(NO)_2Cl_4]^{-1}$
3 $[Ru(NO)(H_2O)Cl_4]^{-1}$
4 $[Ru(NO)Cl_5]^{-2}$
5 $[Re(NO)CN_5]^{-2}$
6 $[Re(NO)ClCN_4]^{-2}$
7 $[Rh(NO)_2Cl_4]^{-1}$
8 $[Rh(NO)(H_2O)Cl_4]^{-1}$
9 $[Ru(NO)CN_5]^{-2}$
10 $[Ru(NO)Br_5]^{-2}$
11 $[Rh(NS)Cl_5]^{-2}$
12 $[Os(NO)Cl_5]^{-2}$
13 $[Cr(NO)Cl_5]^{-2}$
14 $[Re(NO)Cl_5]^{-2}$
15 $[Os(NS)Cl_4(TeCN)]^{-2}$
16 $[Ru(NS)I_5]^{-2}$
17 $[Re(NS)Cl_4(SeCN)]^{-2}$
18 $[Os(NS)Cl(SCN)_4]^{-2}$
19 $[Ir(NO)Cl_5]^{-2}$

There is no particular limitation on spectral sensitizing dyes for use in the present invention.

Although the amount of the sensitizing dyes added varies depending on the form and the size of silver halide grains, they are used in an amount ranging from 4×10^{-6} to 8×10^{-3} mol per mol of silver halide. For example, when the size of silver halide grains is from 0.2 to 1.3 μm, the amount added is preferably within the range of from 2×10^{-7} to 3.5×10^{-6} mol per m^2 of surface area of silver halide grain, and more preferably within the range of from 6.5×10^{-7} to 2.0×10^{-6} mol.

The light-sensitive silver halide emulsion for use in the present invention may be spectrally sensitized to blue, green, red or infrared light having relatively long wavelengths by use of sensitizing dyes. The sensitizing dyes which can be used include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, styryl dyes, hemicyanine dyes, oxonol dyes and hemioxonol dyes.

The useful sensitizing dyes for use in the present invention are described, for example, in Research Disclosure, Item 17643 IV-A, page 23 (December, 1978), ibid., Item 1831 X, page 437 (August, 1978), U.S. Patents 4,425,425 and 4,425,426, and references cited therein.

In particular, sensitizing dyes having the spectral sensitivity suitable for spectral characteristics of various scanner light sources can be advantageously selected.

For example, the following sensitizing dyes are advantageously selected:

A) For argon laser light sources, simple merocyanine dyes described in JP-A-60-162247, JP-A-2-48653, U.S. Patent 2,161,331, West German Patent 936,071 and JP-A-5-11389;
B) For helium-neon laser light sources, trinuclear cyanine dyes shown in JP-A-50-62425, JP-A-54-18726 and JP-A-59-102229;
C) For LED light sources and red semiconductor lasers, thiacarbocyanine dyes described in JP-B-48-42172, JP-B-51-9609, JP-B-55-39818, JP-A-62-284343 and JP-A-2-105135; and
D) For infrared semiconductor laser light sources, tricarbocyanine dyes described in JP-A-59-191032 and JP-A-60-80841, and dicarbocyanine dyes containing 4-quinoline nuclei described in JP-A-59-192242 and general formulas (IIIa) and (IIIb) of JP-A-3-67242.

These sensitizing dyes may be used alone or in combination. Combinations of the sensitizing dyes are often used particularly for supersensitization. The emulsion may contain a dye having no spectral sensitizing function themselves, or substances which do not substantially absorb visible light and exhibit supersensitization, together with the sensitizing dye.

The sensitizing dye, the combination of the dyes showing supersensitization, and the substances exhibiting supersensitization are described in Research Disclosure, 176, 17643 IV-J, page 23 (December, 1978).

For the argon light sources, S1-1 to S1-13 described in JP-A-8-211571 are preferably used.

For the helium-neon laser light sources, sensitizing dyes represented by general formula (I) described in JP-A-6-75322, page 7, column 11, line 42 to page 8, the last line are particularly preferred. Specifically, compounds I-1 to I-35 described therein are preferred. In addition to these, compounds described in general formula (I) of JP-A-6-75322 and I-1 to I-34 of general formula (I) of JP-A-7-287338 are both preferably used.

For the LED light sources and the infrared semiconductor lasers, it is particularly preferred to use dyes of S3-1 to S3-8 described in JP-A-8-211571.

For the infrared semiconductor laser light sources, dyes of S4-1 to S4-9 described in JP-A-8-211571 are preferably used in addition to these.

For white light used for camera work, sensitizing dyes of general formula (IV) described in JP-A-6-313937 are preferred, and specifically, IV-1 to IV-20 described therein are preferably used. Besides, dyes of general formulas (III) and (IV) described in JP-A-4-19647 are preferred, and specifically, III-1 to III-20 and IV-1 to IV-11 described therein are preferably used.

For preventing a reduction in sensitivity or fog in manufacturing processes, during storage or during photographic processing of the silver halide photographic materials, various compounds can be added to the photographic emulsion for use in the present invention. That is, the compounds which can be added include many compounds known as antifogging agents or stabilizers such as azoles, for example, benzothiazolium salts, nitroindazole compounds, chlorobenzimidazole compounds, bromobenzimidazole compounds, mercaptotetrazole compounds, mercaptothiazole compounds, mercaptobenzothiazole compounds, mercaptothiadiazole compounds, aminotriazole compounds, benzothiazole compounds and nitrobenzotriazole compounds; mercaptotriazine compounds; thioketo compounds such as oxazolinethione; azaindene compounds such as triazaindene compounds, tetraazaindene compounds (particularly, 4-hydroxy-substituted (1,3,3a,7)tetraazaindene compounds) and pentaazaindene compounds; benzenethiosulfonic acid, benzenesulfinic acid and benzenesulfonic acid amide. Of these, benzotriazole compounds (for example, 5-methylbenzotriazole) and nitroindazole compounds (for example, 5-nitroindazole) are preferred. Further, these compounds may be added to processing solutions. Furthermore, compounds releasing inhibitors during development described in JP-A-62-30243 can be added as stabilizers or for preventing black peppers.

Techniques can also be used in which polymer latexes are added to the silver halide emulsion layer or a backing layer to improve dimension stability. These techniques are described, for example, in JP-B-39-4272, JP-B-39-17702 and JP-B-43-13482. Besides, dispersions of water-insoluble or slightly soluble synthetic polymers can be added for improving the dimension stability. For example, polymers comprising alkyl (meth)acrylate, alkoxyacryl (meth)acrylate or glycidyl (meth)acrylate alone or combinations thereof, or combinations of them with acrylic acid or methacrylic acid as monomer components can be used.

Plasticizers, for example, polymers or emulsions such as alkyl acrylate latexes and polyols such as trimethylol propane, can be added to the emulsion layer of the photographic material for use in the present invention to improve pressure characteristics.

The photographic emulsion layer or other hydrophilic colloidal layers of the photographic materials produced according to the present invention may contain various surfactants for the various purposes of coating aids, static charge prevention, improvement in slipperiness, emulsified dispersion, adhesion prevention and improvement in photographic characteristics (for example, development acceleration, contrast enhancement and sensitization).

Examples of such surfactants include nonionic surfactants such as saponin (steroid series), alkylene oxide derivatives (for example, polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, and polyethylene oxide adducts of silicones), glycidol derivatives (for example, alkenylsuccinic acid polyglycerides and alkylphenol polyglycerides), fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic surfactants containing an acid group such as carboxyl, sulfo, phospho, sulfuric ester and phosphoric ester groups, such as alkylcarbonates, alkylsulfonates, alkylbenezenesulfonates, alkylnaphthalenesulfonates, alkylsulfuric esters, alkylphosphoric esters, N-acyl-N-alkyltaurines, sulfosuccinic esters, sulfoalkyl polyoxyethylene alkylphenyl ethers and polyoxyethylene alkylphosphoric esters; amphoteric surfactants such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric or phosphoric esters, alkylbetaines and amino oxides; and cationic surfactants such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts such as pyridinium and imidazolium, and phosphonium or sulfonium salts containing aliphatic or heterocyclic rings.

