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(54) Method of processing light-sensitive silver halide color photographic material.

(57) A method of processing silver halide color photographic light-sensitive material in which the stabilizing solution contains a hexamethylenetetramine group and at least one compound out of those listed in the specification as F-1 to F-10, but free from formaldehyde is disclosed. Due to the re-crystallization and the scratches-on-films problems, so-called, slit-type-developer must have been keeping a certain width of the slits. This method of the invention enabled that slits openigs to be less than 5 cm^2, so that the stabilizing solution keeps its ability for a long time.

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FIELD OF THE INVENTION

The present invention relates to a method of processing a light-sensitive silver halide color photographic material. More particularly, it relates to a method of processing a light-sensitive silver halide color photographic material, that makes use of a stabilizing solution having a good storage stability and also can obtain stable photographic performances.

BACKGROUND OF THE INVENTION

Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 131138/1988 and so forth have disclosed processing methods in which processing solutions are brought into contact with air as less as possible and processing is carried out using them in necessary minimum quantities (hereinafter called slit processing). Such methods have the advantage that the processing solutions are not easily oxidized because of a small area (an aperture area) in which a processing solution comes into contact with air.

When, however, the area in which a processing solution comes into contact with air is made as small as possible as typically seen in the slit processing, the components of a processing solution may be concentrated and dried at the aperture through which a light-sensitive material is transported, to cause deposition of crystals, so that the light-sensitive material disadvantageously tends to cause jamming or be scratched when it passes through the transport aperture of each processing tank or bath.

This tendency is seen particularly at the part with which a fixing solution or stabilizing solution for color negative films is concerned. This tendency is little seen in the case of bleach-fixing solution or stabilizing solution used for the processing of usual color photographic papers, and is seen in the processing in mini-labs where light-sensitive materials are processed in a small quantity. The above problems may become remarkable as the aperture area is made smaller, in particular, when the aperture is formed into a slit. These facts were found as a result of studies by the present inventors.

Thus, under the existing circumstances, irrespective of the advantage that making the aperture area small can prevent the oxidation of processing solutions, the slit processing has been little put into practical use because of the aforesaid disadvantages.

SUMMARY OF THE INVENTION

Accordingly, a first object of the present invention is to provide a method of processing a light-sensitive silver halide color photographic material, that enables stable processing without causing jamming or occurrence of scratches due to the deposition of crystals or the like even when the aperture area is made small.

A second object of the present invention is to provide a method of processing a light-sensitive silver halide color photographic material, that makes use of a stabilizing solution having a stable storage stability without regard to how many or few light-sensitive materials are processed. Other objects of the present invention will become apparent from the following description.

As a result of intensive studies, the present inventors have accomplished the present invention. The method of processing a light-sensitive silver halide color photographic material according to the present invention, that can achieve the above objects of the present invention is a method of processing a light-sensitive silver halide color photographic material, comprising processing a light-sensitive silver halide color photographic material with a processing solution having a fixing ability, and thereafter subsequently processing the light-sensitive material with a stabilizing solution, wherein;

said stabilizing solution contains substantially no formaldehyde and contains a hexamethylenetetramine compound and at least one compound selected from the compounds represented by Formulas F-1 to F-10 as will be described later; and

the area in which said stabilizing solution comes into contact with air at each aperture is not larger than 5 cm^2 per liter of stabilizing solution in a processing bath containing said stabilizing solution.

BRIEF DESCRIPTION OF THE DRAWINGS

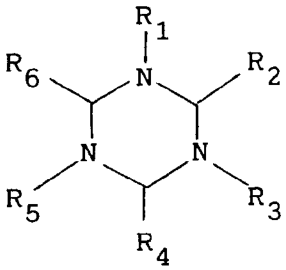
Figs. 1 and 2 are each a schematic illustration of an automatic processor preferably used in the present invention, where Fig. 2 illustrates only a bath having a fixing ability and a stabilizing bath.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, the method of processing a light-sensitive silver halide color photographic material is characterized by a method of processing a light-sensitive silver halide color photographic material, comprising processing a light-sensitive silver halide color photographic material with a processing solution having a fixing ability, and thereafter subsequently processing the light-sensitive material with a stabilizing solution, wherein;

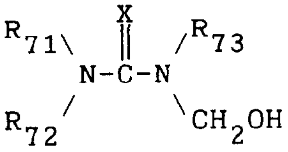
said stabilizing solution contains substantially no formaldehyde and contains a hexamethylenetetramine compound and at least one compound selected from the compounds represented by the following Formulas F-1 to F-10; and

the area in which said stabilizing solution comes into contact with air at each aperture is not larger than 5 cm^2 per liter of stabilizing solution in a processing bath containing said stabilizing solution. Formula F-1

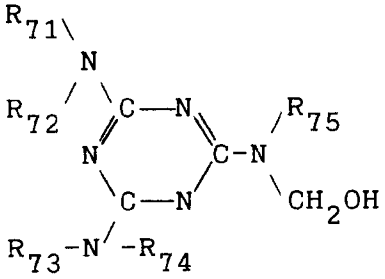


wherein R_1 to R_6 each represent a hydrogen atom or a monovalent organic group.

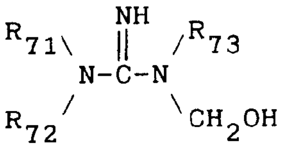
Formula F-2



Formula F-3

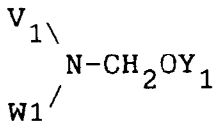


Formula F-4



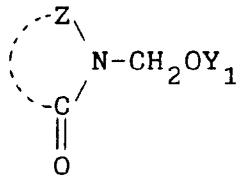
wherein R_{71} to R_{75} each represents a hydrogen atom or a methylol group; and X represents an oxygen atom or a sulfur atom.

Formula F-5



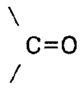
$$\begin{matrix} V_1\backslash & \\ & N-CH_2OY_1 \\ W1/ & \end{matrix}$$

Formula F-6



wherein V_1 and W_1 each represent a hydrogen atom, a lower alkyl group or an electron withdrawing group, and V_1 and W_1 may combine to form a nitrogen-containing heterocyclic group of 5 or 6 members; Y_1 represents a hydrogen atom or a group capable of being split off upon hydrolysis; and Z represents a group of non-metal atoms necessary for completing a single or condensed nitrogen-containing heterocyclic group together with a nitrogen atom and

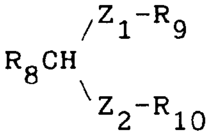
a



$$>C=O$$

group

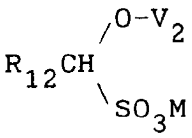
Formula F-7



$$R_8CH\begin{matrix} /Z_1-R_9 \\ \backslash Z_2-R_{10} \end{matrix}$$

wherein R_8 represents a hydrogen atom or an aliphatic group; R_9 and R_{10} each represent an aliphatic group or an aryl group, and R_9 and R_{10} may combine each other to form a ring; and Z_1 and Z_2 each represent an oxygen atom, a sulfur atom or $-N(R_{11})-$, provided that Z_1 and Z_2 are not oxygen atoms at the same time, where R_{11} represents a hydrogen atom, a hydroxyl group, an aliphatic group or an aryl group.

Formula F-8

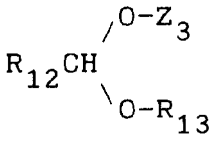


$$R_{12}CH\begin{matrix} /O-V_2 \\ \backslash SO_3M \end{matrix}$$

Formula F-9

$$W_2\text{-O-(-CH}_2\text{O-)}_n\text{-Y}_2$$

Formula F-10

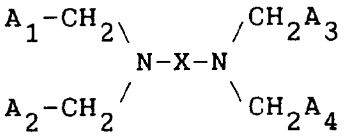


$$R_{12}CH\begin{cases} O-Z_3 \\ O-R_{13} \end{cases}$$

wherein R_{12} represents a hydrogen atom or an aliphatic hydrocarbon group; V_2 represents a group capable of being split off upon hydrolysis; M represents a cation; W_2 and Y_2each represent a hydrogen atom or a group capable of being split off upon hydrolysis; n represents an integer of 1 to 10; and Z_3 and R_{13} each represent a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a group capable of being split off upon hydrolysis, and Z_3 and R_{13} may combine to form a ring.

A preferred embodiment of the present invention is characterized in that the total silver coating weight per 1 m^2 of the light-sensitive silver halide color photographic material is not less than 2.0 g, that the processing solution having a fixing ability contains a thiocyanate, that the processing solution having a fixing ability is a fixing solution, that the solution in the processing step right anterior to the step in which the processing solution having a fixing ability is used is a bleaching solution, and that the bleaching solution contains a ferric complex salt of an aminopolycarboxylic acid represented by the following Formula A or B.

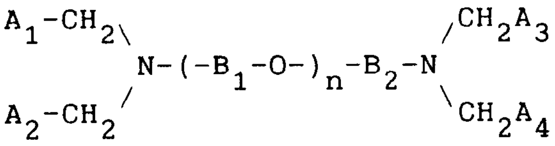
Formula A



$$\begin{matrix} A_1-CH_2 \\ A_2-CH_2 \end{matrix} \rangle N-X-N \langle \begin{matrix} CH_2A_3 \\ CH_2A_4 \end{matrix}$$

wherein A_1 to A_4 may be the same or different and each represent $-CH_2OH$, $-COOM$ or $PO_3M_1M_2$, where M, M_1 and M_2 each represent a hydrogen atom, an alkali metal atom or an ammonium group; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms.

Formula B



$$\begin{matrix} A_1-CH_2 \\ A_2-CH_2 \end{matrix} \rangle N-(-B_1-O-)_n-B_2-N \langle \begin{matrix} CH_2A_3 \\ CH_2A_4 \end{matrix}$$

wherein A_1 to A_4 are the same as those defined in Formula A; n represent an integer of 1 to 8; B_1 and B_2 may be the same or different and each represent a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms.

