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## (54) Silver halide photographic material and method for processing the same

(57) A silver halide photographic light-sensitive material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one protective layer provided on the emulsion layer, wherein: the silver halide emulsion comprises a silver halide emulsion chemically sensitized with either or both of a selenium compound and a tellurium compound; at least one of the silver halide emulsion layer and other hydrophilic colloid layer(s) contains at least one hydrazine derivative; and the outermost layer of the protective layer(s) contains one or more kinds of alkylpolysiloxane. Also disclosed is a method for processing the silver halide photographic light-sensitive material with a developing solution having a pH of less than 11.0.

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## Description

### FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material and, in particular, to a silver halide photographic material having an improved pressure resistance in an image formation system which shows superhigh contrast photographic characteristics (particularly with a $\gamma$ value of 10 or more). The present invention also relates to a method for processing the silver halide photographic light-sensitive material.

### BACKGROUND OF THE INVENTION

An image formation system which shows superhigh contrast photographic characteristics (particularly with a $\gamma$ value of 10 or more) is required in the field of graphic arts to obtain good image reproduction of continuous gradation by halftone images or good reproduction of line images.

An image formation system has been desired which comprises developing a photographic material using a processing solution having an excellent storage stability, to thereby provide superhigh contrast photographic characteristics. For example, a system has been proposed which comprises processing a surface latent image type silver halide photographic material containing a specific acylhydrazine compound with a developing solution containing 0.15 mol/liter or more of a sulfite preservative and having a pH value of from 11.0 to 12.3 to form a superhigh contrast negative image having a $\gamma$ value of more than 10 as disclosed in U.S. Patents 4,166,742, 4,168,977, 4,221,857, 4,224,401, 4,243,739, 4,272,606 and 4,311,781. This novel image formation system is characterized in that silver iodobromide or silver iodochlorobromide can be used in contrast to conventional superhigh contrast image formation methods in which only silver chlorobromide having a high silver chloride content can be used. Furthermore, the system has a relatively good storage stability because it can contain a large amount of a sulfite preservative as opposed to the conventional lith developing solution which can contain only a slight amount of a sulfite preservative.

However, a developing solution having a pH value of 11 or more is liable to be air oxidized, unstable and cannot stand a storage or use for a long period of time.

Accordingly, a system which provides superhigh contrast and has good processing stability has been desired. For example, a system which provides superhigh contrast and has good processing stability even when processed with a developing solution having a pH value of less than 11.0 has been realized by incorporating an accelerator into a photographic material using a hydrazine compound having a specific structure as disclosed in JP-A-7-244350 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-7-248563, JP-A-7-270957, JP-A-7-248563 and JP-A-8-95185.

On the other hand, chemical sensitization of a silver halide emulsion with a selenium compound and a tellurium compound is advantageous in providing superhigh contrast properties with a developing solution having a pH of less than 11.0 but has been disadvantageous in pressure resistance.

Pressure marks are often generated in a silver halide photographic material by handling such as transporting of a photographic material during photographing, development processing, printing and projecting, as well as during a producing process such as coating, drying and processing. Such pressure marks originate in the contact areas of a photographic material with various devices, or originate from the contact abrasion of a photographic material with dusts, fiber dusts, etc., or from the contact abrasion of photographic materials one another such as between a surface and a backing surface.

As a means to improve the fluctuation in density due to such pressures, a method of relieving the pressure before it reaches silver halide grains is known, for example, a method of incorporating a plasticizer such as a polymer latex and a polyhydric alcohol into a photographic material, a method of reducing the silver halide/gelatin ratio in a silver halide emulsion layer, a method of thickening a protective layer, and a method of adding a sliding agent or colloidal silica to a protective layer.

There are disclosed in British Patent 738,618 a method of using heterocyclic compounds, in British Patent 738,637 a method of using alkyl phthalates, in British Patent 738,689 a method of using alkyl esters, in U.S. Patent 2,960,404 a method of using polyhydric alcohols, in U.S. Patent 3,121,060 a method of using carboxyalkyl celluloses, in JP-A-49-5017 a method of using paraffins and carboxylates, and in JP-B-53-28086 (the term "JP-B" as used herein means an "examined Japanese patent publication") a method of using alkyl acrylates and organic acids.

However, the addition of a plasticizer lower the mechanical strength of an emulsion layer, therefore, the use amount thereof is limited, and a method of reducing the silver halide/gelatin ratio in a silver halide emulsion layer has drawbacks such that development progress is delayed or rapid processing suitability is impaired.

Further, a polyhydroxybenzene compound is introduced into a silver halide photographic material containing a hydrazine derivative for various purposes as disclosed in U.S. Patents 4,332,108, 4,385,108 and 4,377,634. A technique for preventing pressure induced sensitization is disclosed in JP-A-62-21143.

The reduction of the replenishing rate of a developing solution is now strongly desired in the printing industry for the environmental protection.

However, if the thickness of a protective layer is thick, the resulting maximum density lowers when processed with a reduced replenishing rate, therefore, the thickness of a protective layer is necessary to be thin.

Pressure marks become a problem at that time, and the compatibility of the performance stability with pressure resistance in a reduced replenishing rate of a photographic material has been desired.

## SUMMARY OF THE INVENTION

An object of the present invention is, therefore, to provide a silver halide photographic light-sensitive material which can stably provide superhigh contrast properties with a reduced replenishing rate of a developing solution and which is improved in pressure marks generated by the contact abrasion with various substances.

Another object of the present invention is to provide a method for processing the silver halide photographic light-sensitive material.

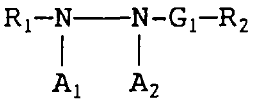
Other objects and effects of the present invention will be apparent from the following description.

The above objects of the present invention have been achieved by providing a silver halide photographic light-sensitive material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one protective layer provided on the emulsion layer, wherein:

(a) the silver halide emulsion comprises a silver halide emulsion chemically sensitized with either or both of a selenium compound and a tellurium compound;
(b) at least one of the silver halide emulsion layer and other hydrophilic colloid layer(s) contains at least one hydrazine derivative; and
(c) the outermost layer of the protective layer(s) contains one or more kinds of alkylpolysiloxane.

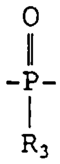
## DETAILED DESCRIPTION OF THE INVENTION

The hydrazine derivative for use in the present invention is preferably represented by the following formula (N):



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

wherein $R_1$ represents an aliphatic, an aromatic group or a heterocyclic group; $R_2$ represents a hydrogen atom, an alkyl group, an aralkyl 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 $-\overset{\overset{O}{\|}}{\underset{\underset{R_3}{|}}{P}}-$ group,

a -CO-CO- group, a thiocarbonyl group, or an iminomethylene group; $A_1$ and $A_2$ each represents a hydrogen atom, or either of them represents a hydrogen atom and the other represents a substituted or unsubstituted alkylsulfonyl group, or a substituted or unsubstituted arylsulfonyl group, or a substituted or unsubstituted acyl group; and $R_3$ has the same meaning as defined in $R_2$ and may be different from $R_2$.

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

The aromatic group represented by $R_1$ in formula (N) is a monocyclic or bicyclic aryl group containing, e.g., a benzene ring or a naphthalene ring. The heterocyclic group represented by $R_1$ is a monocyclic or bicyclic, aromatic or non-aromatic heterocyclic group, and may be condensed with an aryl group to form a heteroaryl group. Examples of the aromatic group include a pyridine ring, a pyrimidine ring, an imidazole ring, a pyrazole ring, a quinoline ring, an isoquinoline ring, a benzimidazole ring, a thiazole ring, and a benzothiazole ring.

$R_1$ is preferably an aryl group. $R_1$ may be substituted, and representative substituents include, for example, an alkyl group (including an active methyl group), an alkenyl group, an alkynyl group, an aryl group, a group containing a heterocyclic ring, a group containing a quaternary nitrogen atom-containing heterocyclic ring (e.g., pyridinio), a hydroxyl group, an alkoxyl group (including a group containing an ethylene oxy group or a propylene oxy group as a repeating unit), an aryloxy group, an acyloxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a urethane group, a carboxyl group, an imido group, an amino group, a carbonamido group, a sulfonamido group, a ureido group, a thioureido group, a sulfamoylamino group, a semicarbazido group, a thiosemicarbazido group, a group containing a hydrazino group, a group containing a quaternary ammonio group, a mercapto group, an (alkyl, aryl or heterocyclic) thio group, an (alkyl or aryl)sulfonyl group, an (alkyl or aryl)sulfinyl group, a sulfo group, a sulfamoyl group, an acylsulfamoyl group, an (alkyl or aryl)sulfonylureido group, an (alkyl or aryl)sulfonylcarbamoyl group, a halogen atom, a cyano group, a nitro group, a phosphoric acid amido group, a group having a phosphate structure, a group having an acylurea structure, a group containing a selenium atom or a tellurium atom, and a group having a tertiary or quaternary sulfonium structure.

Preferred substituents include a straight chain, branched or cyclic alkyl group (preferably having from 1 to 20 carbon atoms), an aralkyl group (preferably having from 1 to 20 carbon atoms), an alkoxyl group (preferably having from 1 to 20 carbon atoms), a substituted amino group (preferably a substituted amino group having from 1 to 20 carbon atoms), an acylamino group (preferably having from 2 to 30 carbon atoms), a sulfonamido group (preferably having from 1 to 30 carbon atoms), a ureido group (preferably having from 1 to 30 carbon atoms), a carbamoyl group (preferably having from 1 to 30 carbon atoms), and a phosphoric acid amido group (preferably having from 1 to 30 carbon atoms).

The alkyl group represented by $R_2$ in formula (N) is preferably an alkyl group having from 1 to 10 carbon atoms, and the aryl group represented by $R_2$ in formula (N) is preferably a monocyclic or bicyclic aryl group, for example, an aryl group which contains a benzene ring.

The heterocyclic group is a 5- or 6-membered compound containing at least one nitrogen, oxygen or sulfur atom, for example, an imidazolyl group, a pyrazolyl group, a triazolyl group, a tetrazolyl group, a pyridyl group, a pyridinio group, a quinolinio group or a quinolinyl group. A pyridyl group and a pyridinio group are particularly preferred.

An alkoxyl group having from 1 to 8 carbon atoms is preferred as the alkoxyl group, a monocyclic aryloxy group is preferred as the aryloxy group, an unsubstituted amino group, an alkylamino group having from 1 to 10 carbon atoms, an arylamino group and a heterocyclic amino group are preferred as the amino group.

$R_2$ may be substituted, and groups exemplified as substituents for $R_1$ are applied to preferred substituents for $R_2$.

Preferred groups of the groups represented by $R_2$ are, when $G_1$ represents a -CO- group, a hydrogen atom, an alkyl group (e.g., methyl, trifluoromethyl, difluoromethyl, 2-carboxytetrafluoroethyl, pyridiniomethyl, 3-hydroxypropyl, 3-methanesulfonamidopropyl, phenylsulfonylmethyl), an aralkyl group (e.g., o-hydroxybenzyl), and an aryl group (e.g., phenyl, 3,5-dichlorophenyl, o-methanesulfonamidophenyl, o-carbamoylphenyl, 4-cyanophenyl, 2-hydroxymethylphenyl), and a hydrogen atom and an alkyl group are particularly preferred of them.

Further, when $G_1$ represents an $-SO_2-$ group, preferred groups represented by $R_2$ are an alkyl group (e.g., methyl), an aralkyl group (e.g., o-hydroxybenzyl), an aryl group (e.g., phenyl), and a substituted amino group (e.g., dimethylamino).

When $G_1$ represents a -COCO- group, $R_2$ preferably represents an alkoxyl group, an aryloxy group or an amino group, particularly preferably represents a substituted amino group (e.g., 2,2,6,6-tetramethylpiperidin-4-ylamino, propylamino, anilino, o-hydroxyanilino, 5-benzotriazoleamino, N-benzyl-3-pyridinioamino). Further, $R_2$ may be a group such that the $-G_1-R_2$ moiety is cleaved from the remainder of the molecule and a cyclization reaction occurs to form a ring structure in which the atoms of the $-G_1-R_2$ moiety is contained, and the example thereof is disclosed in JP-A-63-29751.

$A_1$ and $A_2$ each represents a hydrogen atom, an alkyl-or arylsulfonyl group having 20 or less carbon atoms (preferably phenylsulfonyl or substituted phenylsulfonyl having the total of the Hammett's substituent constant of -0.5 or more), an acyl group having 20 or less carbon atoms (preferably benzoyl or substituted benzoyl having the total of the Hammett's substituent constant of -0.5 or more, or straight chain, branched or cyclic, substituted or unsubstituted aliphatic acyl (substituents include, e.g., halogen, ether, sulfonamido, carbonamido, hydroxyl, carboxyl, sulfonic acid)).

$A_1$ and $A_2$ most preferably represent a hydrogen atom.

The substituents represented by $R_1$ and $R_2$ in formula (N) may further be substituted and preferred substituents include those exemplified as the substituents for $R_1$. The substituent may be substituted multiple times. That is, the substituent may be further substituted, the substituted substituent may be further substituted, the substituent of the substituted substituent may be further substituted .... Preferred examples of each substituents also include those exemplified above as substituents for $R_1$.

$R_1$ or $R_2$ in formula (N) may have a ballast group or a polymer which are normally used in immobile photographic additives such as couplers. Such a ballast group has 8 or more carbon atoms and is a group which is photographically relatively inactive. Such a group can be selected from, for example, an alkyl group, an aralkyl group, an alkoxyl group, a phenyl group, an alkylphenyl group, a phenoxy group and an alkylphenoxy group. Further, those disclosed, for example, in JP-A-1-100530 can be exemplified as such a polymer.

$R_1$ or $R_2$ in formula (N) may include a group which is adsorbed onto silver halide grains. Examples of such an adsorptive group include an alkylthio group, an arylthio group, a thiourea group, a thioamido group, a mercapto heterocyclic group and a triazole group, as disclosed in U.S. Patents 4,385,108, 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 adsorptive group onto silver halide grains may be precursors and those disclosed in JP-A-2-285344 can be exemplified as examples of such precursors.

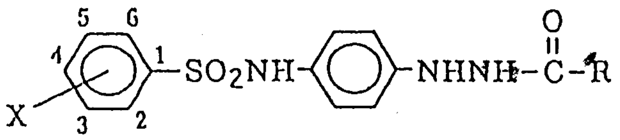
$R_1$ or $R_2$ in formula (N) may include a plurality of hydrazino groups as substituents. In such a case, the compound represented by formula (N) represents a polymer of hydrazino groups, specifically those disclosed in JP-A-64-86134, JP-A-4-16938 and JP-A-5-197091 can be exemplified as such compounds.

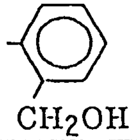
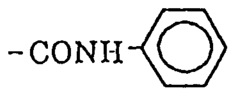
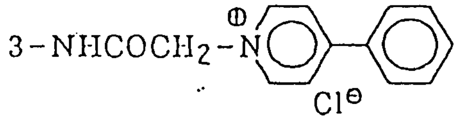
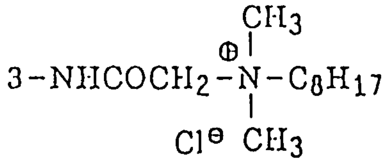
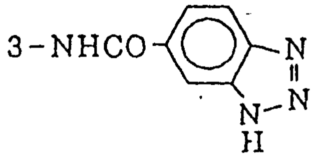
Particularly preferred embodiments of the hydrazine derivative for use in the present invention are described below.

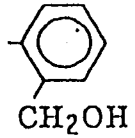
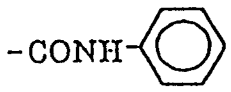
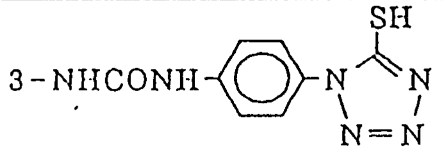
$R_1$ particularly preferably represents a substituted phenyl group, in which a ballast group, an adsorptive group onto silver halide grains, a group containing a quaternary ammonio group, a group containing an ethylene oxy repeating unit, an alkyl-, aryl- or heterocyclic thio group, a group capable of dissociating in an alkaline development processing solution (e.g., carboxyl, sulfo, acylsulfamoyl), or a hydrazino group capable of forming a polymer is preferably substituted via a sulfonamido group, an acylamino group, a ureido group or a carbamoyl group. $R_1$ most preferably represents a phenyl group substituted with a benzenesulfonamido group, and the benzenesulfonamido group preferably has a substituent selected from the above described groups.

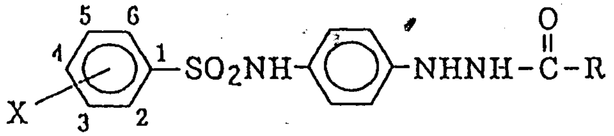
$G_1$ in formula (N) preferably represents a -CO- group or a -COCO- group, and particularly preferably a -CO- group. When $G_1$ represents a -CO- group, $R_2$ represents a hydrogen atom, a substituted alkyl group, or a substituted aryl group (preferred substituents include an electron attractive group or an o-hydroxymethyl group), and when $G_1$ represents a -COCO-group, $R_2$ particularly preferably represents a substituted amino group.

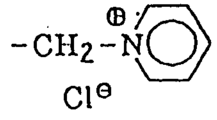
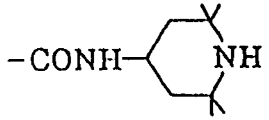
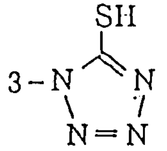
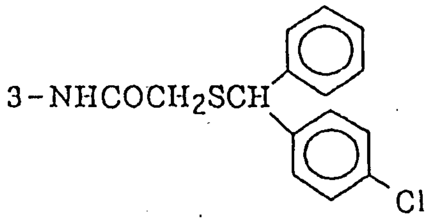
Specific examples of the compound represented by formula (N) are shown below, but the present invention is not limited thereto.