Gelatin is used as a binder material for the photographic material for use in the present invention. However, hydrophilic colloids can also be used in combination therewith. Examples of such hydrophilic colloids include gelatin derivatives, cellulose derivatives, graft polymers of gelatin and other polymers, and other proteins, saccharide derivatives, cellulose derivatives and synthetic hydrophilic polymer substances such as homopolymers or copolymers.

Gelatin is advantageously used as a binder or a protective colloid for the photographic emulsion, but other hydrophilic colloids can also be used. Examples thereof include gelatin derivatives, graft polymers of gelatin and other polymers, proteins such as albumin and casein, cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfate, saccharide derivatives such as sodium alginate and starch derivatives, and many kinds of synthetic hydrophilic polymer substances such as homopolymers or copolymers of polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole.

As gelatin, acid-treated gelatin, as well as lime-treated gelatin, may be used, and hydrolyzed products of gelatin and enzyme-decomposed products of gelatin can also be used.

In the present invention, a homopolymer of polymethyl methacrylate or copolymers of methyl methacrylate and methacrylic acid as described in U.S. Patents 2,992,101, 2,701,245, 4,142,894 and 4,396,706, organic compounds such as starch, and finely divided grains of inorganic compounds such as silica, titanium dioxide and barium strontium sulfate can be used as matte agents. The grain size thereof is preferably from 1.0 to 10 μm, and particularly from 2 to 5 μm.

In the silver halide photographic material for use in the present invention, the photographic emulsion layer or other layers may be colored with dyes for absorbing light within the particular wavelength range, namely conducting halation or irradiation, or providing filter layers to control spectral composition of light to be incident on the photographic emulsion layer. Such dyes include oxonol dyes having pyrazolone nuclei or barbituric acid nuclei, hemioxonol dyes, azo dyes, azomethine dyes, anthraquinone dyes, arylidene dyes, styryl dyes, triarylmethane dyes, merocyanine dyes and cyanine dyes.

The oxonol dyes, the hemioxonol dyes and the merocyanine dyes are useful among others. Specific examples of the dyes which can be used are described in West German Patent 616,007, British Patents 584,609 and 1,117,429, JP-B-26-7777, JP-B-39-22069, JP-B-54-38129, JP-A-48-85130, JP-A-49-99620, JP-A-49-114420, JP-A-49-129537 and Photo. Abstr., 128 ('21). In particular, for illuminated room dot to dot work photographic materials, these dyes are preferably used. Further, fine solid grain dispersions of dyes described in JP-A-7-168311, pages 23 to 30 may also be used. In the silver halide photographic materials according to the present invention, when dyes or ultraviolet absorbers are added to the hydrophilic colloidal layers, they may be mordanted with cationic polymers or the like.

As coating aids for an undercoat layer, nonionic surfactants of the polyethylene oxide series can be preferably used in combination with polymers having cation sites.

Preferred examples of the polymer providing the cation sites include anion conversion polymers.

As the anion conversion polymers, various known quaternary ammonium salt (or phosphonium salt) polymers can be used. The quaternary ammonium salt (or phosphonium salt) polymers are widely known as mordant polymers or antistatic agent polymers in the following publications.

They include water-dispersed latexes as described in JP-A-59-166940, U.S. Patent 3,958,995, JP-A-55-142339, JP-A-54-126027, JP-A-54-155835, JP-A-53-30328 and JP-A-54-92274, polyvinylpyridinium salts described in U.S. Patents 2,548,564, 3,148,061 and 3,756,814, water-soluble quaternary ammonium salt polymers described in U.S. Patent 3,709,690, and water-insoluble quaternary ammonium salt polymers described in U.S. Patent 3,898,088.

In order to prevent them from moving from a desired layer to another layer or into a processing solution to influence photographically undesirable effect, it is particularly preferred that monomers each having at least 2 (preferably, 2 to 4) ethylenic unsaturated groups are copolymerized to use as crosslinked aqueous polymer latexes.

For fixation of dyes, solid dispersing methods described in JP-A-55-155350 and WO88/04794 are also effective.

The photographic material for use in the present invention can contain developing agents such as hydroquinone derivatives and phenidone derivatives for the various purposes of stabilizers, accelerators and the like.

In the photographic material for use in the present invention, the photographic emulsion layer and other hydrophilic layers may contain inorganic or organic hardening agents. Examples of the hardening agents include chromium salts (such as chromium alum and chromium acetate), aldehydes (such as formaldehyde and glutaraldehyde), N-methylol compounds (such as dimethylolurea), dioxane derivatives, active vinyl compounds (such as 1,3,5-triacryloylhexahydro-s-triazine and 1,3-vinylsulfonyl-2-propanol), active halogen compounds (such as 2,4-dichloro-6-hydroxy-s-triazine) and mucohalogen acids (such as mucochloric acid). They can be used alone or in combination.

In the photographic material for use in the present invention, the photographic emulsion layer and other hydrophilic layers may contain hydroquinone derivatives (so-called DIR-hydroquinone) which releases a development inhibitor corresponding to the density of images in development.

Specific examples thereof include compounds described in U.S. Patents 3,379,529, 3,620,746, 4,377,634 and 4,332,878, JP-A-49-129536, JP-A-54-67419, JP-A-56-153336, JP-A-56-153342, JP-A-59-278853, JP-A-59-90435, JP-A-59-90436 and JP-A-59-138808.

The silver halide emulsion layer and other layers of the photographic material for use in the present invention preferably contain a compound having an acid group. The compound having an acid group include organic acids such as salicylic acid, acetic acid and ascorbic acid, and polymers or copolymers having acid monomers such as acrylic acid, maleic acid and phthalic acid as repeating units. With respect to these compounds, the descriptions of JP-A-61-223834, JP-A-61-228437, JP-A-62-25745 and JP-A-62-55642 can be referred to. Of these compounds, ascorbic acid is particularly preferred for low molecular weight compounds, and water dispersed latexes of copolymers composed of acid monomers such as acrylic acid and crosslinking monomers each having at least 2 unsaturated groups such as divinylbenzene are particularly preferred for polymers.

The silver halide emulsions thus prepared are applied to a support such as a cellulose acetate film and a polyethylene terephthalate film by processes such as the dipping process, the air knife process, the bead process, the extrusion doctor process, and the duplicating process, followed by drying.

There is no particular limitation on various additives for the photographic material for use in the present invention. For example, ones described in the following portions can be preferably used.