Another preferred embodiment of the present invention is characterized in that the stabilizing solution is a final processing solution and contains substantially no ammonium salt.

The present inventors made intensive studies in consideration of the facts that, regarding the problems previously discussed, firstly the crystals tend to be deposited at the apertures through which color photographic materials are transported, as the aperture area is made smaller so that the oxidation can be prevented, and secondly the deposition of crystals often occurs in color negative processing steps and also is remarkable at the cross-over from a fixing bath to a stabilizing bath and the cross-over between stabilizing baths comprised of two baths. As a result, they have discovered that the above problems are greatly concerned with the formaldehyde contained in the stabilizing solution, and that the deposition of crystals less occurs at the apertures through which color photographic materials are transported, when a thiocyanate is contained in the fixing solution. They have further discovered that the present invention constituted as herein disclosed can effectively prevent the deposition of crystals although crystals tend to be deposited when the total silver coating weight per 1 m^2 of the light-sensitive silver halide color photographic material is not less than 2.0 g, the processing solution having a fixing ability contains a thiocyanate, the bleaching solution contains a ferric complex salt of an aminopolycarboxylic acid represented by Formula A or B and the stabilizing solution contains substantially no ammonium salt. Thus they have accomplished the present invention.

The present invention will be described below in greater detail.

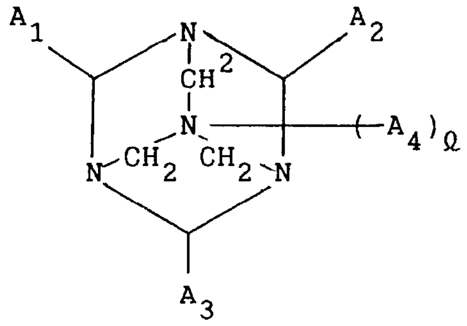
In the processing method making use of the processing solution of the present invention, preferable processing steps may include the following:

(1) Color developing → Bleach-fixing → Stabilizing;
(2) Color developing → Bleaching → Fixing → Stabilizing;
(3) Color developing → Bleaching → Bleach-fixing → Stabilizing;
(4) Color developing → Bleach-fixing → Fixing → Stabilizing;
(5) Color developing → Bleach-fixing → Bleach-fixing → Stabilizing; and
(6) Color developing → Bleaching → Bleach-fixing → Fixing → Stabilizing.

The steps of (1) and (2) are preferred, and the steps of (2) are particularly preferred. More specifically, when a processing solution having a bleaching ability or a processing solution having a fixing ability is referred to in the present invention, such a processing solution may include a bleach-fixing solution, a combination of a bleaching solution and a fixing solution, a combination of a bleaching solution and a bleach-fixing solution, a combination of a bleach-fixing solution and a fixing solution, and a combination of a bleach-fixing solution and a bleach-fixing solution, which are selected according to the processing steps as described above.

The hexamethylenetetramine compound used in the stabilizing solution in the present invention may preferably include a compound, or a salt thereof, represented by the following Formula A-1.

Formula A-1



In Formula A-1, A_1 to A_4 each represent a hydrogen atom, an alkyl group, an alkenyl group or a pyridyl group. The symbol Ω represents an integer of 0 or 1. The groups represented by A_1 to A_4 may include those having a substituent. The groups represented by A_1 to A_4 each may include those having a substituent. The substituent can be exemplified by a carbamoyl group, a halogen atom such as a chlorine atom, an aryl group such as a phenyl group, a hydroxyl group, a carboxyl group, and an oxycarbonyl group such as a methoxycarbonyl group.

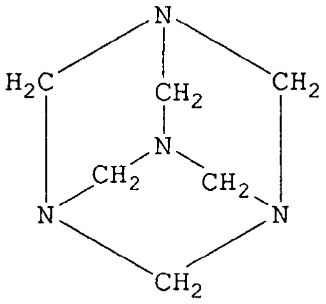
The alkyl group represented by A_1 to A_4 each may preferably be an alkyl group having a carbon chain of 1 to 5 carbon atoms.

The salt of the compound represented by Formula A-1 may include inorganic acid salts such as a hydrochloride, a sulfate and a nitrate, organic acid salts such as phenol salts, double salts or complex salts with metal salts, salt hydrates, and inner salts.

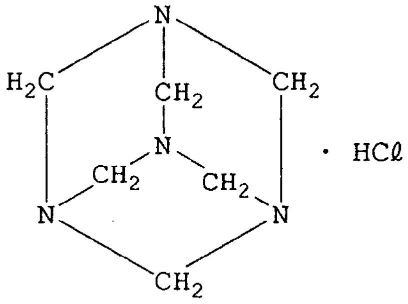
The compound represented by Formula A-1 may specifically include those disclosed in Beilsteins Handbuch der Organishen Chemie, Second Enlarged Edition, Vol 26, pp.200-212. Among them, those soluble in water are preferred in the present invention.

Typical examples of the compound, or a salt thereof, represented by Formula A-1 are shown below.