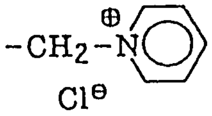
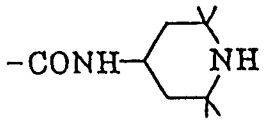
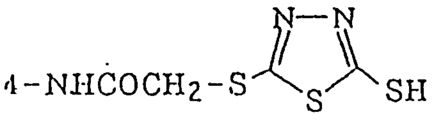
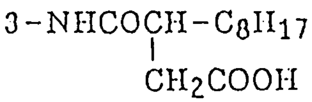
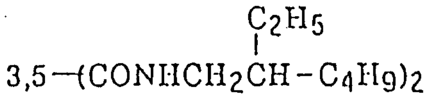


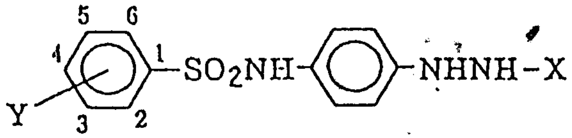
|  | X= \ R= | $-H$ | $-C_2F_4-COOH$<br>(or $-C_2F_4COO^{\ominus}K^{\oplus}$) |  |  |
|---|---|---|---|---|---|
| 1 | $3-NHCO-C_9H_{19}(n)$ | 1a | 1b | 1c | 1d |
| 2 | $3-NHCONH \wedge S-C_7H_{15}(n)$ | 2a | 2b | 2c | 2d |
| 3 |  | 3a | 3b | 3c | 3d |
| 4 |  $3-NHCOCH_2-\overset{\oplus}{N}(CH_3)_2-C_8H_{17}\ Cl^{\ominus}$ | 4a | 4b | 4c | 4d |
| 5 |  | 5a | 5b | 5c | 5d |

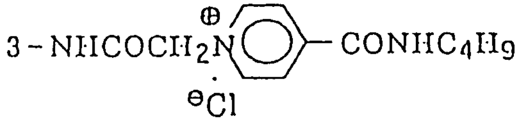
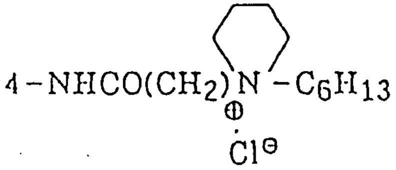
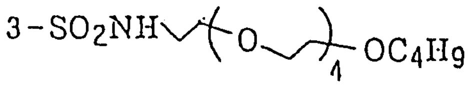
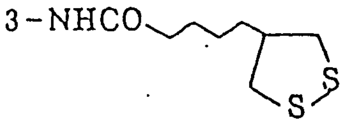
|  | R= / X= | -H | $-C_2F_4-COOH$<br>(or $-C_2F_4COO^{\ominus}K^{\oplus}$) |  |  |
|---|---|---|---|---|---|
| 6 |  | 6a | 6b | 6c | 6d |
| 7 | 2,4-$(CH_3)_2$-<br>3-$SC_2H_4-(OC_2H_4)_4-OC_8H_{17}$ | 7a | 7b | 7c | 7d |

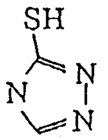


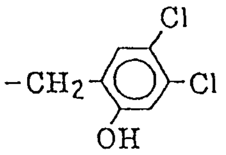
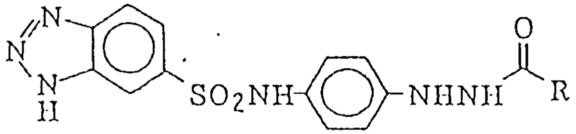
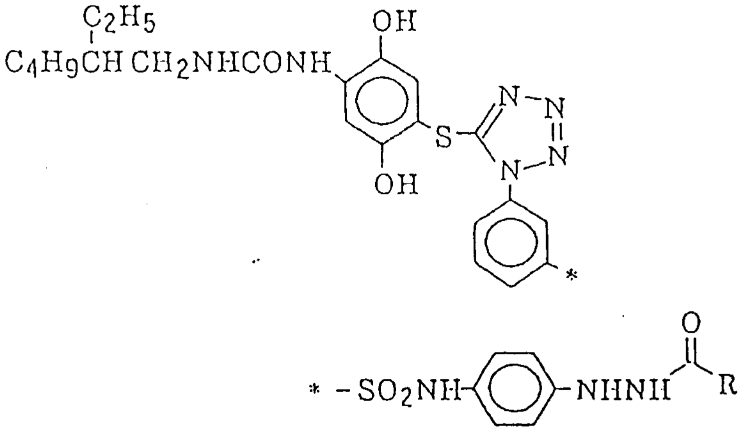
| | X = / R = | $-H$ | $-CF_2H$ |  $-CH_2-N^{\oplus}$ $Cl^{\ominus}$ |  $-CONH-$ |
|---|---|---|---|---|---|
| 8 | $3-CONHCH_2\underset{\vert}{\overset{C_2H_5}{C}}H-C_4H_9$ | 8a | 8e | 8f | 8g |
| 9 | $6-OCH_3-3-C_5H_{11}(t)$ | 9a | 9e | 9f | 9g |
| 10 |  | 10a | 10e | 10f | 10g |
| 11 |  | 11a | 11e | 11f | 11g |

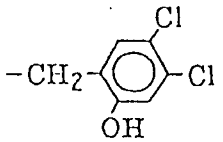
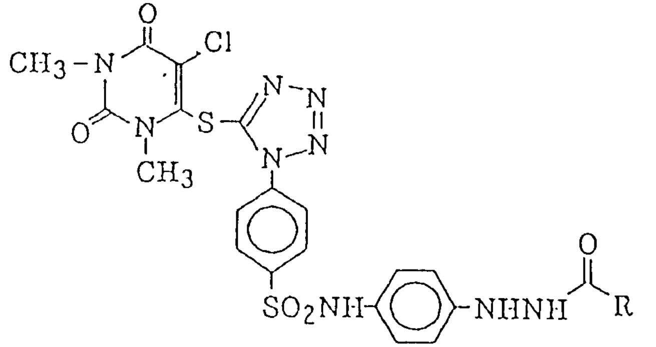
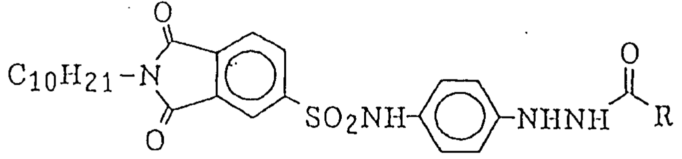
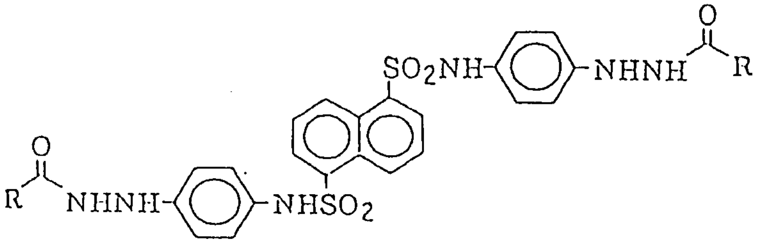
| | X= \ R= | -H | $-CF_2H$ |  |  |
|---|---|---|---|---|---|
| 12 |  | 12a | 12e | 12f | 12g |
| 13 |  $3-NHCOCH(CH_2COOH)-C_8H_{17}$ | 13a | 13e | 13f | 13g |
| 14 |  $3,5-(CONHCH_2CH(C_2H_5)-C_4H_9)_2$ | 14a | 14e | 14f | 14g |

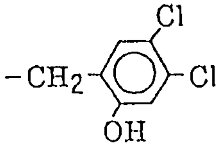
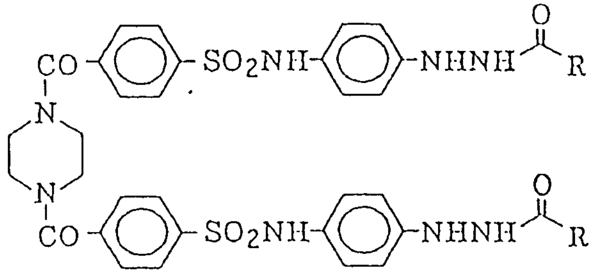
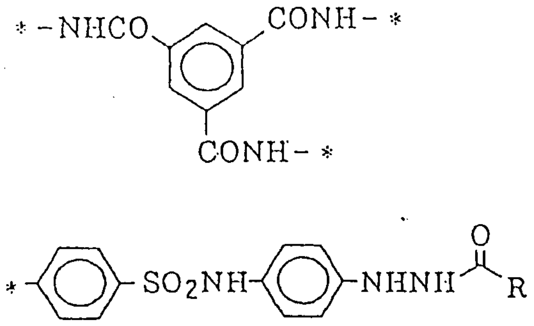


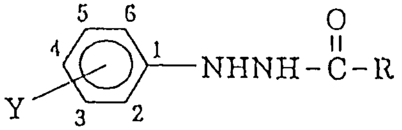
| | Y = ╲ X = | -CHO | $-COCF_3$ | $-SO_2CH_3$ | $-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ |
|---|---|---|---|---|---|
| 15 |  | 15a | 15h | 15i | 15j |
| 16 |  | 16a | 16h | 16i | 16j |
| 17 |  | 17a | 17h | 17i | 17j |
| 18 | $3,4\text{-}(COO\overset{CH_3}{\overset{\|}{C}H}COOC_4H_9)_2$ | 18a | 18h | 18i | 18j |
| 19 |  | 19a | 19h | 19i | 19j |

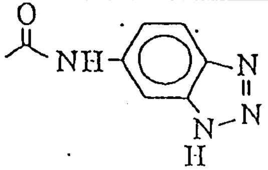
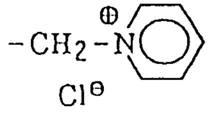
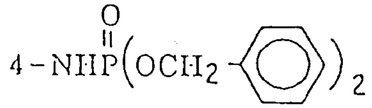
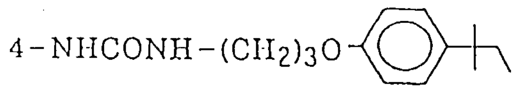
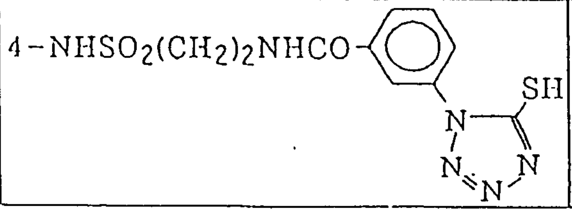
|  | X= / Y= | -CHO | $-COCF_3$ | $-SO_2CH_3$ | $-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ |
|---|---|---|---|---|---|
| 20 | $3-NHSO_2NH-C_8H_{17}$ | 20a | 20h | 20i | 20j |
| 21 | 2-Cl-5-  | 21a | 21h | 21i | 21j |

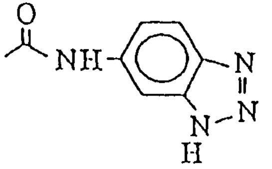
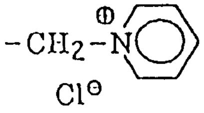
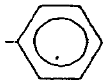
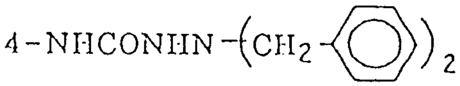
|  | R= | $-H$ | $-CF_2H$ |  | $-CONHC_3H_7$ |
|---|---|---|---|---|---|
| 22 |  | 22a | 22e | 22k | 22l |
| 23 |  | 23a | 23e | 23k | 23l |

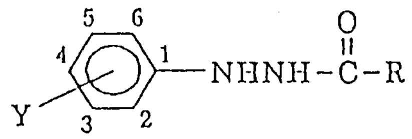
| | R= | -H | $-CF_2H$ |  | $-CONHC_3H_7$ |
|---|---|---|---|---|---|
| 24 |  | 24a | 24e | 24k | 24l |
| 25 |  | 25a | 25e | 25k | 25l |
| 26 |  | 26a | 26c | 26k | 26l |

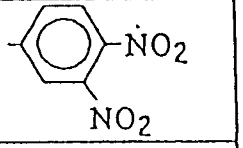
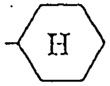
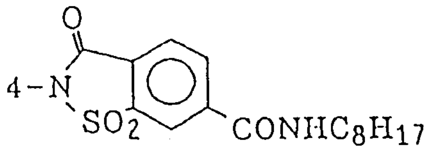
|  | R= | $-H$ | $-CF_2H$ |  | $-CONHC_3H_7$ |
|---|---|---|---|---|---|
| 27 |  | 27a | 27e | 27k | 27l |
| 28 |  | 28a | 28e | 28k | 28l |

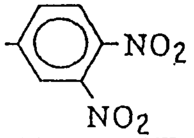
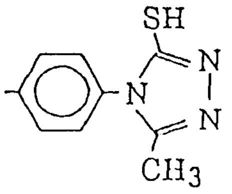
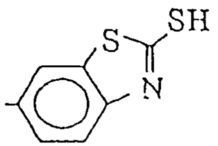


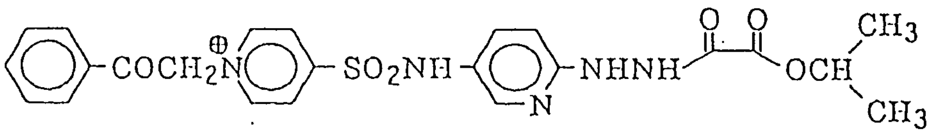
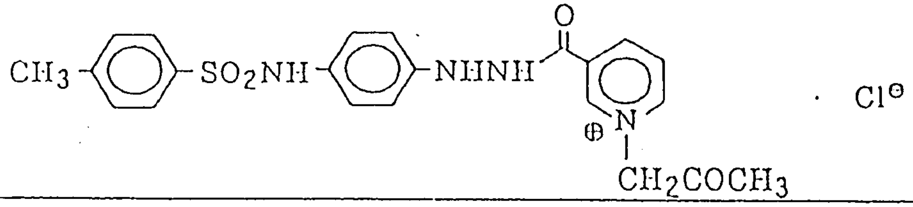
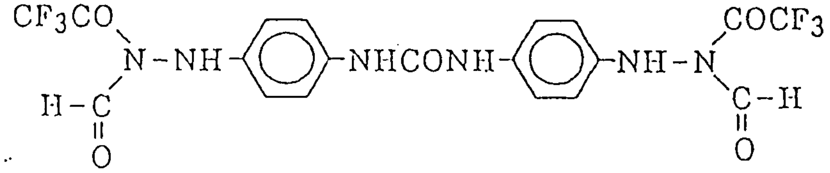
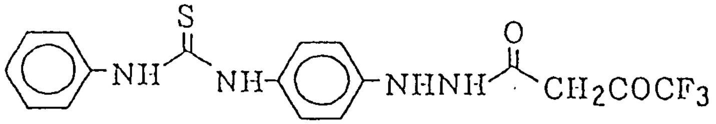
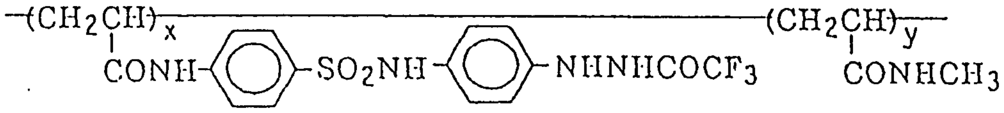
| | R=<br>Y= | -H | $-CH_2OCH_3$ |  |  |
|---|---|---|---|---|---|
| 29 | $4-NH\overset{\overset{S}{\|}}{C}NH-C_8H_{17}(n)$ | 29a | 29m | 29n | 29f |
| 30 |  | 30a | 30m | 30n | 30f |
| 31 |  | 31a | 31m | 31n | 31f |
| 32 | 4-OH<br>$3-NHCOCH_2\overset{\overset{C_2H_5}{\|}}{C}H-C_4H_9$ | 32a | 32m | 32n | 32f |
| 33 |  | 33a | 33m | 33n | 33f |

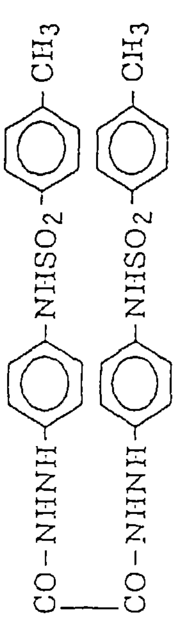
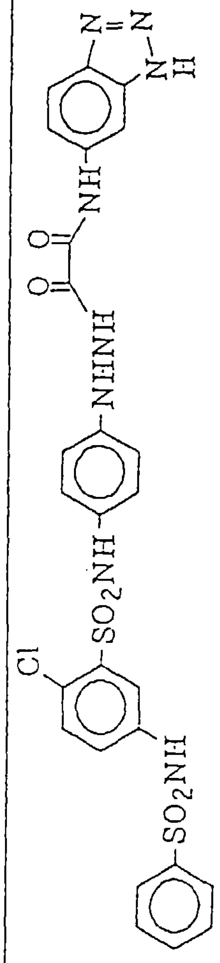
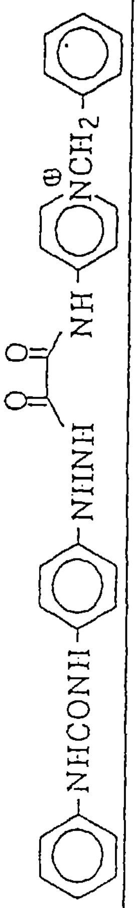
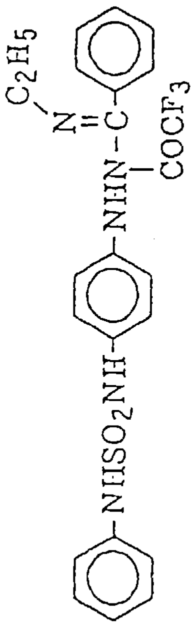
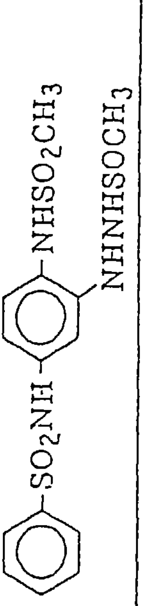
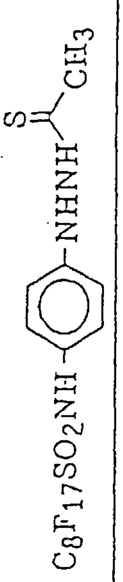
| | R= <br> Y= | -H | $-CH_2OCH_3$ |  |  |
|---|---|---|---|---|---|
| 34 | 4-$OCH_2$-  | 34a | 34m | 34n | 34f |
| 35 |  | 35a | 35m | 35n | 35f |



| | Y = \ R = | -H | $-C_3F_6-COOH$ | $-CONHCH_3$ |  |
|---|---|---|---|---|---|
| 36 | $2-NHSO_2CH_3-$<br>$4-NHCONH(CH_2)_3S-$  | 36a | 36o | 36p | 36q |
| 37 | $2-OCH_3-$<br>$4-NHSO_2C_{12}H_{25}$ | 37a | 37o | 37p | 37q |
| 38 | $3-NHCOC_{11}H_{23}-$<br>$4-NHSO_2CF_3$ | 38a | 38o | 38p | 38q |
| 39 |  | 39a | 39o | 39p | 39q |
| 40 | $4-OCO(CH_2)_2COOC_6H_{13}$ | 40a | 40o | 40p | 40q |

| | Y= \ R= | $-H$ | $-C_3F_6-COOH$ | $-CONHCH_3$ |  |
|---|---|---|---|---|---|
| 41 | 4-NHCONH-  | 41a | 41o | 41p | 41q |
| 42 | 4-NHCO-  | 42a | 42o | 42p | 42q |

| | |
|---|---|
| 43 |  |
| 44 |  |
| 45 |  |
| 46 |  |
| 47 | <br>x/y=3/97<br>average molecular weight: about 100,000 |

| | |
|---|---|
| 48 |  |
| 49 |  |
| 50 |  |
| 51 |  |
| 52 |  |
| 53 |  |

In addition to the above hydrazine derivatives, the following hydrazine derivatives can also preferably be used in the present invention. Further, the hydrazine derivative for use in the present invention can be synthesized according to various methods disclosed in the following patents and the like.