Item	Corresponding Portion
1) Nucleating Accelerators	Compounds of general formulas (I), (II), (III), (IV), (V) and (VI) described in JP-A-6-82943; general formulas (II-m) to (II-p) and compounds II-1 to II-22 described in JP-A-2-103536, page 9, upper right column, line 13 to page 16, upper left column, line 10, and compounds described in JP-A-1-179939
2) Spectral Sensitizing Dyes	Spectral sensitizing dyes described in JP-A-2-12236, page 8, lower left column, line 13 to lower right column, line 4; JP-A-2-103536, page 16, lower right column, line 3 to page 17, lower left column, line 20; JP-A-1-112235; JP-A-2-124560; JP-A-3-7928; JP-A-5-11389; and JP-A-4-330434
3) Surfactants	JP-A-2-12236, page 9, upper right column, line 7 to lower right column, line 7; and JP-A-2-18542, page 2, lower left column, line 13 to page 4, lower right column, line 18
4) Antifoggants	Thiosulfinic acid compounds described in JP-A-2-103536, page 17, lower right column, line 19 to page 18, upper right column, line 4 and page 18, lower right column, line 1 to line 5; and JP-A-1-237538
5) Polymer Latexes	JP-A-2-103536, page 18, lower left column, line 12 to line 20
6) Compounds Having Acid Group	JP-A-2-103536, page 18, lower right column, line 6 to page 19, upper left column, line 1
7) Matte Agents Lubricants Plasticizers	JP-A-2-103536, page 19, upper left column, line 15 to upper right column, line 15
8) Hardening Agents	JP-A-2-103536, page 18, upper right column, line 5 to line 17
9) Dyes	Dyes described in JP-A-2-103536, page 17, lower right column, line 1 to line 18; and solid dyes described in JP-A-2-294638 and JP-A-5-11382
10) Binders	JP-A-2-18542, page 3, lower right column, line 1 to line 20
11) Black Pepper Inhibitor	Compounds described in U.S. Patent 4,956,257 and JP-A-1-118832
12) Redox Compounds	Compounds represented by general formula (I) of JP-A-2-301743 (particularly, compound examples 1 to 50; general formulas (R-1), (R-2) and (R-3), and compounds 1 to 75 described in JP-A-3-174143, pages 3 to 20; and compounds described in JP-A-5-257239 and JP-A-4-278939
13) Monomethine Compounds	Compounds of general formula (II) of JP-A-2-287532 (particularly compound examples II-1 to II-26)
14) Dihydroxybenzenes	Compounds described in JP-A-3-39948, page 11, upper left column to page 12, lower left column, and EP-A-452,772

The present invention will be described in more detail with reference to the following Examples, but the invention should not be construed as being limited thereto.

The composition of developer (1) per liter of working solution is shown below:

Developer (1)

Sodium Hydrogencarbonate	34 g (0.40 mol)
Sodium Carbonate Monohydrate	50 g (0.40 mol)
Diethylenetriaminepentaacetic Acid	4 g
Sodium Sulfite	2.5 g (0.02 mol)
Potassium Bromide	2 g
5-Methylbenzotriazole	0.08 g
Sodium Erysorbate Monohydrate	45 g
N-Ethyl-p-aminophenol	7.5 g
The pH was adjusted to 9.7.	

Then, for comparison, 5.0 g of 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone was added in place of N-methyl-p-aminophenol to prepare developer (2).

The pH adjustment was carried out by use of NaOH.

For the above-described developer (1), the carbonate concentration was 0.8 mol/liter, and the sulfite concentration was 0.02 mol/liter. The carbonate concentration and the sulfite concentration of developer (1) were changed to prepare developers (3) to (7).

The carbonate concentration was changed by varying the amounts of sodium hydrogencarbonate and sodium carbonate at the same ratio.

Further, the pH of the developers were also changed by varying the amount of NaOH added. The compositions of the developers are shown in Table 9.

TABLE 9

Developing Solution No.	Carbonate (mol/liter)	Sulfite (mol/liter)	pH	Remark
(1)	0.8	0.02	9.7	
(2)	0.8	0.02	9.7	Comparison
(3)	0.8	0.02	10.0	
(4)	0.4	0.02	9.7	Comparison
(5)	0.4	0.02	10.0	Comparison
(6)	0.8	0.1	9.7	
(7)	0.8	0.1	10.0	

The formulation of fixing solution (1) per liter of working solution is shown below:

Ammonium Thiosulfate	120 g
Disodium Ethylenediaminetetraacetate Dihydrate	0.03 g
Sodium Thiosulfate Pentahydrate	11.0 g
Sodium Metasulfite	19.0 g
Sodium Hydroxide	12.4 g
Acetic Acid (100%)	30.0 g
Tartaric Acid	2.9 g
Sodium Gluconate	1.7 g
Aluminum Sulfate	8.4 g
pH	4.8

The formulation of fixing solution (2) is shown below:

(Fixing Solution (2))

Sodium Thiosulfate	1.0 mol/liter
1,4,5-Trimethyl-1,2,4-triazolium-3-thiolate	0.1 mol/liter
Sodium Bisulfite	30 g/liter
Disodium EDTA Tetraacetate	0.02 g/liter

Methods for producing photographic materials (1) to (4) are described below.

Structural formulas of compounds used are collectively shown after the description of photographic material (4).

Preparation of Photographic Material (1)

A method for preparing Emulsion A is described below.

Solution 2 and solution 3 were concurrently added to solution 1 maintained at a temperature of 38°C and a pH of 4.5 with stirring over 24 minutes to form grains having a size of 0.18 μm. Subsequently, solution 4 and solution 5 were added over 8 minutes, and 0.15 g of potassium iodide was added to terminate the formation of grains.

Thereafter, the grains were normally washed with water by the flocculation process, and gelatin was added thereto, followed by adjustment of pH and pAg to 5.2 and 7.5, respectively. Then, 4 mg of sodium thiosulfate, 2 mg of N,N-dimethylselenourea, 10 mg of chloroauric acid, 4 mg of sodium benzenethiosulfonate and 1 mg of sodium benzenethiosulfinate were added to conduct chemical sensitization at 55°C so as to give optimum sensitivity.

Further, as a stabilizer, 50 mg of 2-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was added, and phenoxyethanol was added as a preservative so as to give 100 ppm. Finally, cubic silver iodochlorobromide grains having a mean grain size of 0.20 μm and a silver chloride content of 80 mol% were obtained (coefficient of variation: 9%).

〈 Solution 1 〉

Water	1.0 liter
Gelatin	20 g
Sodium Chloride	2 g
1,3-Dimethyl-2-imidazolidine-2-thione	20 mg
Sodium Benzenethiosulfonate	3 mg

〈 Solution 2 〉

Water	600 ml
Silver Nitrate	150 g

〈 Solution 3 〉

Water	600 ml
Sodium Chloride	45 g
Potassium Bromide	21 g
Potassium Hexachloroiridate (III) (0.001% aqueous solution)	15 ml
Ammonium Hexabromorhodate (III) (0.001% aqueous solution)	1.5 ml

〈 Solution 4 〉

Water	200 ml
Silver Nitrate	50 g

⟨ Solution 5 ⟩

Water	200 ml
Sodium Chloride	15 g
Potassium Bromide	7 g
$K_4Fe(CN)_6$	30 mg

⟨ Preparation of Silver Halide Photographic Material ⟩

An UL layer, an EM layer, a PC layer and an OC layer were formed, in this order from a support side, on a polyethylene terephthalate film support undercoated with a moisture-proof layer containing vinylidene chloride to prepare a sample.

The preparation of each layer and the coating amount thereof are shown below:

(UL Layer)

A dispersion of polyethyl acrylate was added to an aqueous solution of gelatin in an amount of 30% by weight based on gelatin, and the resulting solution was applied so as to give an amount of gelatin coated of 0.5 g/m^2.

(EM Layer)

To the above-described emulsion A, the following compound (S-1) was added in an amount of 2.5X10^{-4} mol per mol of silver as a sensitizing dye, and 3X10^{-4} mol per mol of silver of the mercapto compound represented by (a) shown below, 3.0X 10^{-3} mol of KBr, 7.0X10^{-4} mol of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 4X10^{-4} mol of the mercapto compound represented by (b), 4X10^{-4} mol of the triazine compound represented by (c), 2X10^{-3} mol of 5-chloro-8-hydroxyquinoline, 7.0X10^{-5} mol of a nucleating agent (HZ-1) (hydrazine derivative), 4.2X10^{-4} mol of nucleating accelerator (AC-1), 9X10^{-3} mol of sodium p-dodecylbenzenesulfonate and 3X10^{-2} mol of hydroquinone were added thereto. Further, 200 mg/m^2 of a dispersion of polyethyl acrylate, 200 mg/m^2 of a latex copolymer of methyl acrylate, sodium 2-acrylamido-2-methylpropanesulfonate and 2-acetoacetoxyethyl methacrylate (88:5:7 in weight ratio), 200 mg/m^2 of colloidal silica having a mean grain size of 0.02 μm and further 200 mg/m^2 of (d) as a hardener were added. The pH of the completed solution was 5.7.