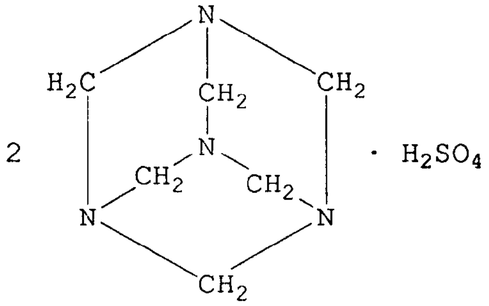
A-1-1



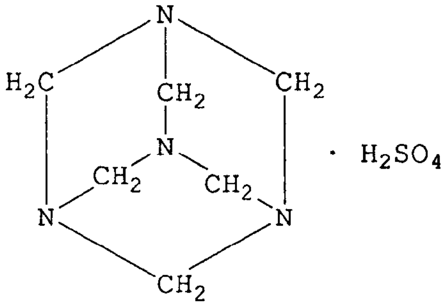
A-1-2



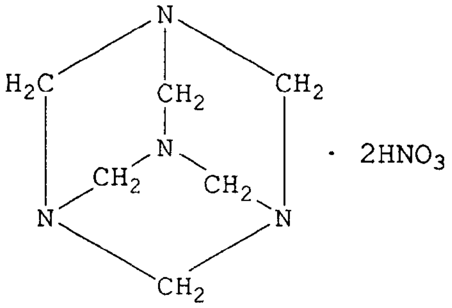
A-1-3



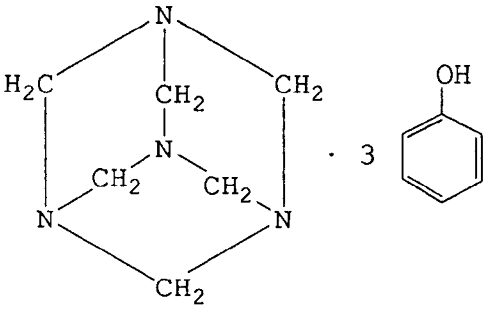
A-1-4



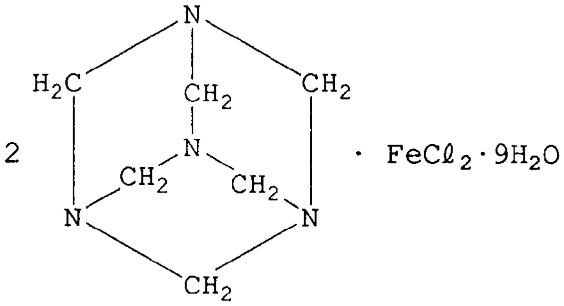
A-1-5



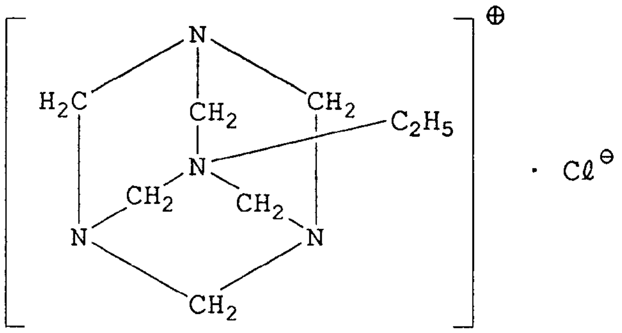
A-1-6



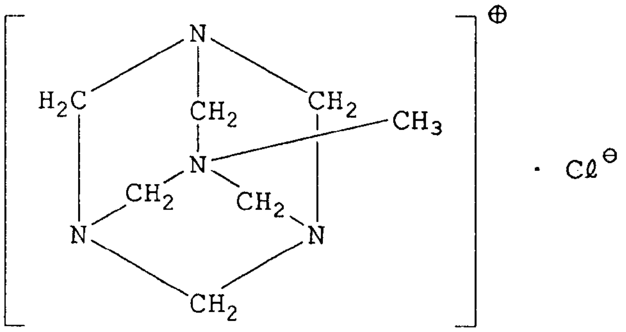
A-1-7



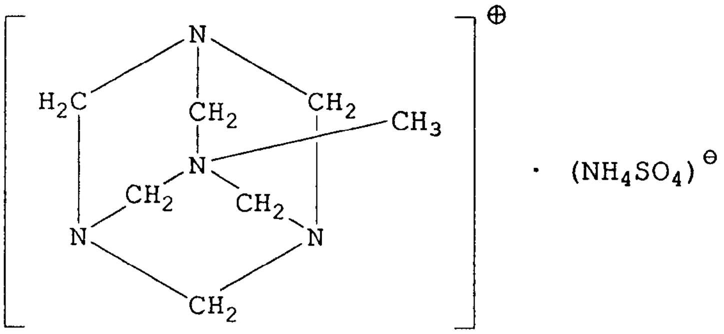
A-1-8



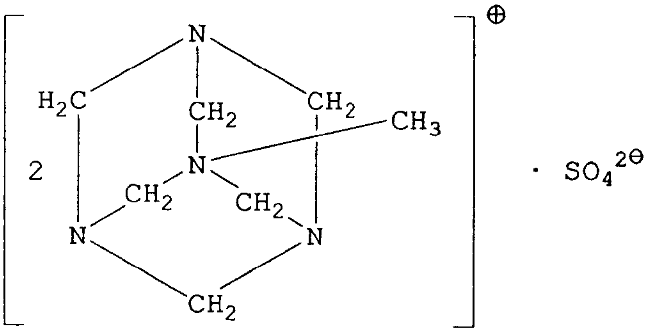
A-1-9



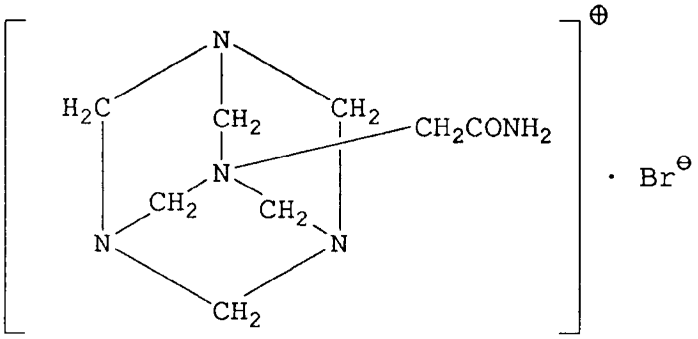
A-1-10



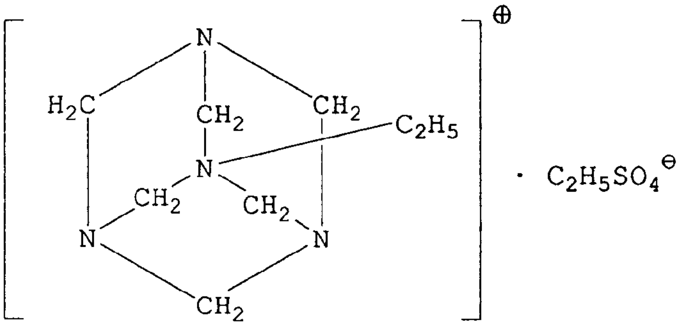
A-1-11



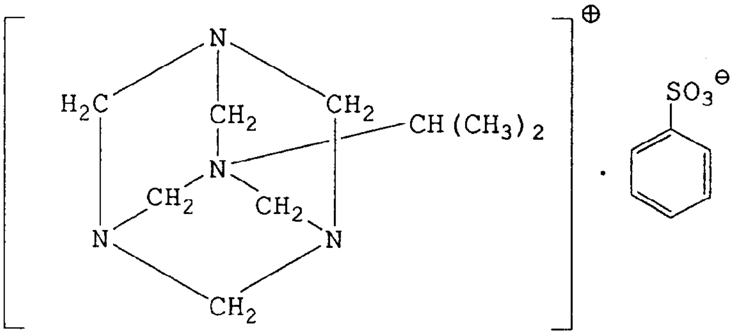
A-1-12



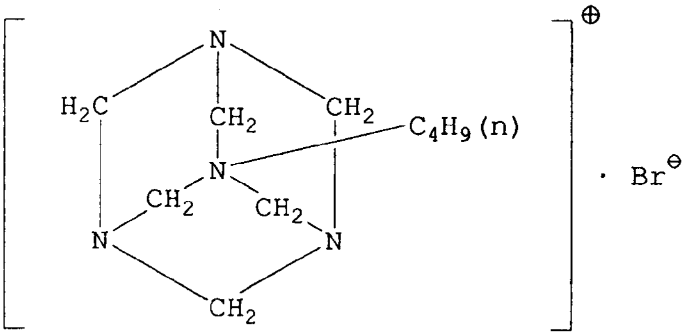
A-1-13



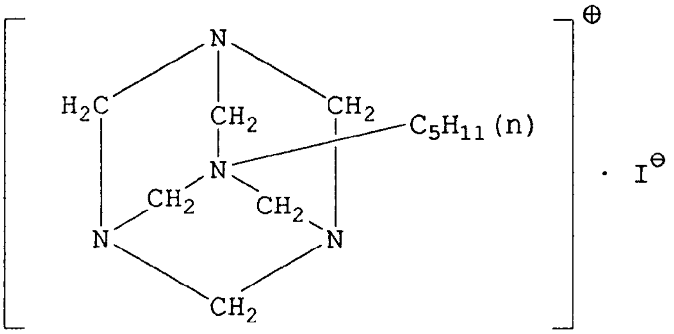
A-1-14



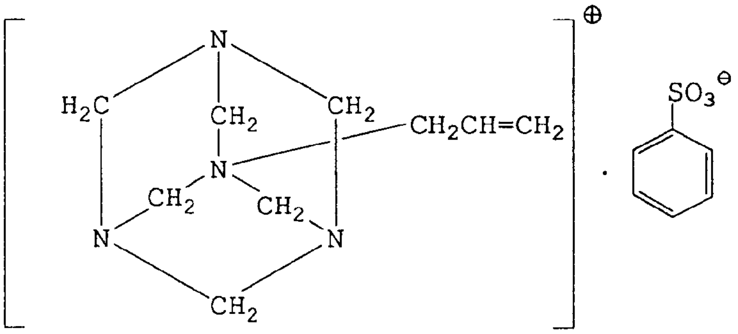
A-1-15



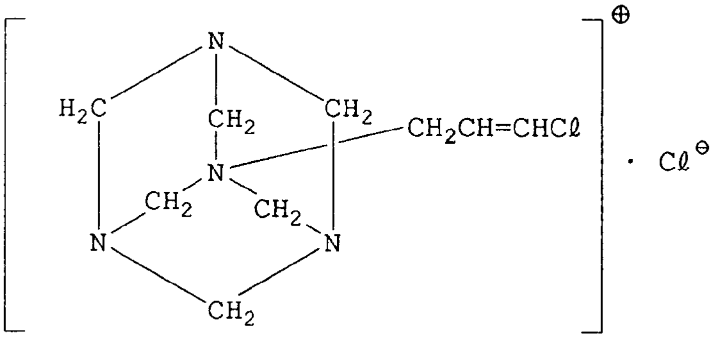
A-1-16



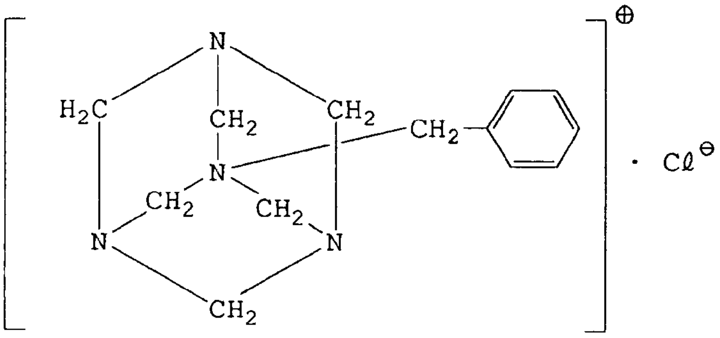
A-1-17



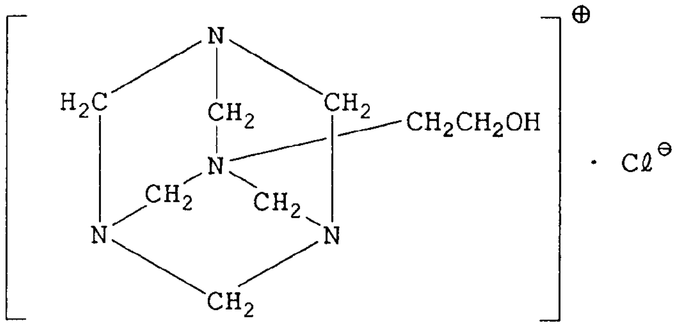
A-1-18



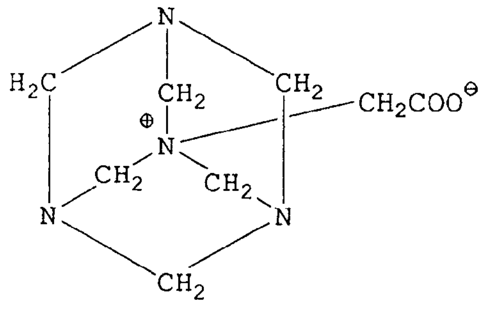
A-1-19



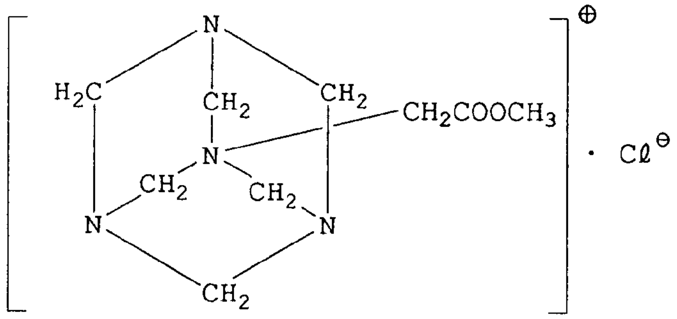
A-1-20



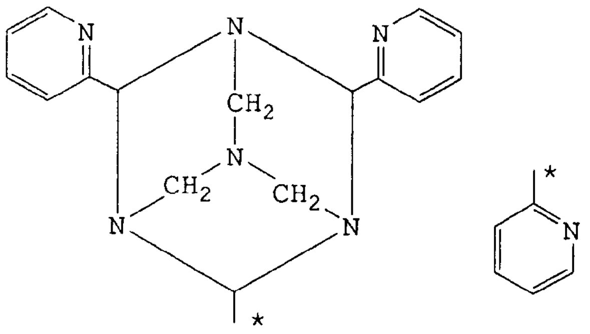
A-1-21



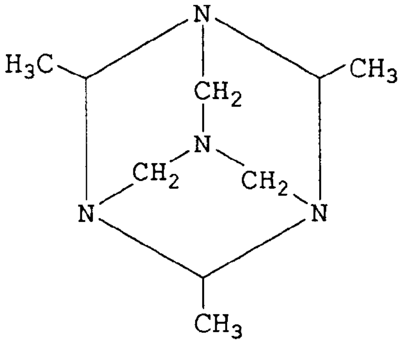
A-1-22



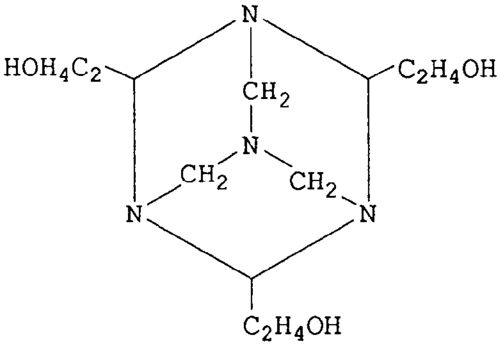
A-1-23



A-1-24



A-1-25



The compound of Formula A-1 is commercially available, or can be readily synthesized using the method described in the above publication.