The compounds represented by (Chemical Formula 1), specifically, the compounds disclosed on pages 3 and 4, of JP-B-6-77138; the compounds represented by formula (I), specifically, compounds 1 to 38 on pages 8 to 18, of JP-B-6-93082; the compounds represented by formula (4), (5) or (6), specifically, compounds 4-1 to 4-10 on pages 25 and 26, compounds 5-1 to 5-42 on pages 28 to 36, and compounds 6-1 to 6-7 on pages 39 and 40, of JP-A-6-230497; the compounds represented by formula (1) or (2), specifically, compounds 1-1) to 1-17 and 2-1) on pages 5 to 7, of JP-A-6-289520; the compounds represented by (Chemical Formula 2) or (Chemical Formula 3), specifically, the compounds disclosed on pages 6 to 19, of JP-A-6-313936; the compounds represented by (Chemical Formula 1), specifically, the compounds disclosed on pages 3 to 5, of JP-A-6-313951; the compounds represented by formula (I), specifically, compounds I-1 to I-38 on pages 5 to 10, of JP-A-7-5610; the compounds represented by formula (II), specifically, compounds II-1 to II-102 on pages 10 to 27, of JP-A-7-77783; the compounds represented by formula (H) or (Ha), specifically, compounds H-1 to H-44 on pages 8 to 15, of JP-A-7-104426; a compound having an anionic group or a nonionic group which forms an intramolecular hydrogen bond with the hydrogen atom of the hydrazine in the vicinity of the hydrazine group, in particular, the compounds represented by formula (A), (B), (C), (D), (E) or (F), specifically, compounds N-1 to N-30, of JP-A-9-22082; and the compounds represented by formula (1), specifically, compounds D-1 to

D-55, of JP-A-9-22082.

The hydrazine derivative of the present invention can be used in the form of a solution in an appropriate organic solvent which is miscible with water, such as alcohols (e.g., methanol, ethanol, propanol, fluorinated alcohol), ketones (e.g., acetone, methyl ethyl ketone), dimethylformamide, dimethyl sulfoxide and methyl cellosolve.

Further, the hydrazine derivative for use in the present invention can also be used in the form of an emulsion dispersion mechanically prepared according to well known emulsifying dispersion methods by dissolving using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate and diethyl phthalate, or using an auxiliary solvent such as ethyl acetate and cyclohexanone, or they can be used in the form of a dispersion prepared according to a solid dispersion method in which powder of a hydrazine derivative is dispersed in water using a ball mill, a colloid mill or ultrasonic wave.

The hydrazine derivative for use in the present invention may be added to any of silver halide emulsion layers or other hydrophilic colloid layers on the silver halide emulsion layer side of the support but they are preferably added to the silver halide emulsion layer(s) or the hydrophilic colloid layers adjacent thereto.

The addition amount of the hydrazine derivative for use in the present invention is preferably from $1 \times 10^{-6}$ mol to $1 \times 10^{-2}$ mol, more preferably from $1 \times 10^{-5}$ mol to $5 \times 10^{-3}$ mol, and most preferably from $2 \times 10^{-5}$ mol to $5 \times 10^{-3}$ mol, per mol of the silver halide.

A nucleation accelerating agent such as amine derivatives, onium salts, disulfide derivatives and hydroxymethyl derivatives are preferably contained in silver halide emulsion layer(s) or other hydrophilic colloid layers of the silver halide photographic material of the present invention.

Examples of the amine derivative for use in the present invention include those disclosed, for example, in JP-A-60-140340, JP-A-62-50829, JP-A-62-222241, JP-A-62-250439, JP-A-62-280733, JP-A-63-124045, JP-A-63-133145 and JP-A-63-286840. The compounds having a group which is adsorbed onto silver halide as disclosed in JP-A-63-124045, JP-A-63-133145 and JP-A-63-286840, and the compounds having a total number of carbon atoms of 20 or more as disclosed in JP-A-62-222241 are more preferably used as the amine derivative.

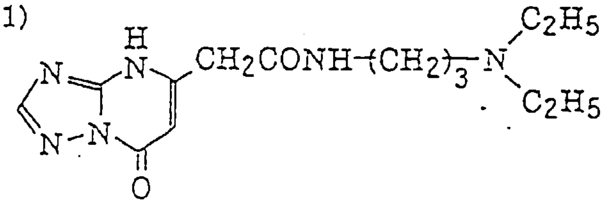
The onium salt is preferably an ammonium salt or a phosphonium salt. Preferred examples of ammonium salts include the compounds disclosed in JP-A-62-250439 and JP-A-62-280733. Also, as preferred examples of phosphonium salts, the compounds disclosed in JP-A-61-167939 and JP-A-62-280733 can be exemplified.

Examples of the disulfide derivative for use in the present invention include, for example, those disclosed in JP-A-61-198147.

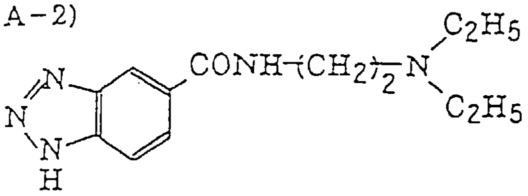
Examples of the hydroxymethyl derivative include those disclosed in U.S. Patents 4,693,956, 4,777,118, European Patent 231,850 and JP-A-62-50829, and diarylmethanol derivatives are preferred of these.

There can be exemplified, as particularly useful nucleation accelerating agents, the compounds represented by formulae (IV) to (VIII), specifically, exemplified compounds IV-1 to IV-36, V-1 to V-22, VI-1 to VI-36 and VIII-1 to VIII-41 disclosed in JP-A-7-287338, and the compounds represented by formulae (A) to (D), specifically, exemplified compounds A-101 to A-147 and A-201 to A-255 disclosed in JP-A-7-287338. Specific examples of nucleation accelerating agents for use in the present invention are shown below, but the present invention is not limited thereto.

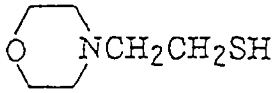
A-1)



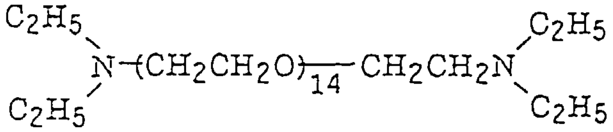
A-2)



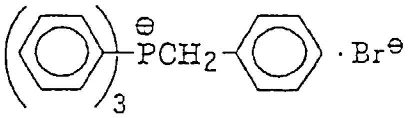
A-3)



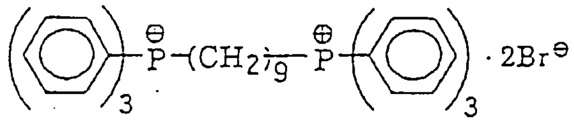
A-4)



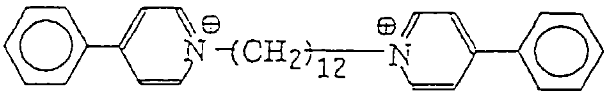
A-5)



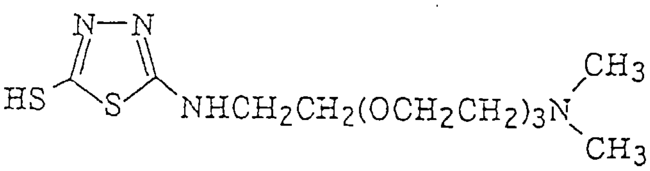
A-6)



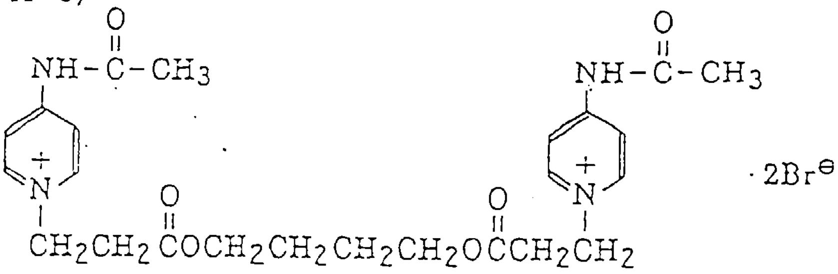
A-7)



A-8)



A-9)



The optimum addition amounts of these compounds vary depending on their kinds, but they are preferably used in an amount of from 1.0 x $10^{-2}$ mol to 1.0 x $10^2$ mol per mol of the hydrazine compound.

These compounds are dissolved in an appropriate solvent ($H_2O$, an alcohol such as methanol and ethanol, acetone, dimethylformamide, methyl cellosolve) and added to a coating solution.

These compounds may be used in combination of two or more kinds.

Silver chloride, silver chlorobromide, silver bromide, silver iodochlorobromide or silver iodobromide can be used as the silver halide in the silver halide emulsion for use in the silver halide photographic light-sensitive material of the present invention, but silver chlorobromide or silver iodochlorobromide having a silver chloride content of 50 mol% or more is preferably used. The silver iodide content thereof is preferably 3 mol% or less, more preferably 0.5 mol% or less. The form of the silver halide grain may be any of a cubic, tetradecahedral, octahedral, amorphous or plate-like form, but a cubic form is preferred. The average grain size of silver halide grains is preferably from 0.1 μm to 0.7 μm, and more preferably from 0.2 μm to 0.5 μm. With respect to the grain size distribution, grains having a narrow grain size distribution such that the variation coefficient represented by the equation ((standard deviation of the grain sizes) /(average grain size)) × 100 is preferably 15% or less, more preferably 10% or less, are preferred.

The interior and the surface layer of the silver halide grains may comprise a uniform layer or different layers.

The photographic emulsions which are used in the present invention can be prepared according to the method disclosed 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) and so on.

Any of a single jet method, a double jet method and a combination of these methods can be used for the reaction of a soluble silver salt with a soluble halogen salt.

A method in which grains are formed in the presence of excess silver ion (a so-called reverse mixing method) can also he used. A method in which the pAg of the liquid phase, in which the silver halide is formed, is kept constant, that is, the controlled double jet method, can also be used as one type of the double jet method. In addition, the grain formation is preferably carried out using a silver halide solvent such as ammonia, thioether or tetra-substituted thiourea. Of these, more preferred are tetra-substituted thiourea compounds and they are disclosed in JP-A-53-82408 and JP-A-55-77737. Preferred thiourea compounds are tetramethylthiourea and 1,3-dimethyl-2-imidazolidinethione.

Silver halide emulsions of a regular crystal form having a narrow grain size distribution can be readily obtained by the controlled double jet method and the grain formation method using a silver halide solvent, which are effective to prepare the silver halide emulsion for use in the present invention.

Moreover, the method in which the addition rates of the silver nitrate and the alkali halide are varied according to the grain growth rate as disclosed in British Patent 1,535,016, JP-B-48-36890 and JP-B-52-16364, and the method in which the concentrations of the aqueous solutions are varied as disclosed in British Patent 4,242,445 and JP-A-55-158124 are preferably and effectively used to rapidly grow grains within the range not exceeding the critical degree of saturation for providing uniform grain size.

The silver halide emulsion of the present invention is chemically sensitized with a selenium compound and/or a tellurium compound. The selenium sensitization and the tellurium sensitization are conducted alone or in combination with a conventionally known chemical sensitization method such as a sulfur sensitization and a noble metal sensitization. When the sensitization is conducted in combination, examples of the combination include a combination of a sulfur sensitization and a selenium sensitization, a combination of a sulfur sensitization and a tellurium sensitization, a combination of a gold sensitization and a selenium sensitization, a combination of a gold sensitization and a tellurium sensitization, a combination of a sulfur sensitization, a gold sensitization and a selenium sensitization, and a combination of a sulfur sensitization, a gold sensitization and a tellurium sensitization.

Various known selenium compounds can be used as a selenium sensitizer in the present invention. The selenium sensitization is usually carried out by adding a labile and/or non-labile selenium compounds and stirring the emulsion at high temperature, preferably 40°C or more, for a certain period of time. The compounds disclosed in JP-B-44-15748, JP-B-43-13489, JP-A-4-25832, JP-A-4-109240, JP-A-4-324855 can be used as the labile selenium compound. The compounds represented by formulae (VIII) and (IX) disclosed in JP-A-4-324855 are particularly preferably used.

The tellurium sensitizer for use in the present invention is a compound which forms silver telluride in the surfaces or interiors of silver halide grains, which silver telluride is presumed to be sensitization speck. The formation rate of the silver telluride in the silver halide emulsion can be examined according to the method disclosed in JP-A-5-313284.

Specific examples of the tellurium sensitizer which can be used in the present invention include those disclosed in the following patents and literatures: U.S. Patents 1,623,499, 3,320,069, 3,772,031, British Patents 235,211, 1,121,496, 1,295,462, 1,396,696, Canadian Patent 800,958, JP-A-4-204640, JP-A-4-271341, JP-A-4-33043 and JP-A-5-303157, J. Chem. Soc. Chem. Commun., 635 (1980), ibid., 1102 (1979), ibid., 645 (1979), J. Chem. Soc. Perkin. Trans., 1, 2191 (1980), S. Patai compiled, The Chemistry of Organic Selenium and Tellurium Compounds, Vol. 1 (1986), and ibid., Vol. 2 (1987). The compounds represented by formulae (II), (III) and (IV) disclosed in JP-A-5-313284 are particularly preferred.

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

The sulfur sensitization for use in the present invention is usually carried out by adding a sulfur sensitizer and stirring the emulsion at high temperature of 40°C or more for a certain period of time. Various known sulfur compounds can be used as a sulfur sensitizer, for example, in addition to sulfur compounds contained in gelatin, various sulfur compounds, e.g., thiosulfates, thioureas, thiazoles and rhodanines. Preferred sulfur compounds are thiosulfates and thioureas. The addition amount of a sulfur sensitizer varies depending on various conditions such as the pH and temperature during chemical ripening and the grain size of the silver halide grains, but is preferably from $10^{-7}$ to $10^{-2}$ mol and more preferably from $10^{-5}$ to $10^{-3}$ mol, per mol of the silver halide.

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

A cadmium salt, a sulfite, a lead salt and a thallium salt may be coexist in the silver halide emulsion for use in the present invention in the process of the formation or physical ripening of the silver halide grains.

A reduction sensitization can be used in the present invention. As a reduction sensitizer, there may be used a stannous salt, an amine compound, formamidinesulfinic acid and a silane compound.

Thiosulfonic acid compounds may be added to the silver halide emulsion of the present invention according to the method disclosed in European Patent 293,917.

The silver halide emulsion in the photographic material of the present invention may be one kind, or two or more kinds of silver halide emulsions (for example, those different in average grain sizes, different in halogen compositions, different in crystal habits, or different in the conditions of chemical sensitization) may be used in combination.

The silver halide grains for use in the silver halide photographic material of the present invention preferably contain at least one kind of a metal selected from the group consisting of rhodium, rhenium, ruthenium, osmium and iridium to attain high contrast and low fog generation. The content thereof is preferably from $1 \times 10^{-9}$ mol to $1 \times 10^{-5}$ mol, more preferably from $1 \times 10^{-8}$ mol to $5 \times 10^{-6}$ mol, per mol of the silver. These metals can be used in combination of two or more. These metals can be included in silver halide grains uniformly or may be distributed locally in grain as disclosed in JP-A-63-29603, JP-A-2-306236, JP-A-3-167545, JP-A-4-76534 and JP-A-6-110146.

Water-soluble rhodium compounds can be used as a rhodium compound for use in the present invention, for example, rhodium(III) halide compounds, or rhodium complex salts having a halogen, an amine or an oxalato as a ligand, such as hexachlororhodium(III) complex salts, hexabromorhodium(III) complex salts, hexaamminerhodium(III) complex salts, trioxalatorhodium(III) complex salts and the like. These rhodium compounds are dissolved in water or an appropriate solvent and used. A conventional method such as a method in which an aqueous solution of hydrogen halide (e.g., hydrochloric acid, hydrobromic acid, hydrofluoric acid) or alkali halide (e.g., KCl, NaCl, KBr, NaBr) is added to stabilize the solution of the rhodium compound can be used. It is also possible to include and dissolve other silver halide grains which have been previously doped with rhodium during the preparation of silver halide instead of using a water-soluble rhodium.

The addition amount of these rhodium compounds is preferably from $1 \times 10^{-8}$ mol to $5 \times 10^{-6}$ mol, and particularly preferably from $5 \times 10^{-8}$ mol to $1 \times 10^{-6}$ mol, per mol of the silver halide.

These compounds can be appropriately added during the preparation of silver halide emulsion grains and at any stage prior to coating of the emulsion, but they are particularly preferably added during emulsion formation to be incorporated into the silver halide grains.

Rhenium, ruthenium and osmium for use in the present invention are added in the form of a water-soluble complex salt as disclosed in JP-A-63-2042, JP-A-1-285941, JP-A-2-20852 and JP-A-2-20855. Particularly preferred compounds are complexes having six ligands represented by the following formula:

$$[ML_6]^{n-}$$

wherein M represents Ru, Re or Os, and n represents 0, 1, 2, 3 or 4.

Herein, counter ions are not important and ammonium or alkali metal ions are used.