(PC Layer)

A dispersion of polyethyl acrylate was added to an aqueous solution of gelatin in an amount of 50% by weight based on gelatin, and the following surfactant (e) and 1,5-dihydroxy-2-benzaldoxime were added so as to be applied in amounts of 5 mg/m^2 and 10 mg/m^2, respectively. The resulting solution was applied so as to give an amount of gelatin coated of 0.5 g/m^2.

⟨ OC Layer ⟩

Gelatin (0.5 g/m^2), 40 mg/m^2 of an irregular SiO_2 matte agent having a mean grain size of about 3.5 μm, 0.1 g/m^2 of methanol silica, 100 mg/m^2 of polyacrylamide, 20 mg/m^2 of silicone oil, 5 mg/m^2 of the fluorine surfactant represented by the following structural formula (f) as a coating aid, 100 mg/m^2 of sodium dodecylbenezenesulfonate and 20 mg/m^2 of the compound represented by the following structural formula (g) were applied.

The coated sample had a back layer and a back protective layer having the following compositions:

(Formulation of Back Layer)

Gelatin	3 g/m^2
Latex, Polyethyl Acrylate	2 g/m^2
Surfactant, Sodium p-Dodecylbenzenesulfonate	40 mg/m^2
Hardener, (d) shown below	200 mg/m^2
SnO_2/Sb (weight ration: 90/10, mean grain size: 0.20 μm)	200 mg/m^2
Dye, Mixture of Dye (a), Dye (b) and Dye (c)	
Dye (a)	70 mg/m^2
Dye (b)	70 mg/m^2
Dye (c)	90 mg/m^2

(Back Protective Layer)

Gelatin	0.8 mg/m^2
Fine Polymethyl Methacrylate Particles (mean particle size: 4.5 μm)	30 mg/m^2
Sodium Dihexyl-α-sulfosuccinate	15 mg/m^2
Sodium p-Dodecylbenzenesulfonate	15 mg/m^2
Sodium Acetate	40 mg/m^2

Preparation of Photographic Material (2)

(Emulsion B)

Emulsion B was prepared in the same manner as with emulsion A, except that the addition amount of the sodium thiosulfate was changed to 2 mg per mol of silver, and that no selenium sensitizer was used.

A sample was prepared in the same manner as in the preparation of photographic material (1) with the exception that the sensitizing dye of photographic material (1) was substituted by S-2 ($5X10^{-4}$ mol/mol Ag) and S-3 ($5X10^{-4}$ mol/mol Ag) shown below, and that emulsion B was used as an emulsion for the EM layer.

Preparation of Photographic Material (3)

(Emulsion C)

A 1.5% aqueous solution of gelatin having a pH of 2.0 maintained at 40°C which contains sodium chloride, $3X10^{-5}$ mol per mol of silver of sodium benzenesulfonate and $5X10^{-3}$ mol of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, and an aqueous solution of sodium chloride containing $2.0X10^{-6}$ mol per mol of silver of $K_2Ru(NO)Cl_5$ were concurrently added by the double jet method at a potential of 95 mV over 3 minutes and 30 seconds by half of the silver amount of final grains to prepare core grains having a size of 0.12 μm. Then, an aqueous solution of silver nitrate and an aqueous solution of sodium chloride containing $6.0X10^{-6}$ mol per mol of silver of $K_2Ru(NO)Cl_5$ were added over 7 minutes in the same manner as described above to prepare cubic silver chloride grains having a mean grain size of 0.15 μm (coefficient of variation: 12%).

Thereafter, the grains were washed with water by the flocculation process well known in the art, and gelatin was added thereto after removal of soluble salts. Compound A and phenoxyethanol were each added in an amount of 60 mg per mol of silver as preservatives, followed by adjustment of pH and pAg to 5.7 and 7.5, respectively. Further, after addition of $4X10^{-5}$ mol per mol of silver of chloroauric acid and $4X10^{-5}$ mol of compound Z, $1X10^{-5}$ mol of sodium thiosulfate and $1X10^{-5}$ mol of potassium selenocyanate were added, and heated at 60°C for 60 minutes to conduct chemical sensitization. Then, $1X10^{-3}$ mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added as a stabilizer (as the final grains, pH=5.7, pAg=7.5, Ru=$4.0X10^{-6}$ mol/mol-Ag).

The following support was coated with EM, PC and OC layers in this order.

(EM)

The following compounds were added to the above-described emulsion C, and the resulting emulsion was applied so as to give a coating amount of gelatin of 0.9 g/m^2 and a coating amount of silver of 2.7 g/m^2, thereby forming a silver halide emulsion layer.

1-Phenyl-5-mercaptotetrazole	1 mg/m^2
Nucleating Accelerator (AC-2)	$3.6X10^{-3}$ mol (/mol-Ag)
N-Oleyl-N-methyltaurine Sodium Salt	10 mg/m^2
Compound-B	10 mg/m^2
Compound-C	10 mg/m^2
Compound-D	10 mg/m^2
n-Butyl Acrylate/2-Acetoacetoxyethyl Methacrylate/Acrylic Acid Copolymer (89/8/3)	760 mg/m^2
Compound-E (Hardener)	105 mg/m^2
Polysodium Styrenesulfonate	57 mg/m^2
Nucleating Agent (HZ-3)	$1.2X10^{-3}$ mol (/mol-Ag)

(PC)

The following compounds were added to an aqueous solution of gelatin, and the resulting emulsion was applied so as to give an amount of gelatin coated of 0.6 g/m^2.

Gelatin (Ca^{++} content: 2700 ppm)	0.6 g/m^2
Sodium p-Dodecylbenzenesulfonate	10 mg/m^2
Sodium Polystyrenesulfonate	6 mg/m^2
Compound-A	1 mg/m^2
Compound-F	14 mg/m^2
n-Butyl Acrylate/2-Acetoacetoxyethyl Methacrylate/Acrylic Acid Copolymer (89/8/3)	250 mg/m^2

(OC)

The following compounds were added to an aqueous solution of gelatin, and the resulting emulsion was applied so as to give an amount of gelatin coated of 0.45 g/m^2.

Gelatin (Ca^{++} content: 2700 ppm)	0.45 g/m^2
Irregular Silica Matte Agent (mean grain size: 3.5 μm, pore size: 25 Å, surface area: 700 m^2/g)	40 mg/m^2
Irregular Silica Matte Agent (mean grain size: 2.5 μm, pore size: 170 Å, surface area: 300 m^2/g)	10 mg/m^2
N-Perfluorooctanesulfonyl-N-propylglycine Potassium	5 mg/m^2
Sodium p-Dodecylbenzenesulfonate	30 mg/m^2
Compound-A	1 mg/m^2
Liquid Paraffin	40 mg/m^2
Solid Disperse Dye-G_1	30 mg/m^2
Solid Disperse Dye-G_2	150 mg/m^2
Polysodium Styrenesulfonate	4 mg/m^2

Then, the opposite surface of the support was concurrently coated with the following coating solutions for a conductive layer and a back layer.

〈Preparation of Coating Solution for Conductive Layer and Coating Thereof〉

The following compounds were added to an aqueous solution of gelatin, and the resulting solution was applied so as to give an amount of gelatin coated of 0.06 g/m^2.

SnO_2/Sb (weight ratio: 9/1; mean grain size: 0.25 μm)	186 mg/m^2
Gelatin (Ca^{++} content: 3000 ppm)	60 mg/m^2
Sodium p-Dodecylbenzenesulfonate	13 mg/m^2
Sodium Dihexyl-α-sulfosuccinate	12 mg/m^2
Sodium Polystyrenesulfonate	10 mg/m^2
Compound-A	1 mg/m^2

〈 Preparation of Coating Solution for Back Layer and Coating Thereof〉

The following compounds were added to an aqueous solution of gelatin, and the resulting solution was applied so as to give an amount of gelatin coated of 1.94 g/m^2.