The compound of Formula A-1 may be used alone or may be used in combination of two or more kinds. It may be added in an amount ranging from preferably 0.01 g to 20 g per liter of the processing solution.

The compounds represented by Formulas F-1 to F-10 used in the present invention will be described below.

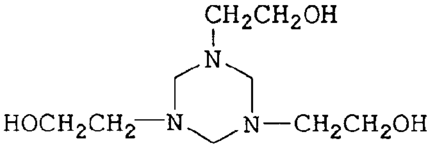
In Formula F-1, R_1 to R_6 each represent a hydrogen atom or a monovalent organic group. The monovalent organic group may include an alkyl group, an aryl group, an alkenyl group, an alkynyl group, an aralkyl group, an amino group, an alkoxyl group, a hydroxyl group, an acyl group, a sulfonyl group, an alkylthio group, an arylthio group, a heterocyclic residual group, a carbamoyl group, a sulfamoyl group and an alkylamino group.

These monovalent organic groups may have a substituent as exemplified by a hydroxyl group, an acyl group, a sulfonyl group, a halogen group, an amino group or a carboxyl group, and preferably a hydroxyl group or a halogen atom. The substituents represented by R_1 to R_6 may preferably have a total carbon atom number of not more than 10.

A group of R_1, R_3 and R_5 and a group of R_2, R_4 and R_6 may be the same or different, provided that all the substituents in any one of the groups R_1, R_3, R_5 and R_2, R_4, R_5 may preferably be hydrogen atoms.

Examples of the compound represented by Formula F-1 are shown below. Examples thereof are by no means limited to these.

F-1-1



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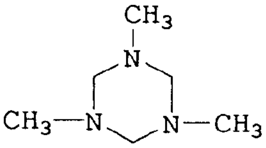

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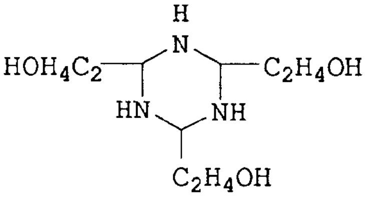

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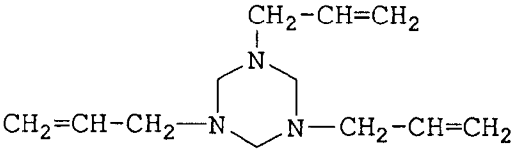
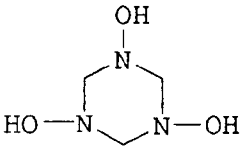


F-1-5



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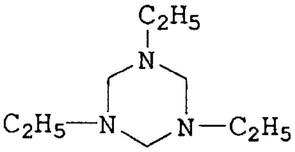
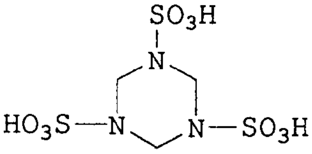


F-1-7



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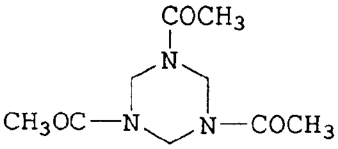

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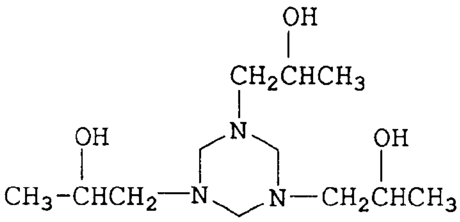

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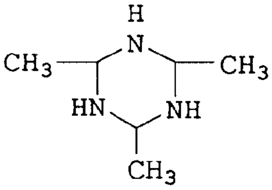
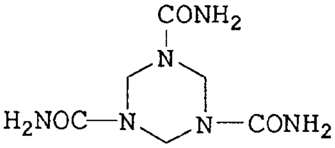


F-1-11



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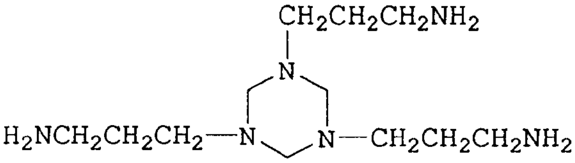
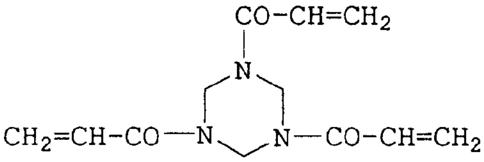
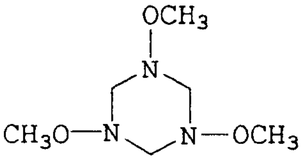


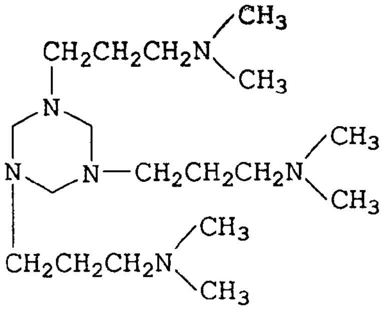
F-1-13



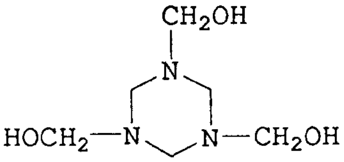
F-1-14



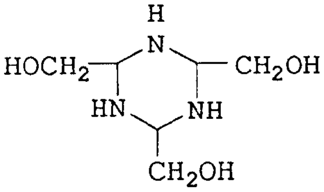
F-1-15



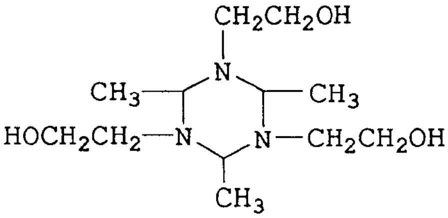
F-1-16



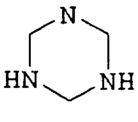
F-1-17



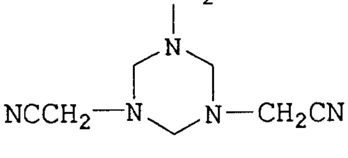
F-1-18



F-1-19



F-1-20



These triazine compounds represented by Formula F-1 may preferably be used in an amount ranging from 0.05 g to 50 g, and more preferably from 0.1 g to 20 g, per liter of the stabilizing solution.

As examples of the methylol compound represented by Formula F-2, F-3 or F-4, the compound may include

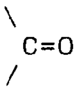
the following:
(F-2-1) Dimethylolurea
(F-2-2) Trimethylolurea
(F-2-3) Monomethylolurea
(F-2-4) Tetramethylolurea
(F-2-5) Dimethylolurea
(F-2-6) Monomethylolthiourea
(F-3-1) Trimethylolmelamine
(F-3-2) Tetramethylolmelamine
(F-3-3) Pentamethylolmelamine
(F-3-4) Hexamethylolmelamine
(F-3-5) Monomethylolmelamine
(F-4-1) Dimethylolguanidine
(F-4-2) Monomethylolguanidine
(F-4-3) Trimethylolguanidine

These may each be added preferably in an amount of 0.05 g to 30 g, and more preferably 0.1 to 15 g, per liter of the stabilizing solution, within the range of which the effect of the present invention can be obtained as intended.

In Formula F-5 and F-6, the electron withdrawing group represented by V_1 and W_1 each may be selected from groups wherein the Hamett's σp value (Lang's Handbook of Chemistry, 12th Ed., Vol. 3, C. Hansch & A. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, John Wiley & Sons, New York, 1979) is positive. They may specifically include an acyl group as exemplified by acetyl, benzoyl or monochoroacetyl; an alkoxycarbonyl group as exemplified by ethoxycarbonyl or methoxycarbonyl; an aryloxycarbonyl group as exemplified by phenoxycarbonyl or p-chlorophenoxycarbonyl; a carbamoyl group as exemplified by N-methylcarbamoyl, N,N-tetramethylenecarbamoyl or N-phenylcarbamoyl; a cyano group; an alkylsulfonyl group as exemplified by methanesulfonyl or ethanesulfonyl; an arylsulfonyl group as exemplified by benzene sulfonyl or p-toluenesulfonyl; and a sulfamoyl group as exemplified by sulfamoyl, N-methylsulfamoyl or N,N-pentamethlenesulfamoyl. The lower alkyl group may include methyl, ethyl or propyl.