Examples of preferred ligands include a halide ligand, a cyanide ligand, a cyanate ligand, a carbonyl ligand, an oxo ligand, a nitrosyl ligand and a thionitrosyl ligand. Specific examples of the complexe for use in the present invention are shown below but the present invention is not limited thereto.

| | | |
|---|---|---|
| $[ReCl_6]^{3-}$ | $[ReBr_6]^{3-}$ | $[ReCl_5(NO)]^{2-}$ |
| $[Re(NS)Br_5]^{2-}$ | $[Re(NO)(CN)_5]^{2-}$ | $[Re(O)_2(CN)_4]^{3-}$ |
| $[RuCl_6]^{3-}$ | $[RuCl_4(H_2O)_2]^{1-}$ | $[RuCl_5(NO)]^{2-}$ |
| $[RuBr_5(NS)]^{2-}$ | $[Ru(CN)_6]^{4-}$ | $[Ru(CO)_3Cl_3]^{2-}$ |
| $[Ru(CO)Cl_5]^{2-}$ | $[Ru(CO)Br_5]^{2-}$ | |
| $[OsCl_6]^{3-}$ | $[OsCl_5(NO)]^{2-}$ | $[Os(NO)(CN)_5]^{2-}$ |
| $[Os(NS)Br_5]^{2-}$ | $[Os(CN)_6]^{4-}$ | $[Os(O)_2(CN)_4]^{4-}$ |

The addition amount of these compounds is preferably from 1 × $10^{-9}$ mol to 1 × $10^{-5}$ mol, and particularly preferably from 1 × $10^{-8}$ mol to 1 × $10^{-6}$ mol, per mol of the silver halide.

These compounds can be appropriately added during the preparation of silver halide emulsion grains and at any stage prior to coating of the emulsion, but they are particularly preferably added during emulsion formation to be incorporated into the silver halide grains.

Various methods can be used for the addition of these compounds during grain formation of silver halide to incorporate them into silver halide grains, for example, a method in which a metal complex powder per se or an aqueous solution dissolved therein a metal complex powder together with NaCl and KCl is previously added to a solution of water-soluble salt or water-soluble halide during grain formation, a method in which a metal complex powder is simultaneously added as the third solution when a solution of silver salt and a solution of halide are mixed to prepare silver halide grains by a triple jet method by three solutions, or a method in which a necessary amount of an aqueous solution of a metal complex is added to a reaction vessel during grain formation. A method of adding a metal complex powder per se or adding an aqueous solution dissolved therein a metal complex powder together with NaCl and KCl, to a water-soluble halide solution is particularly preferred.

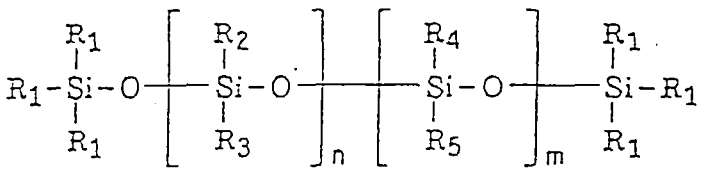
When these compounds are added to the grain surface, a necessary amount of an aqueous solution of a metal complexe can be added to a reaction vessel immediately after grain formation, during or at the time of terminating of physical ripening, or during chemical ripening.

Various iridium compounds can be used in the present invention, for example, hexachloroiridium, hexaammineiridium, trioxalatoiridium, hexacyanoiridium and the like. These iridium compounds are dissolved in water or an appropriate solvent and used. A conventional method such as a method in which an aqueous solution of hydrogen halide (e.g., hydrochloric acid, hydrobromic acid, hydrofluoric acid) or alkali halide (e.g., KCl, NaCl, KBr, NaBr) is added to stabilize the solution of an iridium compound can be used. It is also possible to add and dissolve other silver halide grains which have been previously doped with iridium during the preparation of silver halide instead of using water-soluble iridium.

The silver halide grains according to the present invention may be doped with other heavy metal salts. In particular, doping with an Fe salt, such as $K_4[Fe(CN)_6]$, is advantageously used.

Further, the silver halide grains for use in the present invention may contain a metal atom such as cobalt, nickel, palladium, platinum, gold, thallium, copper, lead or chromium. The preferred addition amount of these metals is from 1 × $10^{-9}$ to 1 × $10^{-4}$ mol per mol of the silver halide. Further, these metals can be added as a metal salt in the form of a single salt, a plural salt or a complex salt during the preparation of grains.

The alkylpolysiloxane represented by formula (S) can be preferably used as the sliding agent contained in the protective layer of the photographic material for use in the present invention:



$$R_1-\overset{R_1}{\underset{R_1}{Si}}-O-\left[\overset{R_2}{\underset{R_3}{Si}}-O\right]_n-\left[\overset{R_4}{\underset{R_5}{Si}}-O\right]_m-\overset{R_1}{\underset{R_1}{Si}}-R_1 \qquad (S)$$

wherein $R_1$ represents an alkyl group having from 1 to 3 carbon atoms or an alkoxyl group having 1 to 2 carbon atoms; and $R_2$, $R_3$, $R_4$ and $R_5$ each represents a hydrogen atom, an aliphatic group or an aryl group (e.g., phenyl).

The aliphatic group preferably represents an alkyl group, a cycloalkyl group, an alkoxyalkyl group, an arylalkyl group, an aryloxyalkyl group or a glycidyloxyalkyl group.

n and m each represents an integer of from 0 to 2,500.

$R_1$, $R_2$, $R_3$, $R_4$ and $R_5$ more preferably represent a methyl group.

Among the compounds represented by formula (S), those having a kinematic viscosity of from 1 to 10,000 are more preferred, and most preferably from 5 to 5,000.

The kinematic viscosity ($\upsilon$) used herein is represented by the following equation:

$$\upsilon = \eta/\rho$$

wherein $\eta$ represents the viscosity of a fluid at 25°C, and $\rho$ represents the density.

The coating amount of the sliding agent for use in the present invention is from 0.01 to 1.0, preferably from 0.05 to 1.0, and particularly preferably from 0.01 to 0.2, in terms of a weight ratio to the weight of the outermost binder layer.

When the protective layer of the photographic material of the present invention comprises two or more layers, the outermost protective layer preferably contains one or more kinds of alkylpolysiloxane.

Any method can be used for the addition of sliding agents in the present invention but, in general, they are directly added to the coating solution for the outermost protective layer as they are, or those insoluble in water are previously dissolved in an organic solvent prior to addition, or they can be previously prepared as a water dispersion or as a dispersion in a hydrophilic colloid solution and added to the coating solution for the outermost protective layer. When they are used as a dispersion, fine dispersion prepared using various surfactants as a dispersant is preferred. Examples of preferred dispersants include sodium salts of dodecylbenzenesulfonic acid, p-nonylphenoxybutanesulfonic acid, $\alpha$-sulfosuccinic acid dioctyl esters or N-methyloleoyltaurine.

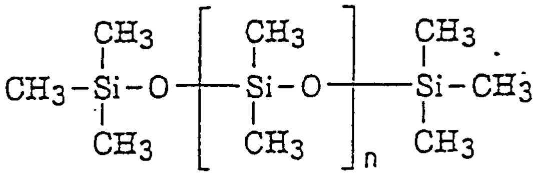
Examples of the organic solvent include alcohols (e.g., methanol, ethanol, propanol), esters (e.g., methyl acetate, ethyl acetate, butyl acetate, methyl formate, ethyl formate, propyl formate) and amides (e.g., dimethylformamide, dimethyl acetoamide). When a sliding agent is dispersed, hydrophilic colloid is preferred and gelatin is particularly effectively used.

For a hydrophilic colloid layer, sliding agents are preferably dispersed using an ultrasonic wave homogenizer or a pulp homogenizer in the presence of an appropriate dispersant to a grain size of preferably from 0.05 to 10 µm.

Specific examples of the sliding agent for use in the present invention are shown below, but the present invention is not limited thereto.

a) Silicone oil KF-96L (1.0), Shin-Etsu Chemical Co., Ltd.
b) Silicone oil KF-96 (10), Shin-Etsu Chemical Co., Ltd.
c) Silicone oil KF-96 (100), Shin-Etsu Chemical Co., Ltd.
d) Silicone oil KF-96 (1,000), Shin-Etsu Chemical Co., Ltd.
e) Silicone oil KF-96 (3,000), Shin-Etsu Chemical Co., Ltd.
f) Silicone oil KF-96H (10,000), Shin-Etsu Chemical Co., Ltd.
g) Silicone oil KF-410, Shin-Etsu Chemical Co., Ltd.

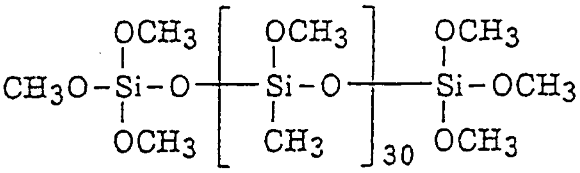
(a)



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3}$$

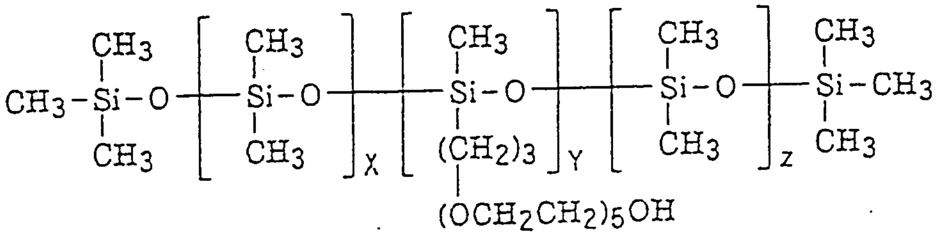
$n = 0 \sim 2500$

(b)



$$\mathrm{CH_3O-\overset{OCH_3}{\underset{OCH_3}{Si}}-O-\left[\overset{OCH_3}{\underset{CH_3}{Si}}-O\right]_{30}-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3}$$

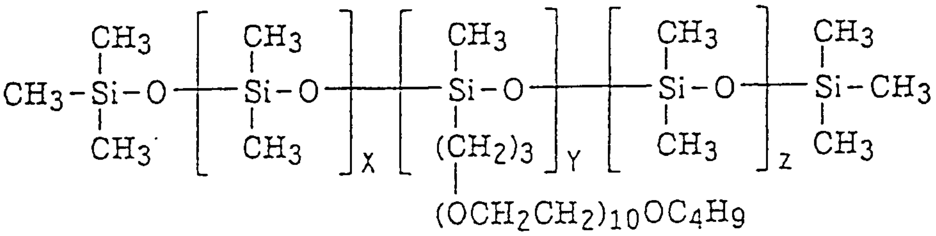
(c)



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_X-\left[\overset{CH_3}{\underset{(CH_2)_3(OCH_2CH_2)_5OH}{Si}}-O\right]_Y-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_Z-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3}$$

$X + Y + Z = 30$

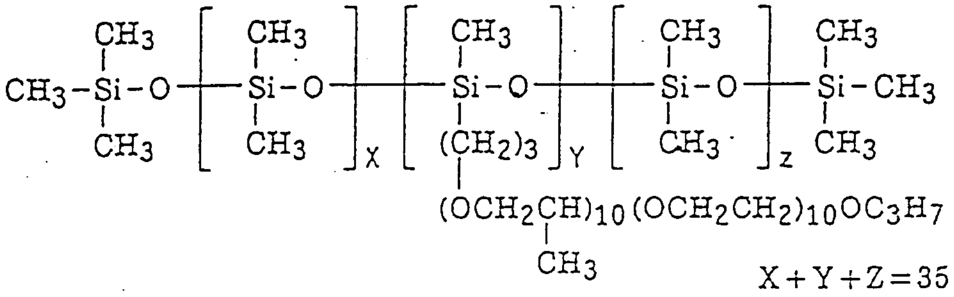
(d)



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_X-\left[\overset{CH_3}{\underset{(CH_2)_3(OCH_2CH_2)_{10}OC_4H_9}{Si}}-O\right]_Y-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_Z-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3}$$

$X + Y + Z = 40$

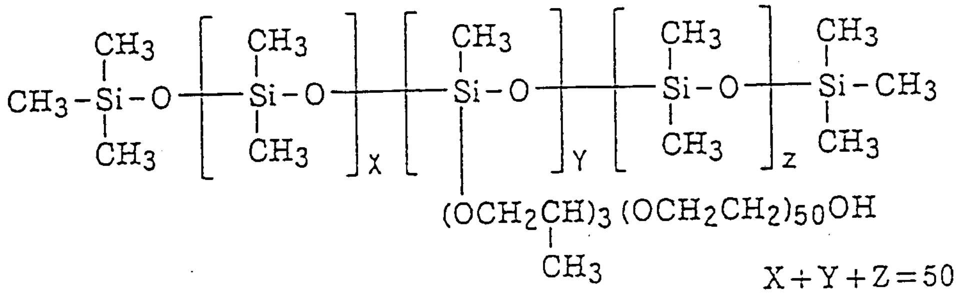
(e)



$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_X-\left[\underset{\mathrm{(CH_2)_3(OCH_2\underset{CH_3}{CH})_{10}(OCH_2CH_2)_{10}OC_3H_7}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Y-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Z-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

$X+Y+Z=35$

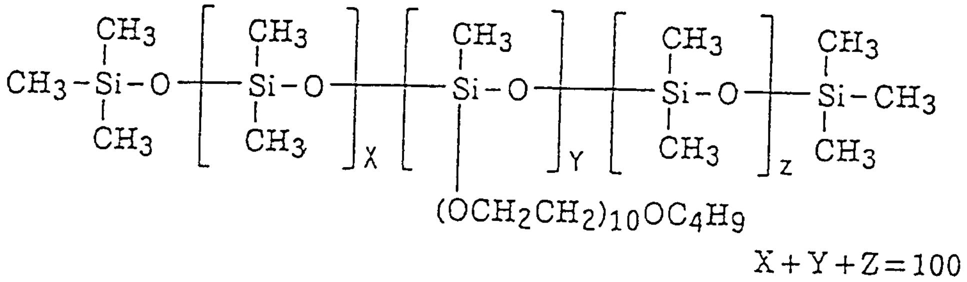
(f)



$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_X-\left[\underset{\mathrm{(OCH_2\underset{CH_3}{CH})_3(OCH_2CH_2)_{50}OH}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Y-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Z-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

$X+Y+Z=50$

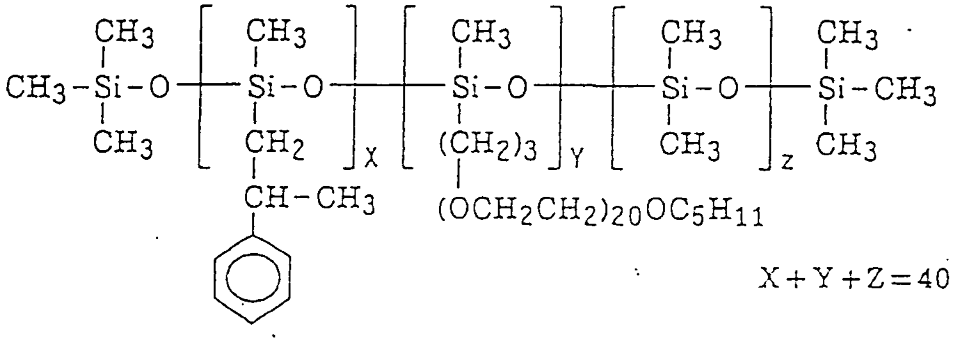
(g)



$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_X-\left[\underset{\mathrm{(OCH_2CH_2)_{10}OC_4H_9}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Y-\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_Z-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

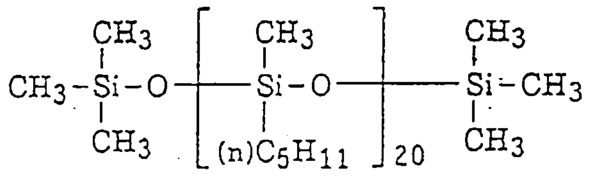
$X+Y+Z=100$

(h)



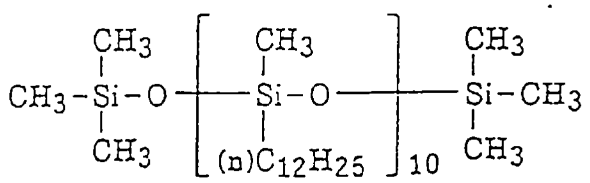
$X+Y+Z=40$

(i)



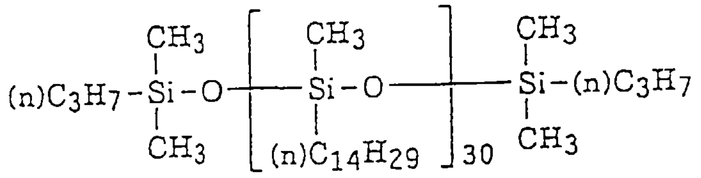
$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{(n)C_5H_{11}}{Si}}-O\right]_{20}-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

(j)



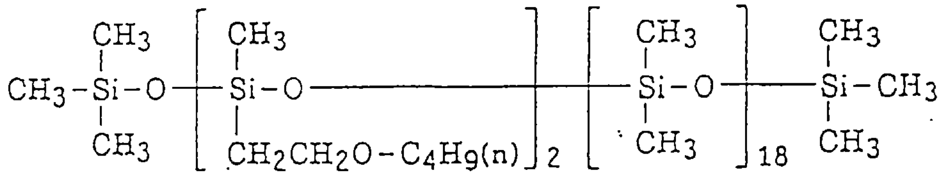
$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{(n)C_{12}H_{25}}{Si}}-O\right]_{10}-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

(k)



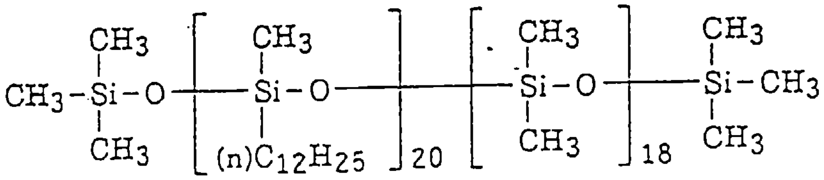
$$(n)C_3H_7-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{(n)C_{14}H_{29}}{Si}}-O\right]_{30}-\overset{CH_3}{\underset{CH_3}{Si}}-(n)C_3H_7$$

(ℓ)



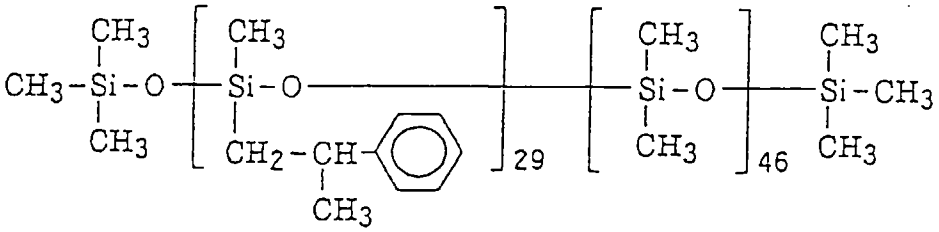
$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_2CH_2O-C_4H_9(n)}{Si}}-O\right]_{2}-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_{18}-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

(m)

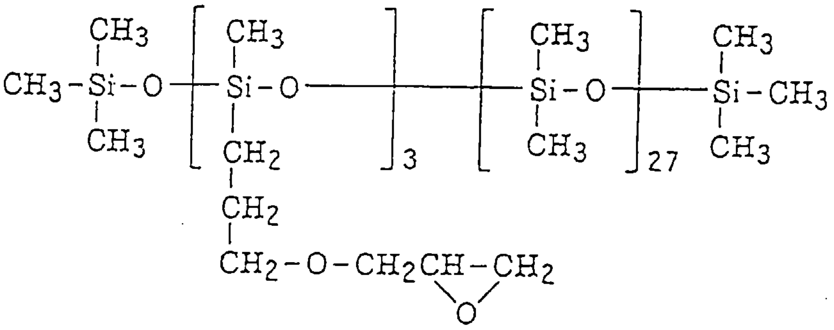


$CH_3-Si(CH_3)_2-O-[Si(CH_3)((n)C_{12}H_{25})-O]_{20}-[Si(CH_3)_2-O]_{18}-Si(CH_3)_2-CH_3$

(n)



(o)



The light-sensitive silver halide emulsion for use in the present invention may be spectrally sensitized using a sensitizing dye to a relatively long wavelength blue light, green light, red light and infrared light. Sensitizing dyes such as a cyanine dye, a merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holopolar cyanine dye, a styryl dye, a hemicyanine dye, an oxonol dye and a hemioxonol dye can be used.