Gelatin (Ca^{++} content: 30 ppm)	1.94 mg/m^2
Fine Polymethyl Methacrylate Particles (mean particle size: 3.4 µm)	15 mg/m^2
Compound-H	140 mg/m^2
Compound-I	140 mg/m^2
Compound-J	30 mg/m^2
Compound-K	40 mg/m^2
Sodium p-Dodecylbenzenesulfonate	7 mg/m^2
Sodium Dihexyl-α-sulfosuccinate	29 mg/m^2
Compound-L	5 mg/m^2
N-Perfluorooctanesulfonyl-N-propylglycine Potassium	5 mg/m^2
Sodium Sulfate	150 mg/m^2
Sodium Acetate	40 mg/m^2
Compound-E (Hardener)	105 mg/m^2

(Support and Undercoat Layer)

A first undercoat layer and a second undercoat layer having the following compositions were formed on both faces of a biaxially oriented polyethylene terephthalate support (thickness: 100 µm).

〈 First Undercoat Layer〉

Core/Shell Type Vinylidene Chloride Copolymer (1)	15 g
2,4-Dichloro-6-hydroxy-s-triazine	0.25 g
Fine Polystyrene Particles (mean particle size: 3 µm)	0.05 g
Compound-M	0.20 g
Colloidal Silica (Snowtex ZL; grain size: 70 to 100 µm; manufactured by Nissan Chemical Industries Ltd.)	0.12 g
Water to make	100 g

Further, 10% by weight of KOH was added thereto, and the pH was adjusted to 6. The resulting solution was applied so as to give a dry film thickness of 0.9 µm at a drying temperature of 180°C for 2 minutes.

〈 Second Undercoat Layer 〉

Gelatin	1 g
Methyl Cellulose	0.05 g
Compound-N	0.02 g
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	0.03 g
Compound-A	$3.5X10^{-3}$ g
Acetic Acid	0.2 g
Water to make	100 g

This coating solution was applied so as to give a dry film thickness of 0.1 µm at a drying temperature of 170°C for 2 minutes. Thus, a sample was prepared.

Preparation of Photographic Material (4)

(Emulsion D)

To a 2% aqueous solution of gelatin containing sodium chloride (0.3%), 1,3-dimethyl-2-imidazolithione (0.002%) and citric acid (0.05%), 250 cc of an aqueous solution of silver nitrate in which 64 g of silver nitrate was dissolved and 250 cc of an aqueous solution of silver halides in which 20 g of potassium bromide and 14 g of sodium chloride containing $K_2Rh(H_2O)Cl_6$ corresponding to $1X10^{-7}$ mol per mol of silver of the whole emulsion and K_3IrCl_6 corresponding to $2X10^{-7}$ mol were dissolved were added by the double jet method at 38°C over 12 minutes with stirring to obtain silver chlorobromide grains having a mean grain size of 0.16 µm and a silver chloride content of 55 mol%, thereby conducting nucleation. Subsequently, 300 cc of an aqueous solution of silver nitrate in which 106 g of silver nitrate was dissolved and 300 cc of an aqueous solution of silver halides in which 28 g of potassium bromide and 26 g of sodium chloride were dissolved were added by the double jet method over 20 minutes to form grains.

Thereafter, a KI solution was added in an amount of $1X10^{-3}$ mol per mol of silver to conduct conversion, and the grains were normally washed with water by the flocculation process. Gelatin was added thereto in an amount of 40 g per mol of silver, followed by adjustment of pH and pAg to 5.9 and 7.5, respectively. Then, 3 mg per mol of silver of sodium benzenethiosulfonate, 1 mg of sodium benzenesulfinate, 2 mg of sodium thiosulfate, 2 mg of a compound represented by the following structural formula (h) and 8 mg of chloroauric acid were added, and heated at 60°C for 70 minutes to conduct chemical sensitization. Thereafter, 150 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as a stabilizer and 100 mg of proxel as a preservative were added, followed by addition of 400 mg of the dye represented by the following structural formula (i). After 10 minutes, the temperature was lowered. The resulting grains were cubic silver iodochlorobromide grains having a mean grain size of 0.22 µm and a silver chloride content of 60 mol% (coefficient of variation: 10%). (Preparation of Coating Solution for Emulsion Layer)

To this emulsion, $2X10^{-4}$ mol per mol of silver of a short-wave cyanine dye represented by the following structural formula (j), $5X10^{-3}$ mol of potassium bromide, $2X10^{-4}$ mol of 1-phenyl-5-mercaptotetrazole, $2X10^{-4}$ mol of a mercapto compound represented by the following structural formula (k), $3X10^{-4}$ mol of a triazine compound represented by the following structural formula (l), $6X10^{-4}$ mol of nucleating accelerator (AC-1) and $2X10^{-4}$ of nucleating agent (HZ-2) were added. Hydroquinone, sodium p-dodecylbenezenesulfonate, colloidal silica (Snowtex C manufactured by Nissan Chemical Industries Ltd.), a dispersion of polyethyl acrylate and 1,2-bis(vinylsulfonylacetamido)ethane were further added so as to be applied in amounts of 100 mg/m², 10 mg/m², 150 mg/m², 500 mg/m² and 80 mg/m², respectively, to prepare a coating solution for an emulsion layer. The pH of the coating solution was adjusted to 5.6.

(Preparation of PC and OC Coating Solutions)

To a gelatin solution containing proxel as a preservative, a compound represented by (n), a compound represented by (o) and a dispersion of polyethyl acrylate were added so as to be applied in amounts of 10 mg/m², 100 mg/m² and 300 mg/m², respectively, to prepare a PC solution.

Further, to a gelatin solution containing proxel as a preservative, an irregular SiO_2 matte agent having a mean grain size of about 3.5 µm, colloidal silica (Snowtex C manufactured by Nissan Chemical Industries Ltd.), liquid paraffin, the fluorine surfactant represented by the following structural formula (p) and sodium p-dodecylbenezenesulfonate as coating aids were added so as to be applied in amounts of 50 mg/m^2, 100 mg/m^2, 30 mg/m^2, 5 mg/m^2 and 30 mg/m^2, respectively, to prepare an OC solution.

A polyethylene terephthalate film both faces of which were undercoated with moisture-proof layers containing vinylidene chloride was coated with these solutions to form an emulsion layer (silver amount: 3.0 g/m^2, gelatin: 1.5 g.m^2) as the lowermost layer, a PC layer (gelatin: 0.5 g/m^2) and an OC layer (gelatin: 0.4 g/m^2). The pH of an emulsion surface of the resulting sample was 5.8.

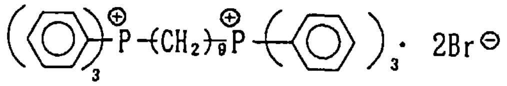
A back layer was formed according to the following formulation.

(Back Layer)

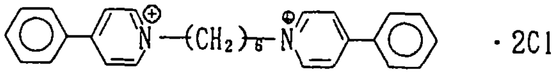
Gelatin	1.5 g/m^2
Surfactant, Sodium p-Dodecylbenzenesulfonate	30 mg/m^2
Hardener for Gelatin	100 mg/m^2
Dyes, Mixture of the Following Dyes (q), (r), (s) and (t)	
Dye (q)	50 mg/m^2
Dye (r)	100 mg/m^2
Dye (s)	30 mg/m^2
Dye (t)	50 mg/m^2
Proxel	1 mg/m^2

Structural formulas of the additives used in photographic materials (1) to (4) are shown below.