The group capable of being split off upon hydrolysis, represented by Y_1 may include a trialkyl-substituted silyl group as exemplified by trimethylsilyl; an acyl group as exemplified by acetyl, benzoyl, monochloroacetyl or trichloroacetyl; a sulfate group; an aminocarbonyl group as exemplified by N,N-dimethylcarbonyl, N-methylcarbonyl or N-phenylcarbonyl; and a sulfonato group as exemplified by methanesulfonato, benzenesulfonato or p-toluenesulfonato.

The nitrogen-containing heterocyclic group of 5 or 6 members formed together with a nitrogen atom and a

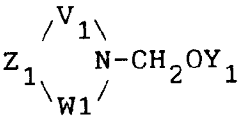


$$>C=O$$

group, represented by Z may include single rings comprised of an elementary constitution such as $[C_1N_4]$, $[C_2N_3]$, $[C_3N_2]$, $[C_4N]$, $[C_2N_4]$, $[C_3N_3]$, $[C_4N_2]$, $[C_5N]$, $[C_2N_2O]$, $[C_3NO]$, $[C_3N_2O]$, $[C_4NO]$, $[C_2N_2S]$, $[C_3NS]$, $[C_3N_2S]$, $[C_2N_2Se]$, $[C_3NSe]$ $[C_4NSe]$ or $[C_3NTe]$, and condensed rings comprised of an elementary constitution such as $[C_3N_2\text{-}C_6]$, $[C_4N\text{-}C_6]$, $[C_4N\text{-}C_3N_2]$, $[C_3N_2\text{-}C_3N_2]$, $[C_3NS\text{-}C_6]$, $[C_5N\text{-}C_5N]$, $[C_5N\text{-}C_6]$ or $[C_4N\text{-}C_6]$. These rings may each be substituted thereon with a group, for example, an alkyl group as exemplified by methyl, ethyl, methoxyethyl, benzyl, carboxymethyl or sulfopropyl; an aryl group as exemplified by phenyl or p-methoxyphenyl; a hydroxyl group; an alkoxyl group as exemplified by methoxy, ethoxy or methoxyethoxy; an aryloxy group as exemplified by phenoxy or p-carboxyphenyl; a carboxyl group, a sulfo group, an alkocycarbonyl group as exemplified by methoxycarbonyl or ethoxycarbonyl; an aryloxycarbonyl group as exemplified by phenoxycarbonyl; an amino group as exemplified by N,N-dimethylamino, N-ethylamino or N-phenylamino; an acylamide group as exemplified by acetamide or benzamide; a carbamoyl group as exemplified by carbamoyl, N-methylcarbamoyl, N,N-tetramethylenecarbamoyl; a sulfonamide group as exemplified by methanesulfonamide or benzenesulfonamide; a sulfamoyl group as exemplified by N-ethylsulfamoyl or N,N-dimethylsulfamoyl; an alkylsulfonyl group as exemplified by methanesulfonyl or ethanesulfonyl; and arylsulfonyl group as exemplified by benzenesulfonyl or p-toluenesulfonyl; or an acyl group as exemplified by acetyl or benzoyl.

In Formula F-5, the nitrogen-containing heterocyclic group of 5 or 6 members that can be formed through combination of V_1 and W_1 each representing a divalent electron withdrawing group may include a compound represented by the following Formula F-5-a.

Formula F-5-a



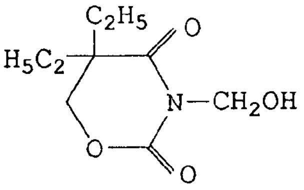
$$Z_1\begin{array}{c}\diagup V_1 \diagdown\\ \diagdown W_1 \diagup\end{array}N\text{-}CH_2OY_1$$

In Formula F-5-a, V_1 and W_1 each represent a -CO-, -CO-O-, -SO-, $-SO_2$ or -CS- group; and Z_1 represents a group of non-metal atoms necessary to complete a single ring or condensed ring of 5 or 6 members formed by the combination of V_1 and W_1.

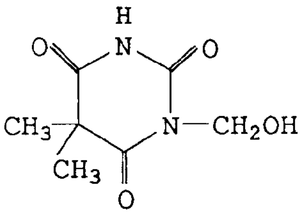
The single ring or condensed ring of 5 or 6 members formed by Z_1 may have thereon any desired substituent. Such a substituent includes, for example, an alkyl group as exemplified by methyl, ethyl, methoxyethyl, benzyl, carboxymethyl or sulfopropyl; an aryl group as exemplified by phenyl or p-methoxyphenyl; a hydroxyl group; an alkoxyl group as exemplified by methoxy, ethoxy or methoxyethoxy; an aryloxy group as exemplified by phenoxy or p-carboxyphenyl; a carboxyl group; a sulfo group; an alkoxycarbonyl group as exemplified by methoxycarbonyl or ethoxycarbonyl; an aryoxycarbonyl group asexemplified by phenoxycarbonyl; an a amino group as exemplified by N,N-dimethylamino, n-ethylamino or N-phenylamino; an acylamide group as exemplified by acetamide or benzamide; a carbamoyl group as exemplified by carbamoyl, N-methylcarbamoyl or N,N-tetramethylenecarbamoyl; a sulfonamide group as exemplified by methanesulfonamide or benzenesulfonamide; a sulfamoyl group as exemplified by N-ethylsulfamoyl or N,N-dimethylsulfamoyl; an alkylsulfonyl group as exemplified by methanesulfonyl or ethanesulfonyl; an arylsulfonyl group as exemplified by benzenesulfonyl or p-toluenesulfonyl; and an acyl group as exemplified by acetyl or benzoyl.

Examples of the compounds represented by Formulas F-5 and F-6 are shown below. Examples thereof are by no means limited to these.

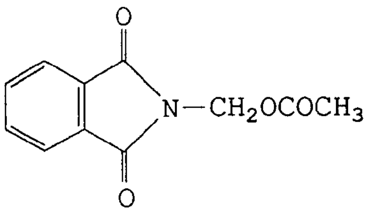
F-5-1



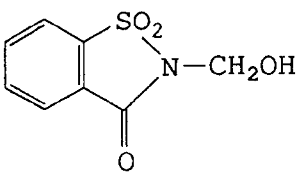
F-5-2



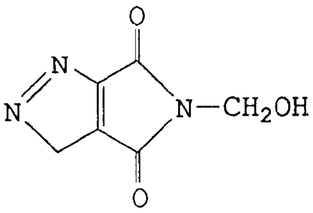
F-5-3



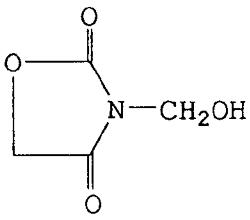
F-5-4



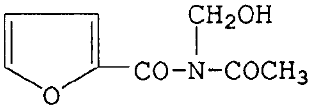
F-5-5



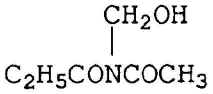
F-5-6



F-5-7



F-5-8



$C_2H_5CO\overset{CH_2OH}{\overset{|}{N}}COCH_3$

F-5-9

HOOC-CH_2NH-CH_2OH

F-5-10

$(CH_3)_2N$-CH_2OH

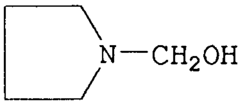
F-5-11

CH_3-NH-CH_2OH

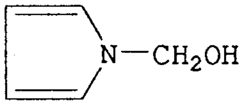
F-5-12

C_2H_5OCONH-CH_2OH

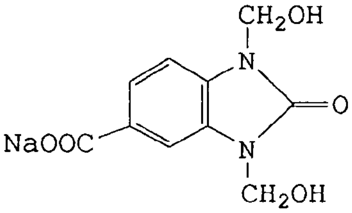
F-5-13



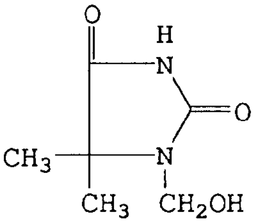
F-5-14



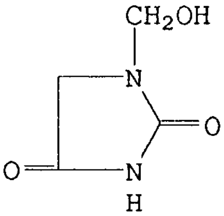
F-6-1



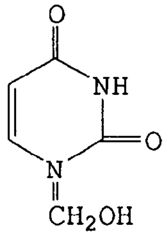
F-6-2



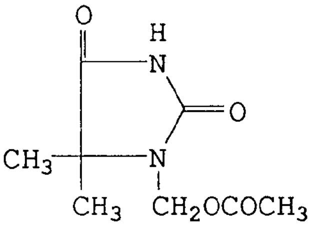
F-6-3



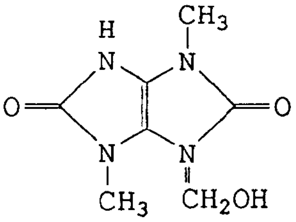
F-6-4



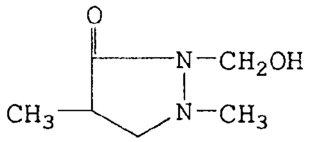
F-6-5



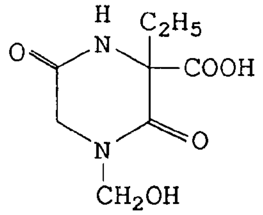
F-6-6



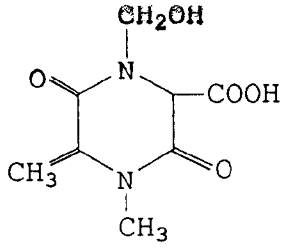
F-6-7



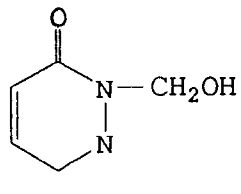
F-6-8



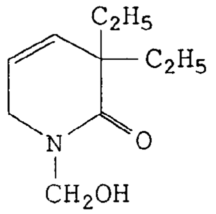
F-6-9



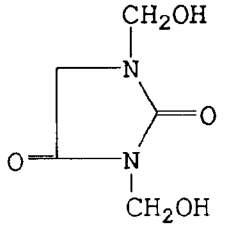
F-6-10



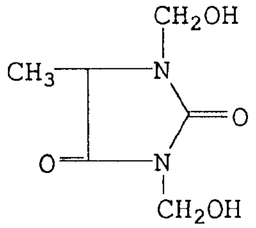
F-6-11



F-6-12



F-6-13



The compound represented by Formula F-5 or F-6 may preferably be added in an amount of 0.01 g to 30 g, more preferably 0.03 g to 15 g, and particularly preferably 0.05 g to 10 g, per liter of the stabilizing solution.