Useful sensitizing dyes for use in the present invention are disclosed in Research Disclosure, Vol. 17643, Item IV-A, p. 23 (December, 1978), ibid., Vol. 1831, Item X, p. 437 (August, 1979) or in the literatures referred to therein.

In particular, sensitizing dyes having spectral sensitivity suitable for spectral characteristics of light sources of various scanners, image setters and process cameras can be advantageously selected.

The following sensitizing dyes can be advantageously selected, for example, from A) for an argon laser light source, compounds (I)-1 to (I)-8 disclosed in JP-A-60-162247, compounds I-1 to I-28 in JP-A-2-48653, compounds I-1 to I-13 in JP-A-4-330434, the compounds disclosed in Example 1 to Example 14, U.S. Patent 2,161,331 and compounds 1 to 7 in West German Patent 936,071, B) for a helium-neon laser light source, compounds I-1 to I-38 disclosed in JP-A-54-18726, compounds I-1 to I-35 in JP-A-6-75322 and compounds I-1 to I-34 in JP-A-7-287338, C) for an LED light source, dyes 1 to 20 disclosed in JP-B-55-39818, compounds I-1 to I-37 in JP-A-62-284343, and compounds I-1 to I-34 in JP-A-7-287338, D) for a semiconductor laser light source, compounds I-1 to I-12 disclosed in JP-A-59-191032, compounds I-1 to I-22 in JP-A-60-80841, compounds I-1 to I-29 in JP-A-4-335342 and compounds I-1 to I-18 in JP-A-59-192242, and E) for tungsten and xenon light sources for a process camera, compounds (1) to (19) represented by formula (I) disclosed in JP-A-55-45015 and compounds 4-A to 4-S, 5-A to 5-Q and 6-A to 6-T in JP-A-6-242547.

These sensitizing dyes may be used either alone or in combination thereof. A combination of sensitizing dyes is often used, in particular, for the purpose of supersensitization. There may be contained in an emulsion together with sensitizing dyes, a dye having no spectral sensitizing function per se or a material which does not substantially absorb visible light but exhibits supersensitization.

Examples of a combination of useful sensitizing dyes and dyes which exhibits supersensitization and examples of the material which exhibits supersensitization are disclosed in Research Disclosure Vol. 176, No. 17643, page 23, Item IV-J (December, 1978), JP-B-49-25500, JP-B-43-4933, JP-A-59-19032 and JP-A-59-192242.

The sensitizing dyes for use in the present invention may be used in combination of two or more thereof. For the inclusion of the sensitizing dyes in the silver halide emulsion of the present invention, they may be directly dispersed in the emulsion, or they may be dissolved in a single or mixed solvent of water, methanol, ethanol, propanol, acetone, methyl cellosolve, 2,2,3,3-tetrafluoropropanol, 2,2,2-trifluoroethanol, 3-methoxy-1-propanol, 3-methoxy-1-butanol, 1-methoxy-2-propanol, N,N-dimethylformamide, etc., and then added to the emulsion.

In addition, various methods can be used for the inclusion of the sensitizing dyes in the emulsion, for example, a method in which the sensitizing dyes are dissolved in a volatile organic solvent, the solution is dispersed in water or hydrophilic colloid and this dispersion is added to the emulsion as disclosed in U.S. Patent 3,469,987, a method in which the sensitizing dyes are dissolved in acid and the solution is added to the emulsion, or the sensitizing dyes are added to the emulsion as an aqueous solution coexisting with acid or base as disclosed in JP-B-44-23389, JP-B-44-27555 and JP-B-57-22091, a method in which the dyes are added to the emulsion as an aqueous solution or colloidal dispersion coexisting with a surfactant as disclosed in U.S. Patents 3,822,135 and 4,006,025, a method in which the dyes are directly dispersed in a hydrophilic colloid and the dispersion is added to the emulsion as disclosed in JP-A-53-102733 and JP-A-58-105141, or a method in which the dyes are dissolved using a compound capable of red-shifting and the solution is added to the emulsion as disclosed in JP-A-51-74624 can be used. Further, ultrasonic waves can be used for dissolution.

The time of the addition of the sensitizing dyes for use in the present invention to the silver halide emulsion for use in the present invention may be at any stage of the preparation of the emulsion which is recognized as useful hitherto. For example, they may be added at any stage if it is before coating, i.e., before grain formation stage of silver halide grains or/and before desalting stage, during desalting stage and/or after desalting and before beginning of chemical sensitization, as disclosed in U.S. Patents 2,735,766, 3,628,960, 4,183,756, 4,225,666, JP-A-58-184142 and JP-A-60-196749, or immediately before or during chemical ripening, after chemical ripening and before coating as disclosed in JP-A-58-113920. Also, as disclosed in U.S. Patent 4,225,666 and JP-A-58-7629, the sensitizing dyes can be used as a single compound alone or in combination with a compound having a different structure, and they can be divided and added separately, for example, one part of them is added during grain formation stage and the remaining is added during chemical ripening or after the completion of chemical ripening, otherwise one part is added prior to chemical ripening or during ripening stage and the remaining after completion of chemical ripening. The kinds of compounds separately added and combinations of compounds may be varied.

The addition amount of the sensitizing dye for use in the present invention is varied depending on the shape, size and halide composition of silver halide grains, the method and degree of chemical sensitization and the kind of antifoggant, but they can be used in an amount of from $4 \times 10^{-6}$ to $8 \times 10^{-3}$ mol per mol of the silver halide. For example, when the grain size of the silver halide grains is from 0.2 to 1.3 μm, the addition amount is preferably from $2 \times 10^{-7}$ to $3.5 \times 10^{-6}$ mol and more preferably from $6.5 \times 10^{-7}$ to $2.0 \times 10^{-6}$ mol per $m^2$ of the surface of the silver halide grains.

Gelatin is advantageously used as a binder for the silver halide emulsion layer and other hydrophilic colloid layers of the present invention, but other hydrophilic colloids can also be used or they can be used in combination with gelatin. Examples thereof include proteins such as gelatin derivatives, graft polymers of gelatin and other polymers, albumin and casein; sugar derivatives such as cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfate, sodium alginate and starch derivatives; and various kinds of synthetic hydrophilic polymers such as homopolymers or copolymers of polyvinyl alcohol, partially acetalated polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole.

Acid-processed gelatin can be used as well as lime-processed gelatin, and hydrolyzed products and enzyme decomposed products of gelatin can also be used.

In the present invention, with respect to the coating amount of gelatin as a binder, the gelatin amount of all the hydrophilic colloid layers on the side of the support on which the silver halide emulsion layer is provided is 3 g/$m^2$ or less, preferably from 1.0 to 3.0 g/$m^2$ or less, and the gelatin amount of all the hydrophilic colloid layers on the side of the support on which the silver halide emulsion layer is provided and all the hydrophilic colloid layers on the opposite side of the support is 6 g/$m^2$ or less, preferably from 2.0 to 6.0 g/$m^2$.

The swelling factor of the hydrophilic colloid layers including emulsion layers and protective layers of the silver halide photographic material according to the present invention is preferably from 80 to 150%, more preferably from 90 to 140%. The swelling factor of the hydrophilic colloid layers is obtained according to the following equation by measuring the thickness of the hydrophilic colloid layers ($d_0$) including emulsion layers and protective layers of the silver halide photographic material, immersing the silver halide photographic material in distilled water of 25°C for 1 minute and determining the swollen thickness ($\Delta d$).

$$\text{Swelling factor (\%)} = \Delta d \div d_0 \times 100$$

As the support of a photographic material for use in the present invention, for example, baryta paper, polyethylene-laminated paper, polypropylene synthetic paper, glass sheet, cellulose acetate, cellulose nitrate, and polyester films, e.g., polyethylene terephthalate can be exemplified. These supports are respectively appropriately selected depending on the intended use of the silver halide photographic material.

There is no particular limitation on various additives for use in the present invention and, for example, those described in the following places can preferably be used.

Polyhydroxybenzene compound:

Line 11, right lower column, page 10 to line 5, left lower column, page 12 of JP-A-3-39948, specifically, compounds (III)-1 to (III)-25 disclosed therein.

Compound which substantially does not have absorption maximum in visible region:

Compounds represented by formula (I) disclosed in JP-A-1-118832, specifically, compounds I-1 to I-26 disclosed therein.

Antifoggant:

Line 19, right lower column, page 17 to line 4, right upper column, page 18 of JP-A-2-103536.

Polymer latex:

Line 12, left lower column, page 18 to line 20, left lower column, the same page of JP-A-2-103536.

Matting agent, sliding agent and plasticizer:

Line 15, left upper column, page 19 to line 15, right upper column, the same page of JP-A-2-103536.

Hardening agent:

Line 5, right upper column, page 18 to line 17, right upper column, the same page of JP-A-2-103536.

Compound having acid radical:

Line 6, right lower column, page 18 to the first line, left upper column, page 19 of JP-A-2-103536.

Conductive material:

Line 13, left lower column, page 2 to line 7, right upper column, page 3 of JP-A-2-18542, specifically, metal oxides in line 2, right lower column, page 2 to line 10, right lower column, the same page, and conductive polymer compounds P-1 to P-7 disclosed therein.

Water-soluble dye:

First line, right lower column, page 17 to line 18, right upper column, the same page of JP-A-2-103536.

Solid dispersion dye:

Solid dispersion dyes disclosed in JP-A-2-294638 and JP-A-5-11382.

Surfactant:

Surfactants disclosed in line 7, right upper column, page 9 to line 3, right lower column, the same page of JP-A-2-12236, PEG-based surfactants disclosed in line 4, left lower column, page 18 to line 7, left lower column, the same page of JP-A-2-103536, and fluorine-containing surfactants disclosed in line 6, left lower column, page 12 to line 5, right lower column, page 13 of JP-A-3-39948, specifically, compounds VI-1 to VI-15 disclosed therein.

Redox compound:

Redox compounds capable of releasing development inhibitor by oxidation disclosed in JP-A-5-274816, preferably redox compounds represented by formula (R-1), (R-2) and (R-3) disclosed therein, specifically, compounds R-1 to R-68 disclosed therein.

Binder:

From first line to line 20, right lower column, page 3 of JP-A-2-18542.

Processing chemicals such as a developing solution and a fixing solution and processing methods according to the present invention are described below but the present invention should not be construed as being limited to the following description and specific examples.

A developing agent for use in a developing solution (hereinafter, a developing starter and a developing replenisher are referred to as a developing solution put together) of the present invention is not particularly limited, but it is preferred to contain a dihydroxybenzene, an ascorbic acid derivative and a hydroquinonemonosulfonate, alone or in combination. Further, from the point of developing capability, combinations of a dihydroxybenzene or an ascorbic acid derivative with an 1-phenyl-3-pyrazolidone, or combinations of a dihydroxybenzene or an ascorbic acid derivative with a p-aminophenol are preferred.

The dihydroxybenzene developing agent for use in the present invention includes hydroquinone, chlorohydroquinone, isopropylhydroquinone and methylhydroquinone, and hydroquinone is particularly preferred. Examples of ascorbic acid derivative developing agents include ascorbic acid, isoascorbic acid, and salts thereof, and sodium erythorbate is particularly preferred from cost for the material.

The 1-Phenyl-3-pyrazolidones or derivatives thereof for use in the present invention as a developing agent include 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone and 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone.

The p-aminophenol based 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.

The dihydroxybenzene developing agent is, in general, preferably used in an amount of from 0.05 to 0.8 mol/liter. When the dihydroxybenzene is used in combination with the 1-phenyl-3-pyrazolidone or the p-aminophenol, the use amount of the former is preferably from 0.05 to 0.6 mol/liter, more preferably from 0.23 to 0.5 mol/liter, and that of the latter is preferably 0.06 mol/ liter or less, more preferably from 0.03 to 0.003 mol/liter.

The ascorbic acid derivative developing agent is, in general, preferably used in an amount of from 0.01 to 0.5 mol/liter, more preferably from 0.05 to 0.3 mol/liter. Further, when the ascorbic acid derivative is used in combination with the 1-phenyl-3-pyrazolidone or p-aminophenol, the use amount of the former is preferably from 0.01 to 0.5 mol/liter, and that of the latter is preferably from 0.005 mol/liter to 0.2 mol/ liter.

A developing solution for processing a photographic material in the present invention can contain commonly used additives (e.g., a developing agent, an alkali agent, a pH buffer, a preservative, a chelating agent, etc.). Specific examples thereof are shown below but the present invention is not limited thereto.

The buffer which is used in a developing solution for developing a photographic material in the present invention includes carbonate, boric acids disclosed in JP-A-62-186259, succharides (e.g., succharose) disclosed in JP-A-60-93433, oximes (e.g., acetoxime), phenols (e.g., 5-sulfosalicylic acid) and tertiary phosphate (e.g., sodium salt, potassium salt), and carbonates and boric acids are preferably used. The use amount of the buffer, in particular carbonate, is preferably 0.1 mol/liter or more, particularly preferably from 0.2 to 1.5 mol/liter.

Examples of the preservatives which can be used in the developing solution for use in the present invention include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite, and sodium formaldehyde bisulfite. Preferred addition amount of the sulfite preservative is 0.20 mol/liter or more, particularly preferably 0.3 mol/liter or more. However, because too much an amount causes silver contamination of the developing solution, the upper limit is preferably 1.2 mol/liter, and particularly preferred addition amount is from 0.35 to 0.7 mol/liter.

A small amount of the ascorbic acid derivative may be used in combination with the sulfite as a preservative for dihydroxybenzene based developing agent. The use of sodium erythorbate is economically preferred. The addition amount thereof is preferably from 0.03 to 0.12, particularly preferably from 0.05 to 0.10, in terms of molar ratio to dihydroxybenzene developing agent. When the ascorbic acid derivative is used as a preservative, it is preferred not to contain a boron compound in the developing solution.

Other additives which can be used in the present invention include, in addition to the above compounds, a development inhibitor such as sodium bromide and potassium bromide; an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol and dimethylformamide; a development accelerator such as alkanolamine, e.g., diethanolamine and triethanolamine, imidazole and derivatives thereof; and a physical development unevenness inhibitor such as a heterocyclic mercapto compound (e.g., sodium 3-(5-mercaptotetrasol-1-yl)benzene sulfonate, 1-phenyl-5-mercaptotetrazole) and the compounds disclosed in JP-A-62-212651.

Further, mercapto based compounds, indazole based compounds, benzotriazole based compounds and benzimidazole based compounds can be used as an antifoggant or a black pepper inhibitor. Specific examples thereof include 5-nitroindazole, 5-p-nitrobenzoylaminoindazole, 1-methyl-5-nitroindazole, 6-nitroindazole, 3-methyl-5-nitroindazole, 5-nitrobenzimidazole, 2-isopropyl-5-nitrobenzimidazole, 5-nitrobenzotriazole, sodium 4-((2-mercapto-1,3,4-thiadiazol-2-yl)thio)butanesulfonate, 5-amino-1,3,4-thiadiazole-2-thiol, methylbenzotriazole, 5-methylbenzotriazole, and 2-mercaptobenzotriazole. The addition amount of these compounds is, in general, from 0.01 to 10 mmol, more preferably from 0.1 to 2 mmol, per liter of the developing solution.

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

Examples of the inorganic chelating agents include sodium tetrapolyphosphate and sodium hexametaphosphate.

On the other hand, examples of the organic chelating agents include organic carboxylic acids, aminopolycarboxylic acids, organic phosphonic acids, aminophosphonic acids, and organic phosphonocarboxylic acids.

Examples of the organic carboxylic acid include acrylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, gluconic acid, adipic acid, pimelic acid, acielaidic acid, sebacic acid, nonanedicarboxylic acid, decanedicarboxylic acid, undecanedicarboxylic acid, maleic acid, itaconic acid, malic acid, citric acid, and tartaric acid.

Examples of the aminopolycarboxylic acids include iminodiacetic acid, nitrilotriacetic acid, nitrilotripropionic acid, ethylenediaminemonohydroxyethyltriacetic acid, ethylenediaminetetraacetic acid, glycol ether tetraacetic acid, 1,2-diaminopropanetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, 1,3-diamino-2-propanoltetraacetic acid, glycol ether diaminetetraacetic acid, and the compounds disclosed 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 the hydroxyalkylidene-diphosphonic acids disclosed in U.S. Patents 3,214,454, 3,794,591 and West German Patent Publication No. 2,227,639, and the compounds disclosed in Research Disclosure, Vol. 181, Item 18170 (May, 1979).

Examples of the aminophosphonic acids include aminotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid, aminotrimethylenephosphonic acid, and the compounds disclosed in Research Disclosure, No. 18170, JP-A-57-208554, JP-A-54-61125, JP-A-55-29883 and JP-A-56-97347.

Examples of the organic phosphonocarboxylic acids include the compounds disclosed 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, No. 18170.

These organic and/or inorganic chelating agents are not limited to the above-described compounds and they may be used in the form of an alkali metal salt or an ammonium salt. The addition amount of these chelating agents is preferably from $1 \times 10^{-4}$ to $1 \times 10^{-1}$ mol, more preferably from $1 \times 10^{-3}$ to $1 \times 10^{-2}$ mol, per liter of the developing solution.