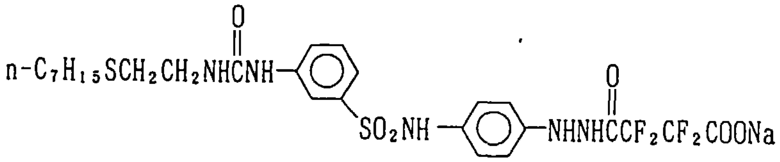
AC－1



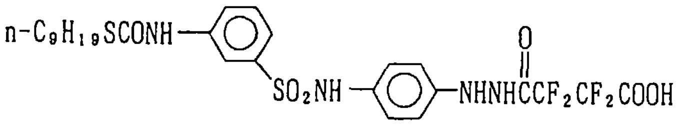
AC－2



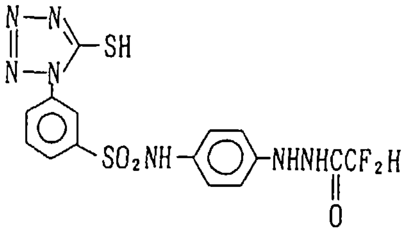
HZ－1



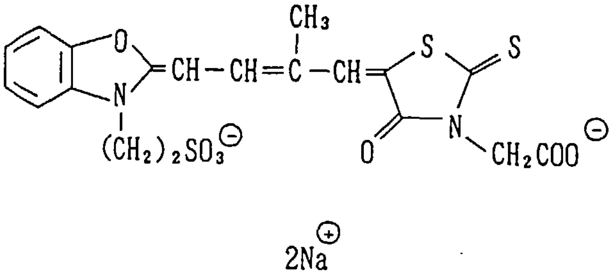
HZ－2



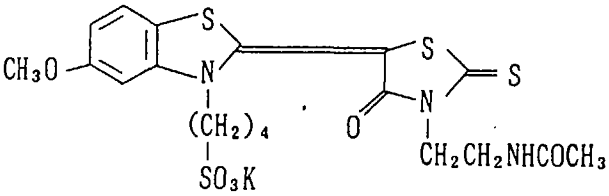
HZ－3



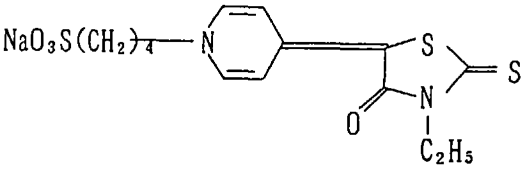
(S－1)


CH₃
O
N
CH－CH＝C－CH＝
S
S
(CH₂)₂SO₃⊖
O
N
CH₂COO⊖
2Na⊕

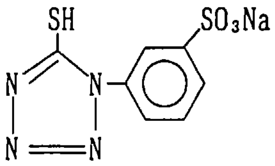
(S－2)


S
CH₃O
N
(CH₂)₄
SO₃K
S
S
O
N
CH₂CH₂NHCOCH₃

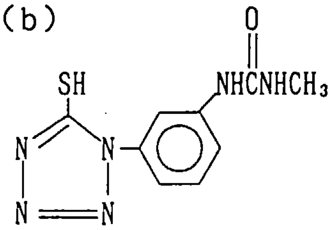
(S－3)


NaO₃S(CH₂)₄
N
S
S
O
N
C₂H₅

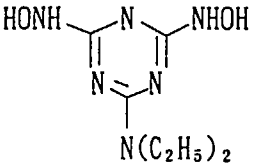
(a)



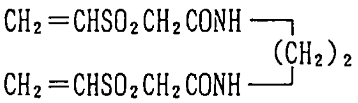
(b)



(c)



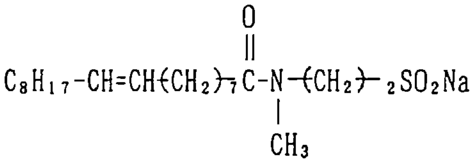
(d)



$$CH_2{=}CHSO_2CH_2CONH{-}(CH_2)_2{-}NHCOCH_2SO_2CH{=}CH_2$$

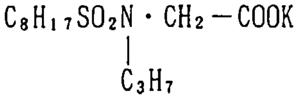
110 mg/m^2

(e)



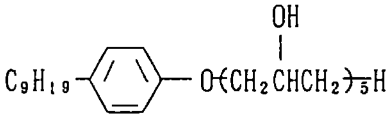
$$C_8H_{17}{-}CH{=}CH{-}(CH_2)_7{-}C(=O){-}N(CH_3){-}(CH_2)_2{-}SO_2Na$$

(f)

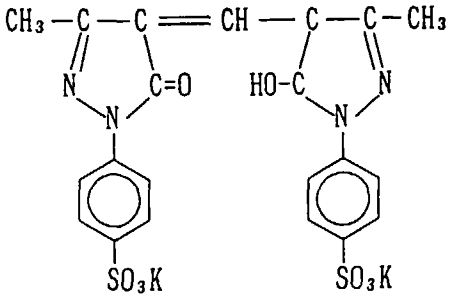


$$C_8H_{17}SO_2N(C_3H_7)\cdot CH_2{-}COOK$$

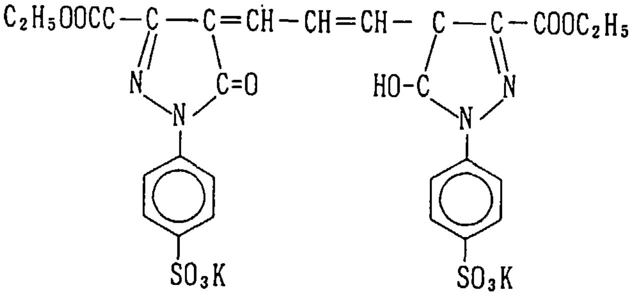
(g)



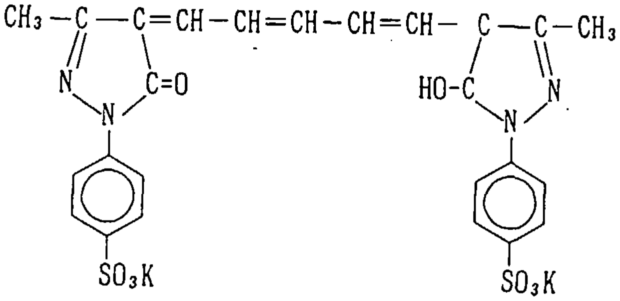
Dye (a)



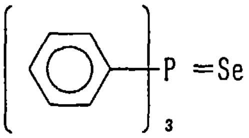
Dye (b)



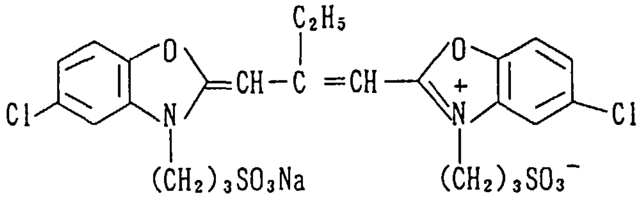
Dye (c)



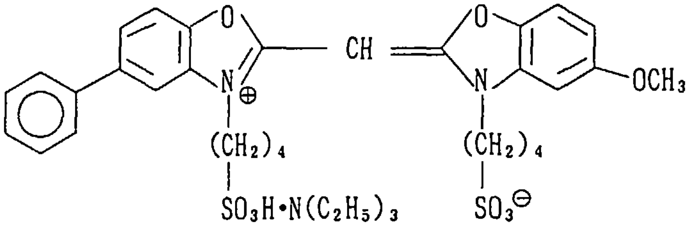
(h)



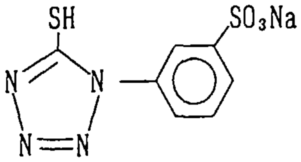
(i)



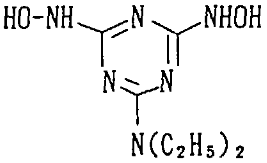
(j)



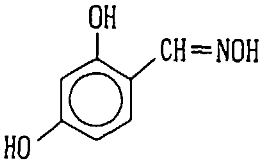
(k)