In Formula F-7, the aliphatic group represented by R_8, R_9 and R_{10} each may include a saturated alkyl group as exemplified by an unsubstituted alkyl group such as methyl, ethyl or butyl or a substituted alkyl group such as benzyl, carboxymethyl, hydroxymethyl or methoxyethyl; an unsaturated alkyl group as exemplified by allyl or 2-butenyl; a cyclic alkyl group as exemplified by cyclopentyl or cyclohexyl.

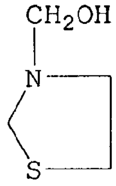
The aryl group represented by R_9, R_{10} and R_{11} each may include substituted or unsubstituted groups. The substituent therefor includes, for example, any desired groups selected from an alkyl group as exemplified by methyl, ethyl, methoxyethyl, benzyl, carboxymethyl or sulfopropyl; an aryl group as exemplified by phenyl or p-methoxyphenyl; a hydroxyl group, an alkoxyl group as exemplified by methoxy, ethoxy or methoxyethoxy, an aryloxy group as exemplified by phenoxy or p-carboxyphenyl; a carboxyl group; a sulfo group; an alkoxycarbonyl group as exemplified by methoxycarbonyl or ethoxycarbonyl; an aryloxycarbonyl group as exemplified by phenoxycarbonyl, an amino group as exemplified by N,N-dimethylamino, N-ethylamino or N-phenylamino; an acylamide group as exemplified by acetamide or benzamide, a carbamoyl group as exemplified by carbamoyl, N-methylcarbamoyl or N,N-tetramethylenecarbamoyl; a sulfonamide group as exemplified by methanesulfonamide or benzenesulfonamide; a sulfamoyl group as exemplified by N-ethylsulfamoyl or N,N-dimethylsulfamoyl; an alkylsulfonyl group as exemplified by methanesulfonyl or ethanesulfonyl; an arylsulfonyl group as exemplified by benzenesulfonyl or p-toluenesulfonyl; an acyl group as exemplified by acetyl or benzoyl; etc.

The ring formed by the combination of R_9 and R_{10} may include heterocyclic groups of 5 to 8 members, which may also include those in which part of bonded carbons has been substituted with other heterocyclic atom.

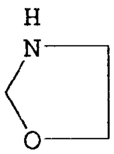
R_8 may preferably be a hydrogen atom.

Examples of the compound represented by Formula F-7 are shown below. Examples thereof are by no means limited to these compounds.

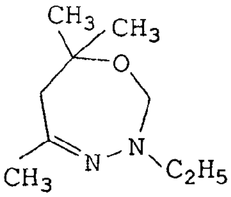
F-7-1



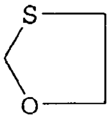
F-7-2



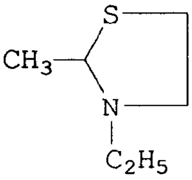
F-7-3



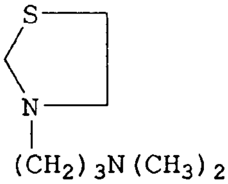
F-7-4



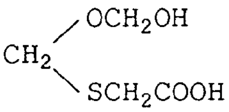
F-7-5



F-7-6

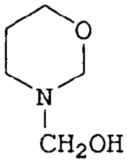


F-7-7

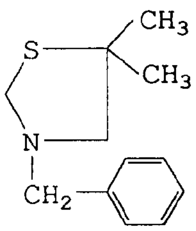


$CH_2(OCH_2OH)(SCH_2COOH)$

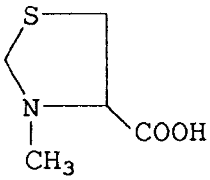
F-7-8



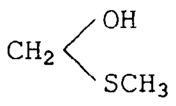
F-7-9



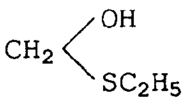
F-7-10



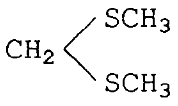
F-7-11



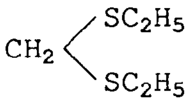
F-7-12



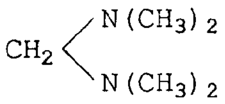
F-7-13



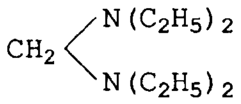
F-7-14



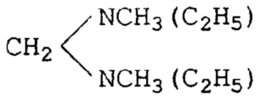
F-7-15



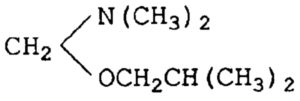
F-7-16



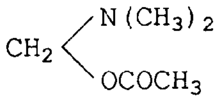
F-7-17



F-7-18



F-7-19



The compound represented by Formula F-7 may preferably be added in an amount of 0.01 g to 30 g, more preferably 0.03 g to 15 g, and particularly preferably 0.05 g to 10 g, per liter of the stabilizing solution.

In the formulas F-8 to F-10, the aliphatic hydrocarbon group represented by R_{12}, R_{13} and Z_3 each may include a saturated alkyl group as exemplified by an unsubstituted alkyl group such as methyl, ethyl or butyl or a substituted alkyl group such as carboxymethyl, methoxymethyl, methoxyethyl, hydroxyethyl or benzyl; an unsaturated alkyl group as exemplified by allyl or 2-butenyl; a cyclic alkyl group as exemplified by cyclopentyl or cyclohexyl.

The aryl group represented by R_{13} and Z_3 each may include substituted or unsubstituted groups. The substituent therefor includes, for example, any desired groups selected from an alkyl group as exemplified by methyl, ethyl, methoxyethyl, benzyl, carboxymethyl or sulfopropyl; an aryl group as exemplified by phenyl or p-methoxyphenyl; a hydroxyl group, an alkoxyl group as exemplified by methoxy, ethoxy or methoxyethoxy, an aryloxy group as exemplified by phenoxy or p-carboxyphenyl; a carboxyl group; a sulfo group; an alkoxycarbonyl group as exemplified by methoxycarbonyl or ethoxycarbonyl; an aryloxycarbonyl group as exemplified by phenoxycarbonyl, an amino group as exemplified by N,N-dimethylamino, N-ethylamino or N-phenylamino; an acylamide group as exemplified by acetamide or benzamide; a carbamoyl group as exemplified by carbamoyl, N-methylcarbamoyl or N,N-tetramethylenecarbamoyl; a sulfonamide group as exemplified by methanesulfonamide or benzenesulfonamide; a sulfamoyl group as exemplified by N-ethylsulfamoyl or N,N-diethylsulfamoyl; an alkylsulfonyl group as exemplified by methanesulfonyl or ethanesulfonyl; an arylsulfonyl group as exemplified by benzenesulfonyl or p-toluenesulfonyl; an acyl group as exemplified by acetyl or benzoyl; etc.

The group capable of being split off upon hydrolysis, represented by V_2, W_2, Y_2 and Z_3 each may include an acyl group as exemplified by acetyl, benzoyl, trifluoroacetyl or monochloroacetyl; and a trialkylsilyl group as exemplified by trimethylsilyl.

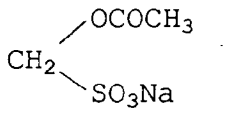
The ring formed by the combination of R_{13} and Z_3 may include heterocyclic groups of 5 to 8 members, which may also include those in which part of bonded carbons has been substituted with other heterocyclic atom. It may specifically include rings such as 1,2-dioxacyclopentane, m-dioxane, trioxane, tetraoxane and benzdioxolan.

The cation represented by M includes, for example, hydrogen ion, an alkali metal ion as exemplified by lithium, sodium or potassium ion; an alkaline earth metal ion as exemplified by magnesium or calcium ion; ammonium ion, an organic ammonium ion as exemplified by triethylammonium or tetramethylammonium ion; and pyridinium ion.

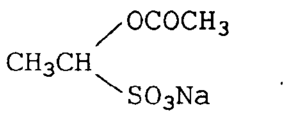
In the formulas F-8 to F-10, the aliphatic hydrocarbon group represent by R_{17} may preferably be a lower alkyl group having 1 or 2 carbon atoms, and also R_{12} may preferably be a hydrogen atom.

Examples of the compounds represented by Formulas F-8 to F-10 are shown below. Examples thereof are by no means limited to these compounds.