Further, the developing solution can contain the following compounds as an agent for preventing silver contamination, in addition to the compounds disclosed in JP-A-56-24347, JP-B-56-46585, JP-B-62-2849 and JP-A-4-362942, triazine having one or more mercapto groups (e.g., the compounds disclosed in JP-B-6-23830, JP-A-3-282457, JP-A-7-175178), pyrimidine having one or more mercapto groups (e.g., 2-mercaptopyrimidine, 2,6-dimercaptopyrimidine, 2,4-dimercaptopyrimidine, 5,6-diamino-2,4-dimercapto-pyrimidine, 2,4,6-trimercaptopyrimidine), pyridine having one or more mercapto groups (e.g., 2-mercaptopyridine, 2,6-dimercaptopyridine, 3,5-dimercaptopyridine, 2,4,6-trimercaptopyridine, the compounds disclosed in JP-A-7-248587), pyrazine having one or more mercapto groups (e.g., 2-mercaptopyrazine, 2,6-dimercaptopyrazine, 2,3-dimercaptopyrazine, 2,3,5-trimercaptopyrazine), pyridazine having one or more mercapto groups (e.g., 3-mercaptopyridazine, 3,4-dimercaptopyridazine, 3,5-dimercaptopyridazine, 3,4,6-trimercaptopyridazine), the compounds disclosed in JP-A-7-175177, and polyoxyalkylphosphonate disclosed in U.S. Patent 5,457,011. These silver contamination preventing agents can be used alone or in combination of two or more, and they are used in an amount of preferably from 0.05 to 10 mmol, more preferably from 0.1 to 5 mmol, per liter of the developing solution.

Further, the compounds disclosed in JP-A-61-267759 can be used as a dissolution aid.

Further, if necessary, the developing solution may contain a toning agent, a surfactant, a defoaming agent and a hardening agent.

The pH of the developing solution is preferably from 9.0 to 12.0, more preferably less than 11.0, and particularly preferably from not less than 9.5 to less than 11.0. As an alkali agent which is used for adjusting pH, common water-soluble inorganic alkali metal salts (e.g., sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate) can be used.

With regard to the cation in a developing solution, a potassium ion does not inhibit development so much as a sodium ion does, and provides less fringes around the blackened portion as compared with a sodium ion. Further, when a developing solution is preserved as a concentrated solution, a potassium salt has, in general, higher solubility and thus preferred. However, since a potassium ion in a fixing solution inhibits fixation in almost the same degree as a silver ion does, if the potassium ion concentration in a developing solution is high, the potassium ion concentration in a fixing solution becomes high by the developing solution carried over with a photographic material, which is not preferred. Accordingly, the molar ratio of the potassium ion to the sodium ion in a developing solution is preferably from 20/80 to 80/20. The ratio of the potassium ion to the sodium ion in a developing solution can be appropriately adjusted within the above range by the counter cation of a pH buffer, a pH adjustor, a preservative, a chelating agent, etc.

The replenishing rate of a developing solution is generally 390 ml or less per $m^2$ of the photographic material, and preferably from 30 to 325 ml, most preferably from 120 to 180 ml, per $m^2$ of the photographic material. The composition and/or the concentration of a developing replenisher may be the same as or different from those of a developing starter.

Ammonium thiosulfate, sodium thiosulfate and sodium ammonium thiosulfate can be used as the fixing agent of fixing processing chemicals in the present invention. The use amount of the fixing agent can be varied appropriately and is generally from about 0.7 to about 3.0 mol/liter.

The fixing solution for use in the present invention may contain a water-soluble aluminum salt and a water-soluble chromium salt, which function as a hardening agent. Preferred compounds are water-soluble aluminum salts, e.g., aluminum chloride, aluminum sulfate, potassium alum, aluminum ammonium sulfate, aluminum nitrate and aluminum lactate. They are preferably contained in an amount of from 0.01 to 0.15 mol/liter in terms of an aluminum ion concentration in the working solution.

When the fixing solution is preserved as a concentrated solution or a solid agent, it may comprise a plurality of parts with a hardening agent being a separate part, or it may comprise one part type including all the components.

The fixing processing chemicals can contain, if desired, a preservative (e.g., sulfite, bisulfite or metabisulfite, in an amount of 0.015 mol/liter or more, preferably from 0.02 mol/liter to 0.3 mol/liter), a pH buffer (e.g., acetic acid, sodium acetate, sodium carbonate, sodium hydrogencarbonate, phosphoric acid, succinic acid and adipic acid, in an amount of from 0.1 mol/liter to 1 mol/liter, preferably from 0.2 mol/liter to 0.7 mol/liter), and a compound having stabilizing capability of aluminum and hard water softening capability (e.g., gluconic acid, iminodiacetic acid, 5-sulfosalicylic acid, glucoheptanic 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 thereof and salts thereof, saccharides and boric acid, in an amount of from 0.001 mol/liter to 0.5 mol/liter, preferably from 0.005 mol/liter to 0.3 mol/liter).

The fixing processing chemicals can contain, if desired, the compounds disclosed in JP-A-62-78551, a pH adjustor (e.g., sodium hydroxide, ammonia, sulfuric acid), a surfactant, a wetting agent and a fixing accelerator. Specific examples of the surfactants include anionic surfactants (e.g., a sulfated product, a sulfonated product), polyethylene based surfactants, and amphoteric surfactants disclosed in JP-A-57-6840, and known defoaming agents can also be used. Specific examples of the wetting agents include alkanolamine and alkylene glycol. Specific examples of the fixing accelerators include alkyl- and aryl-substituted thiosulfonic acid and the salts thereof, the thiourea derivatives disclosed in JP-B-45-35754, JP-B-58-122535 and JP-B-58-122536, an alcohol having a triple bond in the molecule, the thioether compounds disclosed in U.S. Patent 4,126,459, the mercapto compounds disclosed in JP-A-64-4739, JP-A-1-4739, JP-A-1-159645 and JP-A-3-101728, the mesoionic compounds disclosed in JP-A-4-170539, and thiocyanate.

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 pH of the fixing solution rises in processing by mixing of a developing solution thereinto. In such a case the pH of a hardening fixing solution is 6.0 or less, preferably 5.7 or less, and that of a non-hardening fixing solution is 7.0 or less, preferably 6.7 or less.

The replenishing rate of the fixing solution is generally 500 ml/$m^2$ or less, preferably 390 ml/$m^2$ or less, more preferably from 320 to 80 ml/$m^2$, of the photographic material processed. The compositions and/or the concentration of a fixing replenisher may be the same as or different from those of a fixing starter.

Silver recovery from a fixing solution can be carried out according to known fixing solution reclaiming methods, such as electrolytic silver recovery, and the regenerated solution after the silver recovery can be used in the present invention. As such a reclaiming device, Reclaim R-60 produced by Fuji Hunt Co., Ltd. can be exemplified.

Further, the removal of dyes and the like using an adsorptive filter such as an activated carbon is also preferred.

A photographic material is subjected to washing or stabilizing processing after being developed and fixed (hereinafter "washing" includes stabilization processing therein and the solution used therefor is called water or washing water, unless otherwise indicated). The water which is used for washing may be any of tap water, ion exchange water, distilled water and stabilizing solution. The replenishing rate thereof is, in general, from about 8 liters to about 17 liters per $m^2$ of the photographic material, but washing can be carried out with the less replenishing rate. In particular, with a replenishing rate of 3 liters or less (including zero, i.e., washing in a reservoir), not only water saving processing can be carried out but also piping for installation of an automatic processor is not required. When washing is carried out with a reduced amount of water, it is preferred to use a washing tank equipped with a squeeze roller or a crossover roller disclosed in JP-A-63-18350 and JP-A-62-287252. The addition of various kinds of oxidizing agents (e.g., ozone, hydrogen peroxide, sodium hypochlorite, activated halogen, chlorine dioxide, sodium carbonate hydrogen peroxide) and the provision of filters for filtration may be combined to reduce load in environmental pollution which becomes a problem when washing is carried out with a small amount of water and to prevent generation of scale.

As a means of reducing the replenishing rate of the washing water, a multistage countercurrent system (e.g., two stages or three stages) has been known. The replenishing rate of the washing water in this system is preferably from 50 to 200 ml per $m^2$ of the photographic material. This is also effective in an independent multistage system (a method which is not a countercurrent system and fresh solution is replenished separately to multistage washing tanks).

Further, a means of preventing generation of scale may be included in a washing process according to the present invention. A means of preventing generation of scale is not particularly limited and known methods can be used, such as a method of adding antimold agents (a scale preventive), a method by electroconduction, a method of irradiating with ultraviolet ray, infrared ray or far infrared ray, a method of applying a magnetic field, a method of processing by ultrasonic wave, a method of applying a heat, and a method of emptying tanks when they are not used. These scale preventing means may be conducted in accordance with the progress of the processing of photographic materials, may be conducted at regular intervals irrespective of usage conditions, or may be conducted only during the time when processing is not conducted, for example, during night. Alternatively, washing water previously subjected to such a means may be replenished. It is also preferred to conduct different scale preventing means for every given period of time for inhibiting the proliferation of resisting fungi.

An antimold agent is not particularly limited and known antimold agents can be used. Examples thereof include, for example, a chelating agent such as glutaraldehyde and aminopolycarboxylic acid, cationic surfactants and mercaptopyridine oxide (e.g., 2-mercaptopyridine-N-oxide), in addition to the above-described oxidants, and they can be used alone or in combination of two or more.

Methods by electroconduction disclosed in JP-A-3-224685, JP-A-3-224687, JP-A-4-16280 and JP-A-4-18980 can be used in the present invention.

Moreover, known water-soluble surfactants or defoaming agents may be contained in the washing water for preventing generation of foaming irregulars and transfer of stains. In addition, the dye-adsorbents disclosed in JP-A-63-163456 may be included in a washing tank to inhibit contamination by dyes eluted out of photographic materials.

Whole or a part of the overflow from the washing process can be mixed with a processing solution having fixing ability to utilize the mixture as disclosed in JP-A-60-235133. It is also preferred from the environmental protection for the washing solution to be processed by various processes before draining, for example, biochemical oxygen demand (BOD), chemical oxygen demand (COD), iodine consumption, etc., are reduced by a microorganism process (e.g., a process using sulfur oxide fungus or activated sludge, a process using a filter of a porous carrier, such as activated carbon or ceramic, carrying microorganisms) and an oxidation process by electroconduction and oxidants, or silver is precipitated by adding a compound which forms a hardly soluble silver complex such as trimercaptotriazine and filtrated using a filter of a polymer having affinity with silver and to reduce the silver concentration in drained water.

Also, when a photographic material is subjected to stabilizing processing after washing processing, a bath containing compounds disclosed in JP-A-2-201357, JP-A-2-132435, JP-A-1-102553 and JP-A-46-44446 may be used as a final bath. This stabilizing bath may also contain, if desired, ammonium compounds, metal compounds such as Bi and Al, brightening agents, various kinds of chelating agents, film pH adjustors, hardening agents, sterilizers, antimold agents, alkanolamines and surfactants.

Additives such as antimold agents and stabilizing agents which are added to a washing bath and a stabilizing bath can also be solid agents similar to the above-described developing and fixing processing chemicals.

Waste solutions of the developing solution, fixing solution, washing water and stabilizing solution for use in the present invention are preferably subjected to incineration disposal. These waste solutions are also possible to be discarded as concentrated solutions made using concentrators as disclosed in JP-B-7-83867 and U.S. Patent 5,439,560, or as solids.

In the case when the replenishing rate is reduced, it is preferred to prevent evaporation and air oxidation of the solution by minimizing the open area of the processing tank. An automatic processor of roller transporting type is disclosed in U.S. Patents 3,025,779 and 3,545,971 and referred to as merely a roller transporting type processor in the specification of the present invention. A roller transporting type processor comprises four steps of development, fixation, washing and drying and, although the method of the present invention does not exclude other steps (e.g., stopping step), it is most preferred to follow this four step system. Further, a rinsing bath may be provided between development and fixation and/or between fixation and washing.

The development processing for use in the present invention is preferably carried out by development processing of dry to dry of from 25 to 160 seconds, with development and fixing time being 40 seconds or less, preferably from 6 to 35 seconds, the temperature of each processing solutions being from 25 to 50°C, preferably from 30 to 40°C. The temperature and time of washing is preferably from 0 to 50°C and 40 seconds or less, respectively. According to the method of the present invention, photographic materials having been developed, fixed and washed may be dried after the washing water is squeezed out of the materials, that is, through squeeze rollers. The drying step is carried out at a temperature of from about 40 to about 100°C and the time therefor can be appropriately varied depending upon the surrounding conditions. The drying methods are not particularly limited and any known methods can be used, such as a warm air drying method, the heated roller drying method and the far infrared ray drying method disclosed in JP-A-4-

15534, JP-A-5-2256 and JP-A-5-289294 and a plurality of methods can be used in combination.

When the developing and fixing processing chemicals of the present invention are each in a solution form, they are preferably preserved in the packaging materials having a low oxygen permeation as disclosed in JP-A-61-73147. Further, when they are each in a concentrated solution form, they are diluted prior to use with water to a predetermined concentration in the ratio of from 0.2 parts to 3 parts of water per one part of the concentrated solutions.

Whether the developing processing chemicals and fixing processing chemicals of the present invention are each in a solid form, the same effects as in where they are each in a solution form can be obtained. Solid processing chemicals are described below.

The solid chemicals for use in the present invention may be made into known shapes such as powders, pellets, granules, lumps, tablets, compactors, briquettes, sheets, bars or paste. These solid chemicals may be covered with water-soluble coating agents or films to separate components which react with each other on contact, or they may have a multilayer structure to separate components which react with each other, or both types may be used in combination.

Known coating agents and auxiliary granulating agents can be used, but polyvinylpyrrolidone, polyethylene glycol, polystyrene sulfonic acid and vinyl compounds are preferred. Line 48, column 2 to line 13, column 3 of JP-A-5-45805 can be referred to.

When a multilayer structure is used, a component which does not react with the components which react with each other on contact may be sandwiched therebetween and this is made into tablets and briquettes, or components of known structures may be made to similar layer structure and packaged. Methods therefor are disclosed in JP-A-61-259921, JP-A-4-16841, JP-A-4-78848 and JP-A-5-93991.

The bulk density of the solid processing chemicals is preferably from 0.5 to 6.0 g/cm$^3$, in particular, the bulk density of tablets is preferably from 1.0 to 5.0 g/cm$^3$ and that of granules is preferably from 0.5 to 1.5 g/cm$^3$.

Solid processing chemicals according to the present invention can be produced using any known method, for example, those described in JP-A-61-259921, JP-A-4-15641, JP-A-4-16841, JP-A-4-32837, JP-A-4-78848, JP-A-5-93991, 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, JP-A-6-138605 and JP-A-8-286329.

Specifically, a rolling granulating method, an extrusion granulating method, a compression granulating method, a cracking granulating method, a stirring granulating method, a spray drying method, a dissolution coagulation method, a briquetting method, and a roller compacting method can be used.

The solubility of the solid chemicals for use in the present invention can be adjusted by changing the state of the surface (smooth, porous, etc.) and the partial thickness, or making the shape to a hollow doughnut type. Further, it is possible to impart different solubilities to a plurality of granulated products, or it is also possible for materials having different solubilities to take various shapes to coincide with solubilities one another. Multilayer granulated products having different compositions between the inside and the surface can also be used.

Packaging materials of the solid chemicals preferably have low oxygen and water permeability, and those having a bag-like, cylindrical or box-like shape can be used. Packaging materials of foldable shapes as disclosed in JP-A-6-24285, JP-A-6-242588, JP-A-6-247432, JP-A-6-247448, JP-A-6-301189, JP-A-7-5664, and JP-A-7-5666 to JP-A-7-5669 are preferred for saving storage space of waste materials. These packaging materials may be provided with a screw cap, a pull-top or an aluminum seal on takeout ports thereof for processing chemicals, or may be heat-sealed, or other known types may be used, and there are no particular limitations. Waste packaging materials are preferably recycled for reclaiming or reused from the environmental protection view.

Methods of dissolution and replenishment of the solid processing chemicals for use in the present invention are not particularly limited and known methods can be used. Examples of these known methods include a method in which a certain amount of processing chemicals are dissolved and replenished by a dissolving device having a stirring function, a method in which processing chemicals are dissolved by a dissolving device having a dissolving zone and a zone where a finished solution is stocked and the solution is replenished from the stock zone, and methods in which processing chemicals are fed to a circulating system of an automatic processor and dissolved and replenished, or methods in which processing chemicals are fed to a dissolving tank equipped in an automatic processor in accordance with the progress of the processing of photographic materials as disclosed in JP-A-5-119454, JP-A-6-19102 and JP-A-7-261357. In addition to the above methods, any of known methods can be used. The charge of processing chemicals maybe conducted by hands, or automatic opening and automatic charge may be conducted by a dissolving device or automatic processor provided with opening mechanism. The latter is preferred from the working environment. Specifically, there are methods of pushing through, unsealing, cutting off or bursting the takeout port of a package, and the methods disclosed in JP-A-6-19102 and JP-A-6-95331.

## EXAMPLES

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

## EXAMPLE 1

### Preparation of Emulsion N-1

### Solution 1

| | |
|---|---|
| Water | 650 ml |
| Gelatin | 20 g |
| Sodium Chloride | 2.4 g |
| 1,3-Dimethylimidazolidine-2-thione | 16 mg |
| Sodium Benzenesulfonate | 6.4 mg |

### Solution 2

| | |
|---|---|
| Water | 576 ml |
| Silver Nitrate | 150 g |

### Solution 3

| | |
|---|---|
| Water | 517 ml |
| Sodium Chloride | 34 g |
| Potassium Bromide | 31 g |
| Ammonium Hexachloroiridate(III) (0.001% aqueous solution) | 125 ml |
| Potassium Hexachlororhodate(III) (0.001% aqueous solution) | 6 ml |

Solution 2 and Solution 3 each in the amounts corresponding to 90% thereof were simultaneously added to Solution 1 maintained at 42°C and pH 4.5 over a period of 20 minutes with stirring to form nucleus grains. Subsequently, Solution 4 and Solution 5 shown below were added over a period of 8 minutes. Further, the remaining amounts of 10% of Solution 2 and Solution 3 were added over a period of 2 minutes. Moreover, 0.15 g of potassium iodide was added thereto and grain formation was terminated.

Solution 4

| | |
|---|---|
| Water | 200 ml |
| Silver Nitrate | 50 g |

Solution 5

| | |
|---|---|
| Water | 200 ml |
| Sodium Chloride | 13 g |
| Potassium Bromide | 10 g |
| Potassium Hexacyanoferrate(II) (0.1% aqueous solution) | 10 ml |

The mixture was then washed according to the ordinary flocculation method using 3 g of Compound A per mol of silver, and thereto 40 g of gelatin was added.