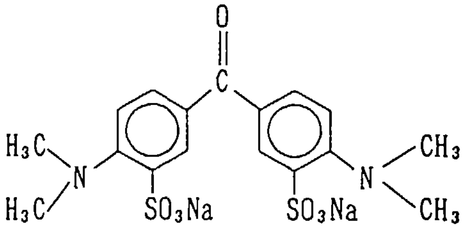
(l)



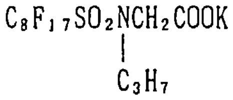
(n)



(o)

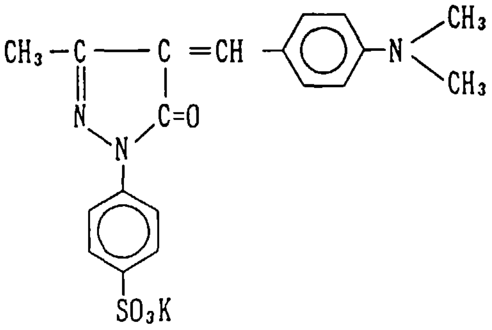


(p)

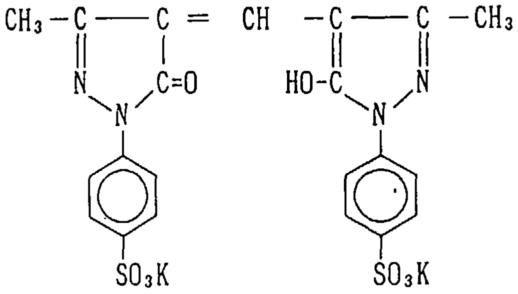


$C_8F_{17}SO_2N(C_3H_7)CH_2COOK$

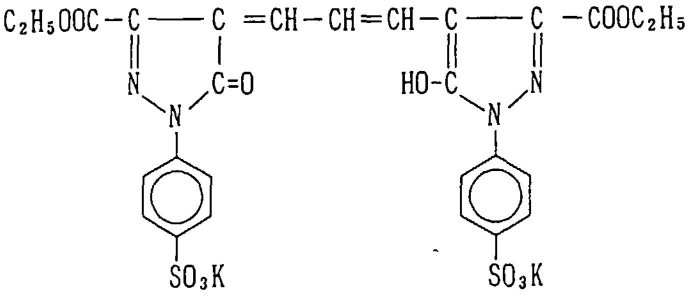
(q)


CH3
C
C
=CH
N
CH3
CH3
N
C=O
N
SO3K

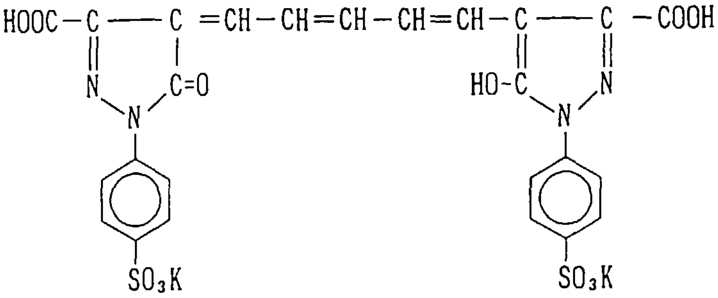
(r)


CH3
C
C
=
CH
C
C
CH3
N
C=O
N
HO-C
N
N
SO3K
SO3K

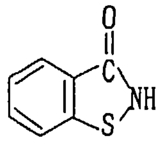
(s)


C2H5OOC
C
C
=CH-CH=CH
C
C
COOC2H5
N
C=O
N
HO-C
N
N
SO3K
SO3K

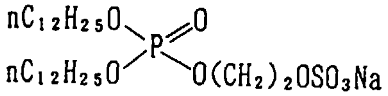
(t)


HOOC
C
C
=CH-CH=CH-CH=CH
C
C
COOH
N
C=O
N
HO-C
N
N
SO3K
SO3K

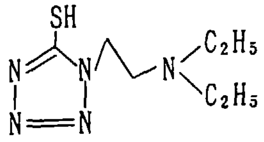
Compound-A



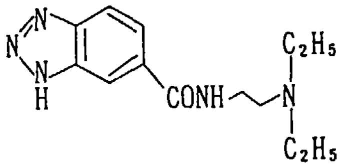
Compound-B



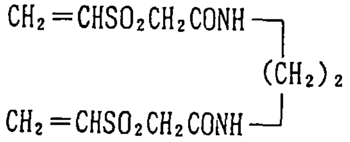
Compound-C



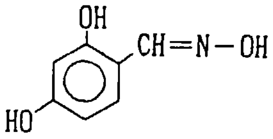
Compound-D



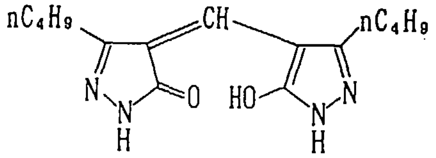
Compound-E



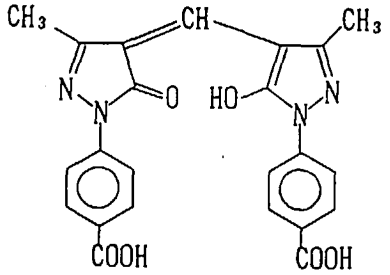
Compound-F



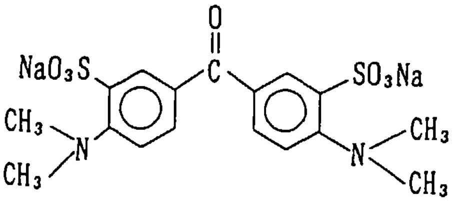
Solid Disperse Dye-G_1



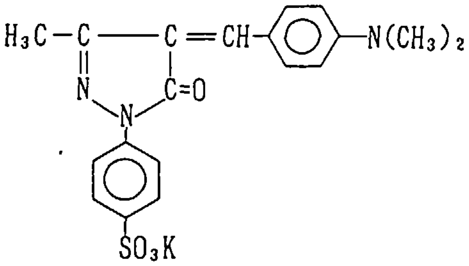
Solid Disperse Dye-G_2



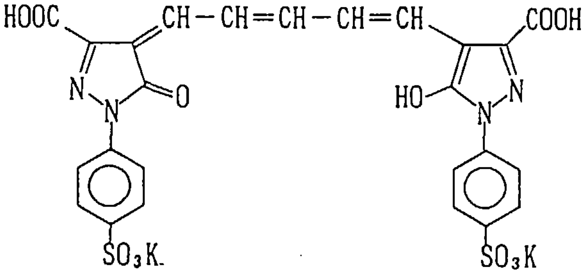
Compound-H



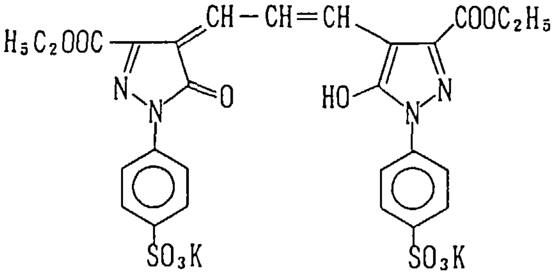
Compound-I



Compound-J



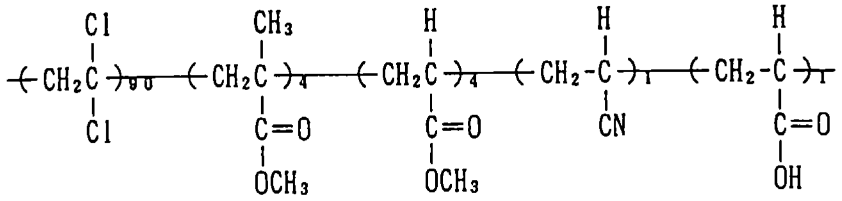
Compound-K



Compound-L

$C_8F_{17}SO_3Li$

Core/Shell Type Vinylidene Chloride Copolymer (1)