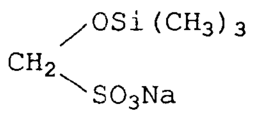
F-8-1



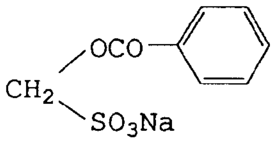
F-8-2



F-8-3



F-8-4



F-9-1

$CH_3COO(CH_2O)_3COCH_3$

F-9-2

$CH_3COO(CH_2O)_2COCH_3$

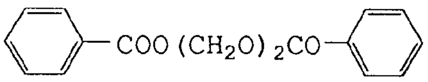
F-9-3

$CH_3COO(CH_2O)_4COCH_3$

F-9-4

$HO(CH_2O)_{10}H$

F-9-5



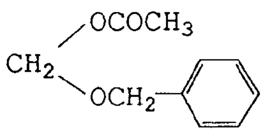
F-9-6

CH_3OCH_2OH

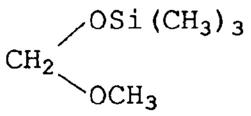
F-9-7

$C\ell CH_2COO(CH_2O)_4COCH_2C\ell$

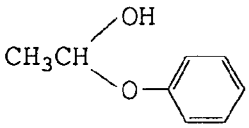
F-10-1



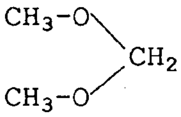
F-10-2



F-10-3

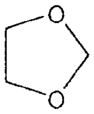


F-10-4

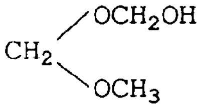


$CH_2(OCH_3)_2$

F-10-5

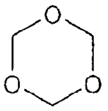


F-10-6

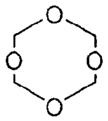


$CH_2(OCH_2OH)(OCH_3)$

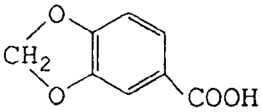
F-10-7



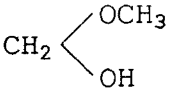
F-10-8



F-10-9

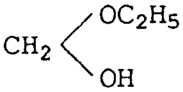


F-10-10



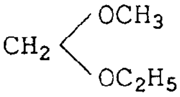
$CH_2(OCH_3)(OH)$

F-10-11



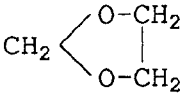
$CH_2(OC_2H_5)(OH)$

F-10-12

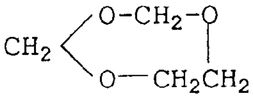


$CH_2(OCH_3)(OC_2H_5)$

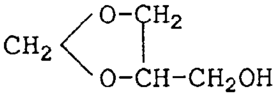
F-10-13



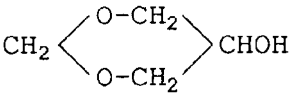
F-10-14



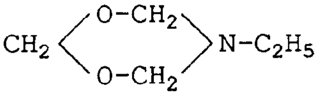
F-10-15



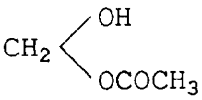
F-10-16



F-10-17

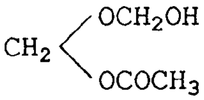


F-10-18



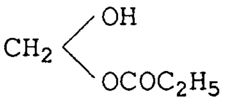
$CH_2(OH)(OCOCH_3)$

F-10-19



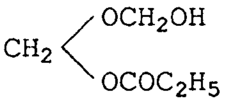
$CH_2(OCH_2OH)(OCOCH_3)$

F-10-20



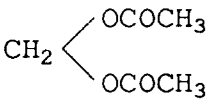
$$CH_2\left\langle\begin{matrix}OH\\OCOC_2H_5\end{matrix}\right.$$

F-10-21



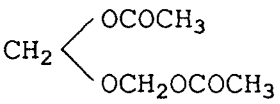
$$CH_2\left\langle\begin{matrix}OCH_2OH\\OCOC_2H_5\end{matrix}\right.$$

F-10-22



$$CH_2\left\langle\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix}\right.$$

F-10-23



$$CH_2\left\langle\begin{matrix}OCOCH_3\\OCH_2OCOCH_3\end{matrix}\right.$$

The compound represented by Formula F-8, F-9 or F-10 may preferably be added in an amount of 0.01 g to 30 g, more preferably 0.03 g to 20 g, and particularly preferably 0.05 g to 15 g, per liter of the stabilizing solution.

In the present invention, what is meant by "substantially no formaldehyde" is that it is in an amount of not more than 1.0 x 10^{-2} mol, preferably not more than 1.0 x 10^{-3}, and particularly preferably 0, per liter of the stabilizing solution.

In the present invention, the stabilizing solution may preferably contain a chelating agent having a chelate stability constant of not less than 8 with respect to iron ions. Herein, the chelate stability constant indicates the constant commonly known from L.G. Sillen & A.E. Martell, "Stability Constants of Metal-ion complexes", The Chemical Society, London (1964), or S. Chaberek & A.E. Martell, "Organic Sequestering Agents", Wiley (1959).

The chelating agent having a chelate stability constant of not less than 8 with respect to iron ions may include organic carboxylic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxyl compounds. The above iron ions refer to ferric ions (Fe^{3+}).

Specific compounds of the chelating agent having a chelate stability constant of not less than 8 with respect to ferric ions can be exemplified by the following. Examples are by no means limited these. That is, they are ethylenediaminediorthohydroxyphenylacetic acid, diaminopropanetetraacetic acid, nitrirotriacetic acid, hydroxyethylenediaminetriacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanoltetraacetic acid, transcyclohexanediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrakismethylenephosphonic acid, nitrirotrimethylenephosphonic acid, 1-hydroxyethylidene1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-diphosphonic acid, sodium pyrophosphate, sodium tetrapolyphosphate, and sodium hexametaphosphate. Particularly preferred are diethylenetriaminepentaacetic acid, nitrilotriacetic acid, nitrilotrimethylenephosphonic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid. In particular, 1-hydroxyethylidene-1,1-diphosphonic aicd is most preferably used.

The above chelating agent may be used preferably in an amount of 0.01 g to 50 g, and more preferably 0.05 g to 20 g, per liter of the stabilizing solution, whithin the range of which good results can be obtained.

The stabilizing solution of the present invention can be preferably used in view of a low possibility of environmental pollution, when it contains substantially no ammonium ion as the cation. Although the deposition of crystals tends to be somewhat less prevented unless the ammonium ion is used, the present invention constituted as herein disclosed can solve such a problem, and also is effective for an improvement in the storage stability of the solution.

Herein, what is meat by "...contains substantially no ammonium ion" is that the stabilizing solution contains ammonium ions in an amount of not more than 0.1 mol/lit., preferably not more than 0.01 mol/lit. This value is preferable as the total amount when ammonium ions are carried over from a previous bath, e.g., the fixing bath, or also when the ammonium ions are beforehand added in the stabilizing solution.

The stabilizing solution may also preferably be incorporated with a sulfite. The sulfite may be any of organic matters and inorganic matters so long as they are capable of releasing sulfite ions. Inorganic salts may preferably be used. Preferred specific compounds may include sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. The above sulfite may preferably be so added that it is in such an amount of at least 1 x 10^{-3} mol/lit. in the stabilizing solution. It may more preferably be so added that it is in an amount of 5 x 10^{-3} mol/lit. to 10^{-1} mol/lit. Its addition is effective particularly for preventing stain. The sulfite may be added directly to the stabilizing solution, and may preferably be added to a stabilizing replenishing solution.

The stabilizing solution may preferably contain a metal salt used in combination of the chelating agent previously described. Such a metal salt may include salts of a metal such as Ba, Ca, Ce, Co, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al or Sr. It can be fed in the form of an inorganic salt such as a halide, a hydroxide, a sulfate, a carbonate, a phosphate or an acetate, or a water-soluble chelating agent. It may preferably be used in an amount ranging from 1×10^{-4} mol to 1×10^{-1} mol, and more preferably from 4×10^{-4} mol to 2×10^{-2}mol, per liter of the stabilizing solution.

To the stabilizing solution, it is possible to add a salt of an organic acid such as citric acid, acetic acid, succinic acid, oxalic acid or benzoic acid, and a pH adjuster such as phosphate, borate, hydrochloric acid or sulfate. These compounds may be used in any combination in an amount necessary for maintaining the pH of the stabilizing solution and in such an amount that its addition does not adversely affect the stability required when color photographic images are stored and the prevention of occurrence of precipitates.

In the present invention, it is also possible to to use in combination any known mildewproofing agent as exemplified by 5-chloro-2-methylisothiazolin-3-one or benzoisothiazoline, so long as the effect of the present invention is not impaired.

The stabilizing solution may contain a surface active agent. The surface active agent may include the compounds represented by Formulas I and II in Japanese Patent O.P.I. Publication No. 250499/1987, and water-soluble organic siloxane compounds.

In the processing according to the present invention, silver may be recovered from the stabilizing solution. The stabilizing solution may also be subjected to a treatment such as ion exchange, electrodialysis (see Japanese Patent O.P.I. Publication No. 28949/1986) or reverse osmosis (see Japanese Patent O.P.I. Publications No. 241053/1985, No. 254151/1987 and No. 132440/1990, which is a preferred embodiment in working the present invention. As the water used in the stabilizing solution, it is also preferred to use water having been deionized. This is because its use can achieve improvments in the mildewproofing properties of the stabilizing solution, the stability of the stabilizing solution and the storage stability of images. The water may be deionized by any methods so long as the washing water may be made to contain Ca and Mg ions in a concentration of 5 ppm or less after processing. For example, it is preferred to use, alone or in combination, treatments using an ion-exchange resin and a reverse osmosis membrane. The ion-exchange resin and the reverse osmosis membrane are described in detail in KOKAI GIHO (Voluntary Technical Publication) 87-1984.

The salt concentration in the stabilizing solution may preferably be not more than 1,000, and more preferably not more than 800 ppm in order to bring about the effect of the present invention.

A soluble iron salt may preferably be present in the stabilizing solution in order to bring about the effect of the present invention. The soluble iron salt may preferably be used in a concentration of at least 5×10^{-3} mol/lit., more preferably in the range of 8×10^{-3} mol/lit. to 150×10^{-3} mol/lit. and still more preferably in the range of 12×10^{-3} mol/lit. to 100×10^{-3} mol/lit., in the stabilizing solution.

In the present invention, the pH of the stabilizing solution may preferably be in the range of 5.5 to 11.0. The pH may more preferably be 7.0 to 10.5, and particularly preferably 8.0 to 10.0, where the storage stability of the solution in use of the compound of the present invention can be more improved. A pH adjuster that can be contained in the stabilizing solution may be any of commonly known alkali agents or acid agents.