The pH and pAg were adjusted to 5.7 and 7.5, respectively, and 1.0 mg of sodium thiosulfate, 4.0 mg of chloroauric acid, 1.5 mg of triphenylphosphine selenide (a selenium sensitizing dye), 8 mg of sodium benzenethiosulfonate, and 2 mg of sodium benzenesulfinate were added thereto and the resulting product was chemically sensitized to provide an optimum sensitivity at 55°C.

Further, 100 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as a stabilizer and phenoxyethanol as a preservative were added, to thereby finally obtain cubic silver chloroiodobromide Emulsion A having a silver chloride content of 70 mol% and an average grain size of 0.25 µm.

Preparation of Coated Sample

To Emulsion A were added Sensitizing Dye (1) in an amount of $3.8 \times 10^{-4}$ mol/mol-Ag and spectral sensitization was conducted. Further, KBr in an amount of $3.4 \times 10^{-4}$ mol/mol-Ag, Compound (1) in an amount of $3.2 \times 10^{-4}$ mol/mol-Ag, Compound (2) in an amount of $8.0 \times 10^{-4}$ mol/mol-Ag, hydroquinone in an amount of $1.2 \times 10^{-2}$ mol/mol-Ag, citric acid in an amount of $3.0 \times 10^{-3}$ mol/mol-Ag, Compound (3) in an amount of $1.0 \times 10^{-4}$ mol/mol-Ag, Compound (4) in an amount of $6.0 \times 10^{-4}$ mol/mol-Ag, 200 mg/m$^2$ of Compound C (a water-soluble polymer latex), 200 mg/m$^2$ of a latex copolymer of methyl acrylate/sodium 2-acrylamido-2-methylpropanesulfonate/2-acetoxyethyl methacrylate (88/5/7 by weight), 200 mg/m$^2$ of a dispersion of polyethyl acrylate, 20 wt% (based on gelatin) of colloidal silica having a particle size of 10 µm and 4 wt% (based on gelatin) of Compound (5) were added thereto.

The pH value of the emulsion was adjusted to 5.6 with citric acid. The thus-obtained coating solution was coated on the polyester support having a thickness of 100 µm and having provided on both sides thereof the first undercoat layer and the second undercoat layer disclosed in Example 1 of JP-A-6-317866 to provide a coated silver weight of 3.7 g/m$^2$ and a coated gelatin weight of 1.6 g/m$^2$. An upper protective layer and a lower protective layer each having the composition shown below were coated on this support and a UL layer having the composition shown below was coated beneath the lower protective layer.

Upper Protective Layer

| | |
|---|---|
| Gelatin | 0.3 g/m$^2$ |
| Phenoxyethanol | 100 ppm (per coating solution) |
| Silica Matting Agent (average particle size: 3.5 µm) | 25 mg/m$^2$ |
| Sliging Agent shown in Table A (gelatin dispersion) | 50 mg/m$^2$ |
| Colloidal Silica (particle size: 10 to 20 µm) | 30 mg/m$^2$ |
| Compound (7) | 5 mg/m$^2$ |
| Sodium Dodecylbenzenesulfonate | 20 mg/m$^2$ |
| Compound (8) | 20 mg/m$^2$ |
| Compound B | added to obtain viscosity of 15 cp |

Lower Protective Layer

| | |
|---|---|
| Gelatin | 0.5 g/m$^2$ |
| Phenoxyethanol | 100 ppm (per coating solution) |
| Compound (9) | 15 mg/m$^2$ |
| 1,5-Dihydroxy-2-benzaldoxime | 10 mg/m$^2$ |
| Polyethyl Acrylate Latex | 150 mg/m$^2$ |
| Compound B | added to obtain viscosity of 20 cp |

UL Layer

| | |
|---|---|
| Gelatin | 0.5 g/m$^2$ |
| Phenoxyethanol | 100 ppm (per coating solution) |
| Polyethyl Acrylate Latex | 150 mg/m$^2$ |
| Compound (5) | 40 mg/m$^2$ |
| Compound (10) | 10 mg/m$^2$ |
| Compound B | added to obtain viscosity of 30 cp |

The support of the samples which were used in the present invention had the backing layer and the conductive layer having the following compositions.

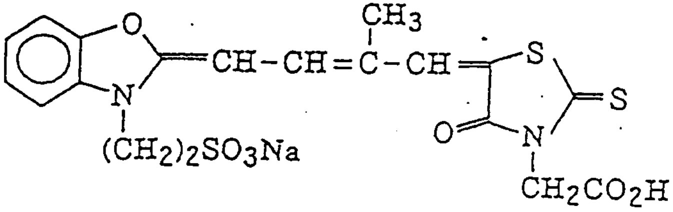
Backing Layer

| | |
|---|---|
| Gelatin | 3.3 g/$m^2$ |
| Phenoxyethanol | 100 ppm (per coating solution) |
| Sodium Dodecylbenzenesulfonate | 80 mg/$m^2$ |
| Compound (11) | 40 mg/$m^2$ |
| Compound (12) | 20 mg/$m^2$ |
| Compound (13) | 90 mg/$m^2$ |
| 1,3-Divinylsulfonyl-2-propanol | 60 mg/$m^2$ |
| Polymethyl Methacrylate Fine Grains (average particle size: 5.0 µm) | 30 mg/$m^2$ |
| Compound (5) | 120 mg/$m^2$ |
| Compound B | added to obtain viscosity of 25 cp |

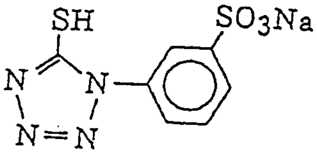
Conductive Layer

| | |
|---|---|
| Gelatin | 0.1 g/$m^2$ |
| Phenoxyethanol | 100 ppm (per coating solution) |
| Sodium Dodecylbenzenesulfonate | 20 mg/$m^2$ |
| $SnO_2$/Sb (9/1 by weight ratio, average grain size: 0.25 µm) | 200 mg/$m^2$ |
| Compound B | added to obtain viscosity of 30 cp |

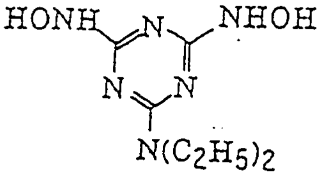
Sensitizing Dye (1)



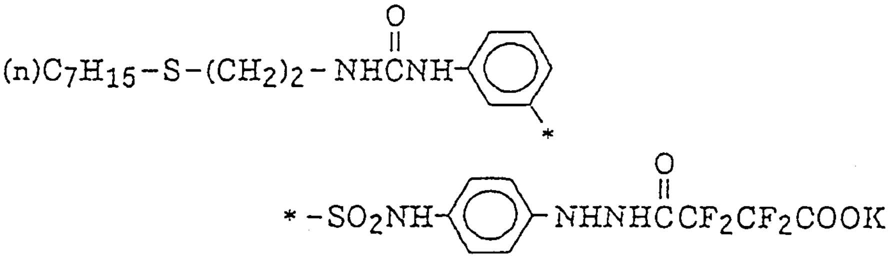
Compound (1)



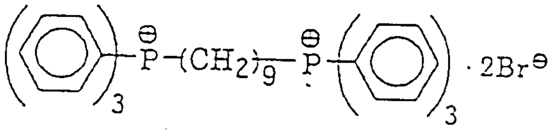
Compound (2)



Compound (3)

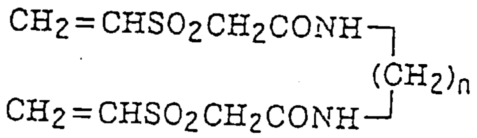


Compound (4)



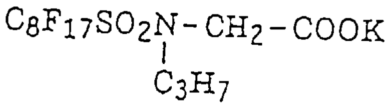
Compound (5)

A 3/1 mixture of n=2/n=3



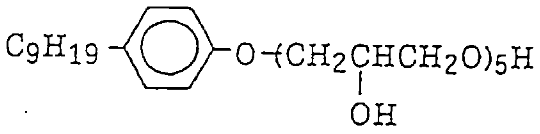
$$CH_2{=}CHSO_2CH_2CONH-(CH_2)_n-NHCOCH_2SO_2CH{=}CH_2$$

Compound (7)

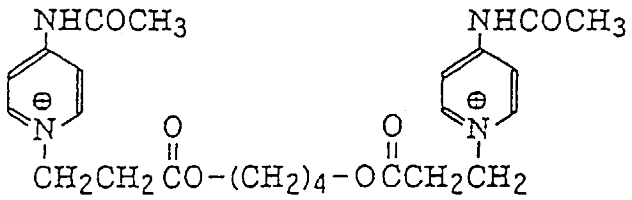


$$C_8F_{17}SO_2N(C_3H_7)-CH_2-COOK$$

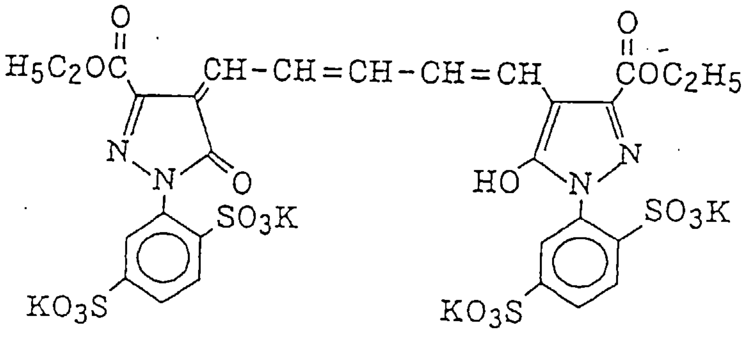
Compound (8)



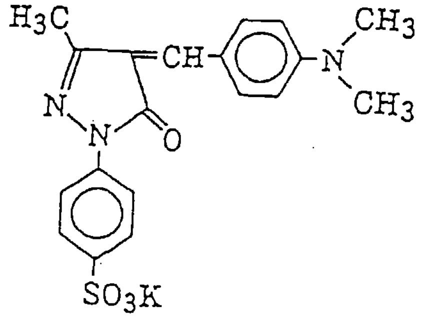
Compound (9)



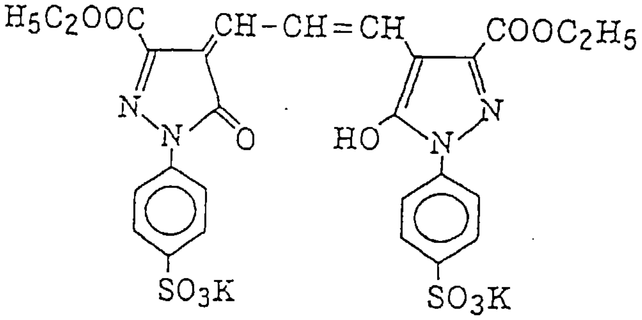
Compound (10)



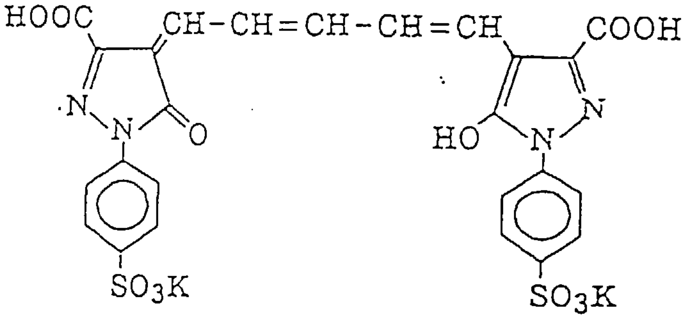
Compound (11)



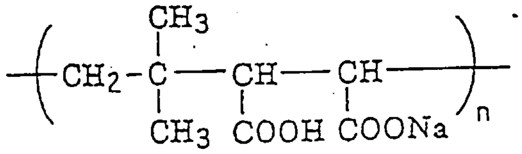
Compound (12)



Compound (13)

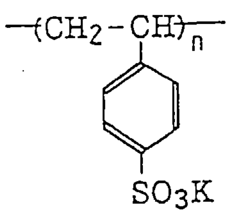


Compound A

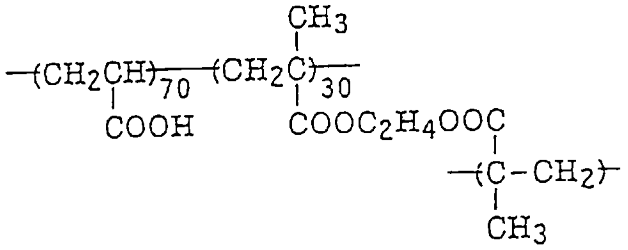


$$-\left(CH_2-C(CH_3)_2-CH(COOH)-CH(COONa)\right)_n-$$

Compound B



Compound C



## Exposure and Development Processing

### (1) Evaluation of Photographic Capabilities

Each of the above samples was exposed with xenon flash light of emission time of $10^{-4}$ sec. through an interference filter which had a peak at 633 nm and through a step wedge, and subjected to development (35°C, 30 sec.), fixation, washing and drying using automatic processor FG-680AG, produced by Fuji Photo Film Co., Ltd. A developing solution and a fixing solution had the following compositions.

Formulation of Developing Solution (Developing Solution A)

| | |
|---|---|
| Potassium Hydroxide | 40.0 g |
| Diethylenetriaminepentaacetic Acid | 2.0 g |
| Potassium Carbonate | 60.0 g |
| Sodium Metabisulfate | 70.0 g |
| Potassium Bromide | 7.0 g |
| Hydroquinone | 40.0 g |
| 5-Methylbenzenetriazole | 0.35 g |
| 4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone | 1.5 g |
| Sodium 2-Mercaptobenzimidazole-5-sulfonate | 0.3 g |
| Sodium 3-(5-Mercaptotetrazol-1-yl)-benzenesulfonate | 0.1 g |
| Sodium Erythorbate | 6.0 g |
| Diethylene Glycol | 5.0 g |
| pH | 10.65 |

Formulation of Fixing Solution (Fixing Solution A)

| | |
|---|---|
| Ammonium Thiosulfate | 359.1 g |
| Disodium Ethylenediaminetetraacetate Dihydrate | 0.09 g |
| Sodium Thiosulfate Pentahydrate | 32.8 g |
| Sodium Sulfite | 64.8 g |
| NaOH | 37.2 g |
| Glacial Acetic Acid | 87.3 g |
| Tartaric Acid | 8.76 g |
| Sodium Gluconate | 6.6 g |
| Aluminum Sulfate | 25.3 g |
| pH (adjusted with sulfuric acid or sodium hydroxide) | 4.85 |
| Water to make | 3 liters |

The reciprocal of the exposure amount required to give a density of 1.5 was taken as the sensitivity and this is shown as a relative sensitivity. The larger the value, the higher is the sensitivity. The gradient of the straight line joining the points of (fog + density 0.3) and (fog + density 3.0) of the characteristic curve was taken as the index ($\gamma$ value) showing the contrast of images. That is, $\gamma$ = (3.0 - 0.3)/ (log(exposure amount giving a density of 3.0) - log(exposure amount giving a density of 0.3)) . The larger the gamma value, the higher is the contrast.

(2) Evaluation of Pressure Marks

The surface of each samples was rubbed with a polystyrene material at 25°C, 60% RH with varying the load, then each sample was development processed and evaluated by five grades.

Grade "5" means that pressure marks were not generated and thus indicates the best level. "1" means that pressure marks were extremely generated and thus indicates the worst quality.

"3" means that the generation of pressure marks is within the limit of practically acceptable level.

(3) PD (practical density)

Test pattern of 175 lpi was outputted on the sample using SG-608 (a product of Dai Nippon Screen Mfg. Co., Ltd.) and the solid density at exposure amount (current value) reproducing 49% dot of the test pattern on the sample as 49% dot was taken as practical density DP.

(4) Evaluation of Running Stability

Exhausted Solution A-1

Running processing of the sample was conducted in such a manner that 100 $m^2$ of the sample was processed per a day using automatic processor FG-680AG produced by Fuji Photo Film Co., Ltd. which was charged with the above described developing solution A and fixing solution A, with setting a replenishing rate of the developing solution to 160 ml per $m^2$ of the sample and that of the fixing solution to 260 ml per $m^2$ of the sample. The temperatures of the developing solution and fixing solution were 35°C and 34°C, respectively, and the developing time was 30 seconds. The above described running processing was conducted for 4 days.

Exhausted Developing Solution A-2

Running processing of the sample was conducted in such a manner that 5 $m^2$ of the sample was processed per a day using automatic processor FG-680AG produced by Fuji Photo Film Co., Ltd. which was charged with the above described developing solution A and fixing solution A, with setting a replenishing rate of the developing solution to 160 ml per $m^2$ of the sample and that of the fixing solution to 260 ml per $m^2$ of the sample. The temperatures of the developing solution and fixing solution were 35°C and 34°C, respectively, and the developing time was 30 seconds. The above described running processing was conducted for 75 days.

Preparation of Sample Nos. 10 and 11

Sample Nos. 10 and 11 were prepared in the same manner as in the preparation of Sample No. 9 except for using Emulsion N-2 and N-3 in place of N-1.

Preparation of Comparative Emulsions N-2 and N-3

The addition amount of potassium hexachlororhodate(III) (0.001% aqueous solution) to Solution 3 of Emulsion N-1 was changed for adjusting sensitivity.

Preparation of Sample No. 12

Sample No. 12 was prepared in the same manner as in the preparation of Sample No. 9 except for omitting Compound (3) from the coated sample.

Preparation of Sample No. 13

Sample No. 13 was prepared in the same manner as in the preparation of Sample Nos. 1 to 7 except for using a comparative compound (liquid paraffin) as the sliding agent.

Preparation of Sample No. 14

Sample No. 14 was prepared in the same manner as in the preparation of Sample No. 2 except for using Emulsion N-4 as the emulsion.

Preparation of Comparative Emulsion N-4

Emulsion N-4 was prepared in the same manner as in the preparation of Emulsion N-1, except that the chemical sensitization was carried out using 7.5 mg of sodium thiosulfate and 10 mg of chloroauric acid instead of triphenylphosphine selenide (a selenium sensitizing dye) to obtain optimal sensitivity.

Preparation of Sample No. 15

Sample No. 15 was prepared in the same manner as in the preparation of Sample No. 2 except for omitting Compound (3) from the coated sample.

Preparation of Sample No. 16

Sample No. 16 was prepared in the same manner as in the preparation of Sample No. 9 except for using Emulsion N-4 as the emulsion.

The results obtained are shown in Tables A and B below.