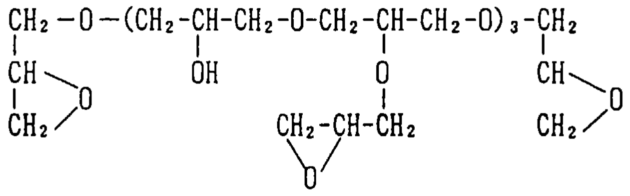


Core: VDC/MMA/MA (80% by weight)

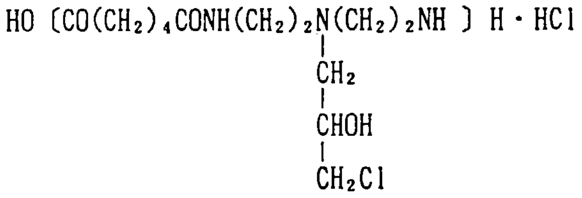
Shell: VDC/AN/AA (20% by weight)

Mean particle size: 70 nm

Compound-M



Compound-N



$HO[CO(CH_2)_4CONH(CH_2)_2N(CH_2CHOHCH_2Cl)(CH_2)_2NH]H \cdot HCl$

EXAMPLE 1

Photographic materials (1) to (4) were processed with developers (1) to (5). As a fixing solution, fixing solution (1) was used in common. Combinations of the photographic materials and the developers used are shown in Table 10. Each of the photographic materials was processed with an FG-680AG automatic processor (manufactured by Fuji Photo Film Co., Ltd.) charged with the developer and the fixing solution at a developing temperature of 35°C at a fixing temperature of 34°C for a developing time of 20 seconds. The sensitivity of sensitometry was relatively compared, taking as 100 a sensitivity at the time when each photographic material was processed with developer (1). The sensitivity evaluation point was indicated using an exposure amount giving a density of 1.5. Further, γ (gamma) was indicated using a slope between two points, 0.3 and 3.0 in density.

The exposure conditions of the respective photographic materials were as follows:

Photographic material (1): exposed to xenon flash light having a light-emitting time of 10^{-6} second through a 633-nm interference filter and a step wedge;

Photographic material (2): exposed to xenon flash light having a light-emitting time of 10^{-5} second through an interference filter having a peak at 488 nm and a step wedge;

Photographic material (3): exposed with a P-627FM printer manufactured by Dainippon Screen Mfg. Co., Ltd. through a step wedge; and

Photographic material (4): exposed to tungsten light of 3200°K through a step wedge.

After sensitometry, running processing was carried out. A consumption photographic material identical to the photographic material for sensitometry was exposed so as to give an exposed area of 100%, and 300 m^2 thereof was processed while replenishing a developing replenisher at a rate of 80 ml/m^2, followed by sensitometry again. Then, the photographic characteristics thereof were compared with those at a start of the running processing. The replenishment rate of the fixing solution was 150 ml/m^2. The results obtained are shown in Table 10.

TABLE 10

Test No.	Photographic Material No.	Starting Develop. Solution No.	Replen. Develop. Solution No.	Sensitivity		γ (Gamma)		Remark
				At Running Start	On Termination	At Running Start	On Termination	
1	1	1	1	100	71	18	9.5	Comparison
2	1	2	2	100	87	9.0	7.5	Comparison
3	1	1	3	100	91	18	16	Invention
4	2	1	3	100	93	20	17	Invention
5	3	1	3	100	95	13	11	Invention
6	4	1	3	100	91	17	16	Invention
7	2	1	1	100	78	20	10	Comparison
8	3	1	1	100	83	13	8.0	Comparison
9	4	1	1	100	78	17	9.5	Comparison
10	1	4	5	100	48	17	6.5	Comparison
11	2	4	5	100	43	19	6.8	Comparison

As is apparent from Table 10, test Nos. 3 to 6 of the present invention were reduced in changes in sensitivity and in a reduction in contrast (γ) due to the running, exhibiting excellent characteristics. Test No. 2 in which the 3-pyrazolidone compound was used as the auxiliary developing agent is unfavorably low in contrast from the start of the running.

EXAMPLE 2

A silver stain inhibitor selected from the exemplified compounds of general formula (1) was added in an amount shown in Table 11 to each of the starting developing solution and the developing replenisher. It was added to both the starting developing solution and the developing replenisher in the same amount. For the running, 300 m^2 of a consumption photographic material was processed, while replenishing a developing replenisher in the same manner as in Example 1, using an unexposed photographic material different from Example 1. Silver stain which adhered to the first processed photographic material on the day after the day when the consumption was conducted was evaluated. No stain adhered at the start, so that only results of evaluation of silver stain on the termination are shown in Table 11. As a fixing solution, fixing solution (2) was used, and the replenishment rate thereof was 150 ml/m^2.

Levels of the silver stain are as follows:

◎	No stain at all
○	Slight stain on the periphery
△	Within the permitted limit
X	Slight stain adhered to the whole surface

XX Considerable stain adhered to the whole surface

The photographic material used was photographic material (1).

TABLE 11

Test No.	Developing Solution No.		Silver Stain Inhibitor		Silver Stain	Remark
	Starting Solution	Replenisher	Compound No.	Amount Added (mmol/l)		
12	1	3	-	-	△	Comparison
13	1	3	11	0.5	○	Invention
14	1	3	23	0.5	◎	Invention
15	1	3	30	0.5	◎	Invention
16	6	7	11	0.5	△	Comparison
17	6	7	23	0.5	△	Comparison
18	1	3	77	0.5	◎	Invention
19	1	3	108	0.5	◎	Invention
20	1	3	117	0.5	◎	Invention

As is apparent from Table 11, the developers having low sulfite concentration and containing the silver stain inhibitor were very good in prevention of silver stain.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

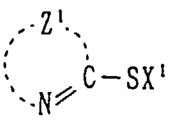
Claims

1. A method for continuously developing an exposed silver halide photographic material containing a hydrazine derivative by an automatic processor,

   wherein the development is carried out by using a developer being substantially free from a dihydroxybenzene compound and containing an ascorbic acid and/or a derivative thereof as a developing agent, an aminophenol derivative as an auxiliary developing agent which exhibits a superadditive property and at least 0.5 mol/liter of a carbonate as a buffer, and

   wherein the developer is replenished with a developing replenisher having a pH at least 0.2 higher than that of the starting developing solution.

2. The method according to claim 1, wherein the developing replenisher contains a silver stain inhibitor represented by the following general formula (1):



(1)

   wherein Z^1 represents a non-metallic atom group necessary to form a 5- or 6-membered nitrogen-containing aromatic heterocyclic ring together with the N and C in general formula (1) and has R^1 and $(SX^2)_n$ as substituent groups, wherein R^1 represents a hydrogen atom, a halogen atom or a substituent group which is connected to the ring by a carbon atom, an oxygen atom, a nitrogen atom or a sulfur atom contained therein, X^1 and X^2 each represents a hydrogen atom or a cation, n is an integer of 0, 1 or 2, and two radicals each formed by eliminating any one hydrogen atom from Z^1 may combine to form a bis form structure.

3. The method according to claim 1, wherein the developing replenisher has a sulfite concentration of not more than 0.05 mol/liter and a pH of from 9.0 to 10.5.

4. The method according to claim 1, wherein the replenishment rate of the developing replenisher is not more than 300 ml/m^2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 1987

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US 5 236 816 A (PUROL MICHAEL D ET AL) 17 August 1993 * abstract; claims 1,7 * * column 6, line 41 - line 46 * ---	1-4	G03C5/30 G03C5/305 G03C1/06 G03C5/31
Y	JP 07 092 625 A (FUJI PHOTO FILM CO LTD) 7 April 1995 & US-A-5503965 (2 April 1996) * column 1, line 35 - column 2, line 5; claims 1-3 * ---	1-4	
Y	EP 0 573 700 A (AGFA GEVAERT NV) 15 December 1993 * page 2, line 44 - page 3, line 24; claims 1,3 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 June 1997	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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