TABLE A

| Sample No. | Emulsion No. | Sliding Agent of the Invention | Trade Name | Kinetic Viscosity (CS) | Coating Amount of Gelatin in Protective Layer (g/m$^2$) | Photographic Capabilities (Developing Solution A) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sensitivity | γ | PD | Pressure Marks |
| 1 | N-1 | a | KF-96L 1.0 | 1 | 0.75 | 100 | 20 | 5.0 | 4 |
| 2 | " | b | KF-96 10 | 10 | " | " | " | " | 5 |
| 3 | " | c | KF-96 100 | 100 | " | " | " | " | 5 |
| 4 | " | d | KF-96 1,000 | 1,000 | " | " | " | " | 5 |
| 5 | " | e | KF-96 3,000 | 3,000 | " | " | " | " | 5 |
| 6 | " | f | KF-96H 10,000 | 10,000 | " | " | " | " | 4 |
| 7 | " | g | KF-410 | 1,500 | " | " | " | " | 4 |
| 8 | " | None | — | — | 1.00 | " | " | " | 5 |
| 9 | " | None | — | — | 0.75 | " | " | " | 1 |
| 10 | N-2 | None | — | — | " | 75 | " | " | 2 |
| 11 | N-3 | None | — | — | " | 50 | " | " | 3 |
| 12 | N-1 | None | — | — | " | 70 | 8 | " | 3 |

TABLE A (cont'd)

| Sample No. | Emulsion No. | Sliding Agent of the Invention | Trade Name | Kinetic Viscosity (CS) | Coating Amount of Gelatin in Protective Layer (g/m$^2$) | Photographic Capabilities (Developing Solution A) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sensitivity | γ | PD | Pressure Marks |
| 13 | N-1 | Comparative compound | Kaydol | Not Measured | 0.75 | 100 | 20 | 5.0 | 3 |
| 14 | N-4 | b | KF-96 | 10 | 0.75 | 80 | 18 | " | 5 |
| 15 | N-1 | b | " | 10 | " | 70 | 8 | " | 5 |
| 16 | N-4 | None | — | — | " | 80 | 18 | " | 3 |

As a sliding agent of the present invention, commercially available polyalkylsiloxane (a product of Shin-Etsu Chemical Co., Ltd.) was used, and as a comparative compound, liquid paraffin (a product of SONNEBORN, U.S.A.; the trade name is shown in the table) was used.

TABLE B

| Sample No. | Exhausted Solution 1 | | | | Exhausted Solution 2 | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| | Sensitivity | γ | PD | Pressure Marks | Sensitivity | γ | PD | Pressure Marks | |
| 1 | 98 | 18 | 4.8 | 4 | 105 | 21 | 5.0 | 3 | Invention |
| 2 | " | " | " | 5 | " | " | " | 5 | " |
| 3 | " | " | " | " | " | " | " | " | " |
| 4 | " | " | " | " | " | " | " | " | " |
| 5 | " | " | " | " | " | " | " | " | " |
| 6 | " | " | " | 4 | " | " | " | 3 | " |
| 7 | " | " | " | 4 | " | " | " | 3 | " |
| 8 | 90 | 14 | 3.8 | 5 | 112 | " | 4.0 | 5 | Comparison |
| 9 | 98 | 14 | 4.8 | 1 | 105 | " | 5.0 | 1 | " |
| 10 | 72 | " | " | 2 | 79 | " | " | 1 | " |
| 11 | 49 | " | " | 3 | 53 | " | " | 2 | " |
| 12 | 70 | 8 | 5.0 | 3 | 70 | 8 | 5.0 | 3 | " |
| 13 | 98 | 18 | 4.8 | 3 | 105 | 21 | 5.0 | 2 | " |
| 14 | 72 | 15 | 4.0 | 5 | 83 | 19 | 5.0 | 5 | " |
| 15 | 70 | 8 | 5.0 | 5 | 70 | 8 | 5.0 | 5 | Comparision |
| 16 | 72 | 15 | 4.0 | 3 | 83 | 19 | 5.0 | 2 | " |

It can be seen from the results in Table A that the samples of the present invention are conspicuously improved in pressure marks and provide superhigh contrast ($\gamma \geq 10$) and even when samples are processed with an exhausted solutions, fluctuations in sensitivity and gradation are less. The sample in which the coating amount of gelatin of the protective layer was increased showed large fluctuations in sensitivity, gradation and PD when processed with an exhausted solutions (Sample No. 8). Pressure resistance cannot be improved to a practically acceptable level by the adjustment of the sensitivity of emulsion, and sensitivity loss is very large (comparison between Sample Nos. 9 to 11). Samples not containing a nucleating agent do not provide superhigh contrast ($\gamma \geq 10$) (Sample Nos. 12 and 15). It is understood that if selenium sensitization is not conducted, sensitivity loss and fluctuations in sensitivity, gradation and PD are large when processed with an exhausted solutions (Sample No. 14).

## EXAMPLE 2

Development processing was carried out using the photographic material prepared in Example 1 under the development processing conditions in Example 1 using the following developing solution B in place of developing solution A used in Example 1.

Formulation of Developing Solution B (Developing Solution B)

| | |
|---|---|
| Potassium Hydroxide | 35.0 g |
| Diethylenetriaminepentaacetic Acid | 2.0 g |
| Potassium Carbonate | 40.0 g |
| Sodium Metabisulfate | 40.0 g |
| Potassium Bromide | 3.0 g |
| Hydroquinone | 25.0 g |
| 5-Methylbenzenetriazole | 0.08 g |
| 4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone | 0.45 g |
| 2,3,5,6,7,8-Hexahydro-2-thioxo-4-(1H)-quinazolinone | 0.04 g |
| Sodium 2-Mercaptobenzimidazole-5-sulfonate | 0.15 g |
| Sodium Erythorbate | 3.0 g |
| Diethylene Glycol | 20.0 g |
| pH | 10.5 |

Exhausted Solution B-1

Running processing of the sample was conducted in such a manner that 100 m$^2$ of the sample was processed per a day using automatic processor FG-680AG produced by Fuji Photo Film Co., Ltd. which was charged with the above developing solution B and fixing solution A, with setting a replenishing rate of both the developing solution and the fixing solution to 320 ml per m$^2$ of the sample. The temperatures of the developing solution and fixing solution were 35°C and 34°C, respectively, and the developing time was 30 seconds. The above described running processing was conducted for 2 days.

Further, even when the processing was conducted while recovering the silver in the fixing solution using Reclaim R-60 produced by Fuji Hunt Co., Ltd. with setting a replenishing rate of the fixing solution to 160 ml per m$^2$ of the sample, similar results were obtained.

Exhausted Developing Solution B-2

Running processing of the sample was conducted in such a manner that 5 m$^2$ of the sample was processed per a day using automatic processor FG-680AG produced by Fuji Photo Film Co., Ltd. which was charged with the above developing solution B and fixing solution A, with setting a replenishing rate of both the developing solution and the fixing solution to 320 ml per m$^2$ of the sample. The temperatures of the developing solution and fixing solution were 35°C and 34°C, respectively, and the developing time was 30 seconds. The above described running processing was conducted for 40 days.

Further, even when the processing was conducted while recovering the silver in the fixing solution using Reclaim R-60 produced by Fuji Hunt Co., Ltd. with setting a replenishing rate of the fixing solution to 160 ml per m$^2$ of the sample, similar results were obtained.

Results

The same results as in Example 1 were obtained even if the above developing solution B was used.

EXAMPLE 3

When the following solid processing chemicals were used as developing and fixing replenishers, similar results were obtained. A dissolving and replenishing device having an automatic opening mechanism for a packaging material of processing chemicals was used for the dissolution and replenishment of solid processing chemicals. Even if solid processing chemicals were used as a tank mother solution, the similar results were obtained.

Further, even when the processing was conducted while recovering the silver in the fixing solution using Reclaim R-60 produced by Fuji Hunt Co., Ltd. with replenishing 160 ml of a fixing replenisher per $m^2$ of the sample, similar results were obtained.

The exhausted solution was prepared in the same manner as in Example 1.

The composition of the solid developing agent is as follows.

| | |
|---|---|
| Sodium Hydroxide (beads, 99.5%) | 11.5 g |
| Potassium Sulfite (raw material powder) | 63.0 g |
| Sodium Sulfite (raw material powder) | 46.0 g |
| Potassium Carbonate | 62.0 g |
| Hydroquinone (briquette) | 40.0 g |
| (The following are briquetted together) | |
| Diethylenetriaminepentaacetic Acid | 2.0 g |
| 5-Methylbenzenetriazole | 0.35 g |
| 4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone | 1.5 g |
| Sodium 2-Mercaptobenzimidazole-5-sulfonate | 0.3 g |
| Sodium 3-(5-Mercaptotetrazol-1-yl)-benzenesulfonate | 0.1 g |
| Sodium Erythorbate | 6.0 g |
| Potassium Bromide | 6.6 g |
| These components are dissolved in water to make | 1 liter |
| pH | 10.65 |

The raw material powders are general industrial products and were used as they were, and beads of alkali metal salts were those commercially available.

Raw materials which were in the form of briquettes were compressed by the application of pressure using a briquetting machine and formed to an amorphous rugby ball type having a length of about 4 to 6 mm, they were crushed and used. With respect to components of small amounts, every components were blended and then made to briquettes.

Ten liter portion of the above processing chemicals was filled in a foldable container made of high density polyethylene and the takeout port was sealed with an aluminum seal. A dissolving and replenishing device having an automatic opening mechanism for a packaging material of processing chemicals was used for the dissolution and replenishment of solid processing chemicals.

## Results

Similar results as in Example 1 were obtained even if the above described developing solution and fixing solution were used.

## EXAMPLE 4

Samples in Example 1 was coated on the polyester support having a thickness of 175 µm and having provided on both sides thereof the first undercoat layer and the second undercoat layer disclosed in Example 1 of JP-A-6-317866, or coated on the polyester support having a thickness of 100 µm or 175 µm and having provided on both sides thereof the first undercoat layer and the second undercoat layer disclosed in Example 3 of JP-A-6-317866. Evaluation was conducted on the same conditions as in Example 1.

## Results

Similar results as in Example 1 were obtained even if the above described supports were used.

EXAMPLE 5

Samples prepared in Example 1 were coated on the following support and evaluated under the same conditions as in Example 1.

Producing Method of Support

(1) Preparation of contact product of trimethylaluminum with water

Seventeen point eight (17.8) grams (71 mmol) of cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 200 ml of toluene and 24 ml (250 mmol) of trimethylaluminum were put in an argon-substituted glass container having a capacity of 500 ml and reacted at 40°C for 8 hours. Then, a solution was obtained by removing the solid component from the reaction product. Further, toluene was distilled off from the solution under reduced pressure at room temperature to obtain a contact product. The molecular weight of the contact product measured by a cryoscopic method was 610.

(2) Production of styrene polymer

A polymerization reaction was conducted at 90°C for 5 hours in a reaction vessel having a capacity of 2 liters using 950 ml of purified styrene, 50 ml of p-methylstyrene, 5 mmol in terms of an aluminum atom of the contact product obtained in the above (1), 5 mmol of triisobutylaluminum, and 0.025 mmol of pentamethylcyclopentadienyl titanium trimethoxide. After the reaction was finished, the catalytic component of the obtained product was decomposed by a methanol solution of sodium hydroxide, the product was washed with methanol repeatedly, and dried to obtain 308 g of a polymer.

The obtained polymer was confirmed by $^{13}C$-NMR to have a cosyndiotactic structure and to contain 9.5 mol% of p-methylstyrene unit. The weight average molecular weight was 438,000 and the ratio of weight average molecular weight/number average molecular weight was 2.51.

(3) Production of support

The styrene polymer obtained in the above (2) was dried under reduced pressure at 150°C, then pelletized by a monoaxial extruder having a vent, and these pellets were crystallized by stirring in air of 130°C. The content of the styrene monomer in crystallized pellets was 1,100 ppm.

Then the pellets were extruded with a device having a T-type die at the tip of an extruder having a filter inside therein. The melting temperature was 300°C.

This molten state sheet was stretched 3.5 times in a machine direction at 110°C and 4 times in a transverse direction at 120°C, and heat treated at 240°C in fixed stretching condition for 10 seconds and in 5% restricted contraction for 20 seconds. The thickness of the obtained film was 100 µm and the haze was 1.0%.

Both surfaces of the syndiotactic polystyrene (SPS) support thus obtained was glow discharged as follows.

Four cylindrical electrodes were fixed on an insulating plate with the distance of 10 cm. Each electrode has a hollow part as a flow route for cooling medium, and has the cross sectional diameter of 2 cm and the length of 150 cm. This electrode plate was fixed in a vacuum tank, biaxially stretched film was traveled so as to face the surface thereof 15 cm apart from the surface of the electrode, and the traveling speed was controlled so that the surface treatment were carried out for 2 seconds.

A heating roll was positioned such that the film contacted by 3/4 round with the heating roll having a diameter of 50 cm and having a temperature controller immediately before the film passes the electrode. Further, the temperature of the film surface was controlled to 115°C by contacting a thermocouple thermometer with the film face between the heating roll and electrode zone.

The pressure within the vacuum tank was 0.2 Torr, and partial pressure of $H_2O$ in the atmosphere was 75%. Discharge frequency was 30 kHz, output was 2,500 W, treating strength was 0.5 $kV \cdot A \cdot min/m^2$. The film was wound around after contacting with a cooling roll having a diameter of 50 cm and having a temperature controller so that the surface temperature of the discharge-treated support was 30°C.

The both surfaces of the support were coated the following undercoat layer.

Undercoat Layer

| | |
|---|---|
| Deionized Alkali-Processed Gelatin (isoelectric point: 5.0) | 10.0 wt part |
| Water | 24.0 wt part |
| Methanol | 961.0 wt part |
| Salicylic Acid | 3.0 wt part |
| Polyamide-Epichlorohydrin Resin (Synthesis Example 1, JP-A-1-3619) | 0.5 wt part |
| Nonionic Surfactant (Compound I-13, JP-B-3-27099) | 1.0 wt part |

This coating solution was coated in an amount of 10 ml/m$^2$ with a wire bar coater and wound after drying at 115°C for 2 minutes.

Results

Samples of the invention and comparative samples were prepared in the same manner as in Example 1 except for using the above described support and processed in the same manner as in Example 1. Similar results as in Example 1 were obtained.

According to the present invention, a silver halide photographic material which can stably provide high contrast with reduced replenishing rate of the developing solution and which is improved in pressure marks by contact friction with various materials, and further a method for processing thereof, can be provided.

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

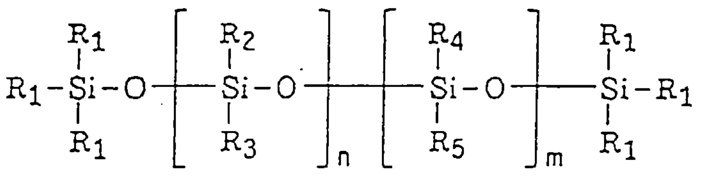
1. A silver halide photographic light-sensitive material comprising a support having thereon at least one light-sensitive silver halide emulsion layer and at least one protective layer provided on the emulsion layer, wherein:

   (a) the silver halide emulsion comprises a silver halide emulsion chemically sensitized with either or both of a selenium compound and a tellurium compound;
   (b) at least one of the silver halide emulsion layer and other hydrophilic colloid layer(s) contains at least one hydrazine derivative; and
   (c) the outermost layer of the protective layer(s) contains one or more kinds of alkylpolysiloxane.

2. The silver halide photographic light-sensitive material as claimed in claim 1, wherein at least one of the silver halide emulsion layer and other hydrophilic colloid layer(s) contains at least one nucleation accelerator selected from the group consisting of amine derivatives, onium salts, disulfide derivatives and hydroxymethyl derivatives.

3. The silver halide photographic light-sensitive material as claimed in claim 1, wherein the protective layer comprises two or more layers and the outermost layer thereof contains one or more kinds of alkylpolysiloxane.

4. The silver halide photographic light-sensitive material as claimed in claim 1, wherein the alkylpolysiloxane is represented by formula (S):



$$R_1-\underset{R_1}{\overset{R_1}{\mathrm{Si}}}-O\left[\underset{R_3}{\overset{R_2}{\mathrm{Si}}}-O\right]_n\left[\underset{R_5}{\overset{R_4}{\mathrm{Si}}}-O\right]_m\underset{R_1}{\overset{R_1}{\mathrm{Si}}}-R_1 \qquad (S)$$

wherein $R_1$ represents an alkyl group having from 1 to 3 carbon atoms or an alkoxyl group having 1 to 2 carbon atoms; and $R_2$, $R_3$, $R_4$ and $R_5$ each represents a hydrogen atom, an aliphatic group or an aryl group.

**5.** The silver halide photographic light-sensitive material as claimed in claim 4, wherein the alkylpolysiloxane has a kinematic viscosity of from 1 to 10,000.

**6.** The silver halide photographic light-sensitive material as claimed in claim 4, wherein the alkylpolysiloxane has a kinematic viscosity of from 5 to 5,000.

**7.** The silver halide photographic light-sensitive material as claimed in claim 1, wherein the alkylpolysiloxane is coated in an amount of from 0.01 to 1.0 in terms of a weight ratio to the weight of the outermost binder layer.

**8.** A method for processing a silver halide photographic material, which comprises developing a silver halide photographic material with a developing solution having a pH of less than 11.0,

wherein the silver halide photographic light-sensitive material comprises a support having thereon at least one light-sensitive silver halide emulsion layer and at least one protective layer provided on the emulsion layer, wherein:

(a) the silver halide emulsion comprises a silver halide emulsion chemically sensitized with either or both of a selenium compound and a tellurium compound;
(b) at least one of the silver halide emulsion layer and other hydrophilic colloid layer(s) contains at least one hydrazine derivative; and
(c) the outermost layer of the protective layer(s) contains one or more kinds of alkylpolysiloxane.

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 97 10 6377

## 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 | EP 0 670 516 A (FUJI PHOTO FILM CO., LTD.) 6 September 1995<br>* page 3, line 3 - line 4 *<br>* page 3, line 39 - line 41 *<br>* page 35, line 52 - page 36, line 41 *<br>* page 51, line 26 - line 29 *<br>* page 52, line 31 - page 54, line 35 *<br>* examples 2-4 *<br>* claims 1,3,6,8 *<br>--- | 1-8 | G03C1/76<br>G03C1/09<br>G03C1/06 |
| Y | US 5 340 695 A (YAMAGUCHI) 23 August 1994<br>* column 1, line 6 - line 11 *<br>* column 3, line 57 - column 4, line 7 *<br>* column 23, line 38 - column 26, line 56 *<br>* column 27, line 28 - column 28, line 18 *<br>* examples 1,2 *<br>* claims 1,2,8,9 *<br>--- | 1,2,4-7 | |
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The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| MUNICH | 24 June 1997 | Binder, R |

CATEGORY OF CITED DOCUMENTS

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