When stabilizing is carried out, its processing temperature may preferably be 15°C to 70°C, and may more preferably be in the range of 20°C to 55°C. The processing time may preferably be not more than 150 seconds, more preferably 3 seconds to 120 seconds, and most preferably 6 seconds to 90 seconds.

The stabilizing solution may be replenished in an amount of preferably not more than 1,000 ml, and more preferably 150 ml to 600 ml.

The stabilizing tank or bath may preferably be comprised of a plurality of baths. It may preferably be comprised of 2 to 6 baths, particularly preferably 2 to 3 baths, and more preferably 2 baths, and may preferably take a counter-current system (a system in which a solution is fed to a post-bath and overflowed from a prebath).

After stabilizing, it is not necessary at all to carry out washing. It, however, is possible to optionally carry out rinsing, surface washing, etc. with use of water in a small quantity for a very short time.

In the present invention, the stabilizing bath has an aperture area of not larger than 5 cm^2 per liter of the stabilizing solution.

Herein, the aperture area refers to the area in which a processing solution comes into contact with air at each aperture, per liter of the processing solution. The aperture area may preferably be smaller than 3.0 cm^2, and particularly preferably 1.5 cm^2, in the case of which the effect of the present invention becomes remarkable. If it is larger than 5 cm^2, the effect of the present invention can not be remarkable.

An automatic processor having an aperture area of not larger than 5 cm^2, used in the present invention may be any automatic processor so long as it has an aperture area of not larger than 5 cm^2. In the present invention, automatic processors preferably used are a slit type automatic processor as disclosed in Japanese Patent O.P.I Publications No. 131138/1988, No. 259661/1988, No. 235939/1988, etc., an automatic processor having a processing zone and a liquid-tank zone, as disclosed in Japanese Patent O.P.I. Publication No. 219807/1989, and an automatic processor of the type light-sensitive materials to be processing are inserted from the side wall of a processing tank, as disclosed in Japanese Patent O.P.I. Publication No. 156139/1989.

In the case when the automatic processor used in the present invention is the slit type automatic processor, a slit-shaped processing path used in its processing is meant to be a path whose cross section is smaller in its thickness than its breadth (i.e., width direction of a light-sensitive material), what is called the slit form, in a view the passageway in a processing bath through which a light-sensitive material is passed is cross-cut at right angles to the direction in which the light-sensitive material is sent forward. The form of the slit may be either rectangular or elliptic in its cross section.

The slit-shaped processing path may preferably have a thickness of 1 mm to 50 mm, and particularly preferably 3 mm to 30 mm.

The speed at which light-sensitive materials are transported through the slit-shaped processing path may preferably be in the range of 10 cm/min. to 300 cm/min. In order to obtain an even and uniform finish, it may particularly preferably be in the range of 20 cm/min. to 200 cm/min., and most preferably 20 cm/min. to 120 cm/min.

A color developing agent used in the step of color developing may include aminophenol compounds and p-phenylenediamine compounds. In the present invention, it is preferred to use p-phenylenediamine compounds having a water-soluble group.

As to such a water-soluble group, at least one group may be present on the amino group or benzene nucleus of the p-phenylenediamine compound. As specific water-soluble groups, the group may preferably include the following:

$$-(CH_2)_n-CH_2OH;$$
$$-(CH_2)_m-NHSO_2-(CH_2)_n-CH_3;$$
$$-(CH_2)_m-O-(CH_2)_n-CH_3;$$
$$-(CH_2CH_2O)_nC_mH_{2m+1};$$

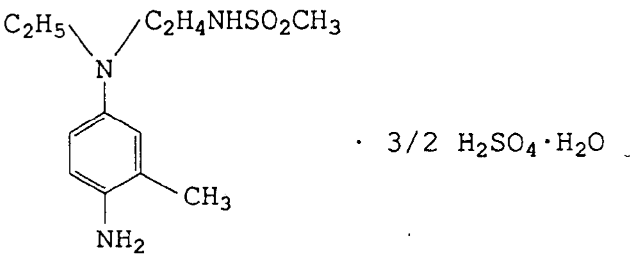
wherein m and n each represent an integer of 0 or more;

a -COOH group, and a SO_3H group.

Specific exemplary compounds of the color developing agent used in the present invention are shown below.

- Exemplary Color Developing Agent -

(DA-1)



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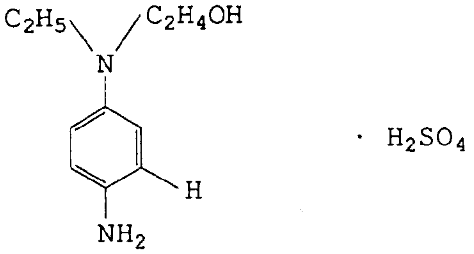

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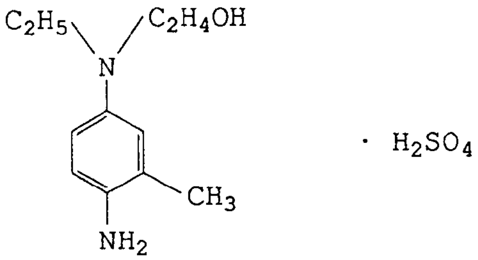

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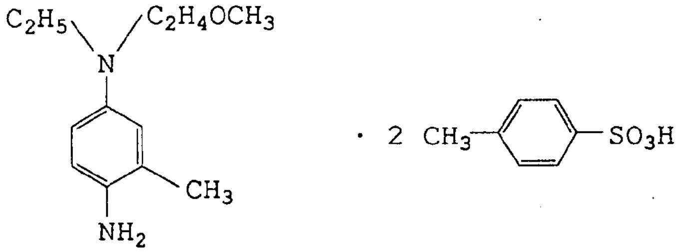
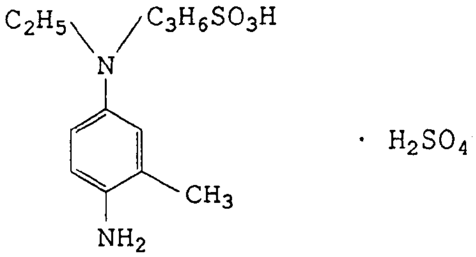


(DA-5)



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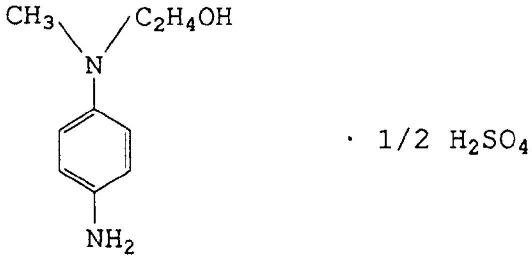

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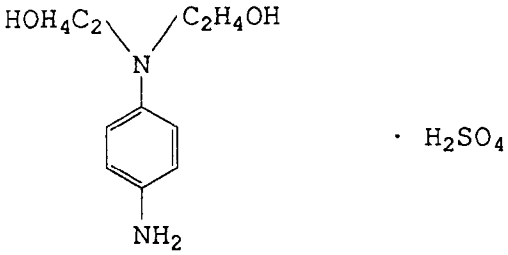

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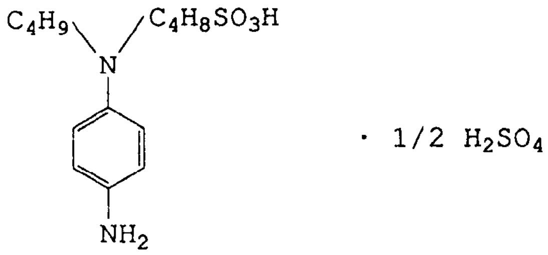

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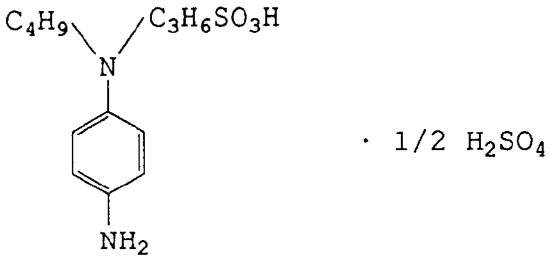

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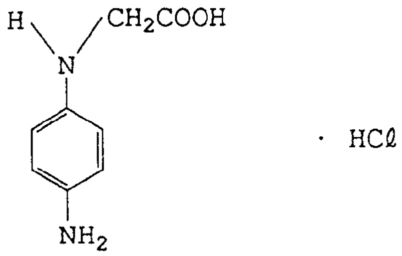

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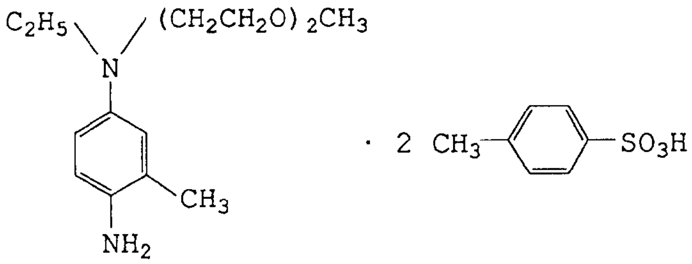

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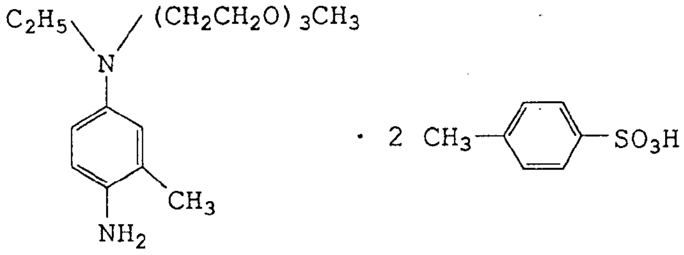

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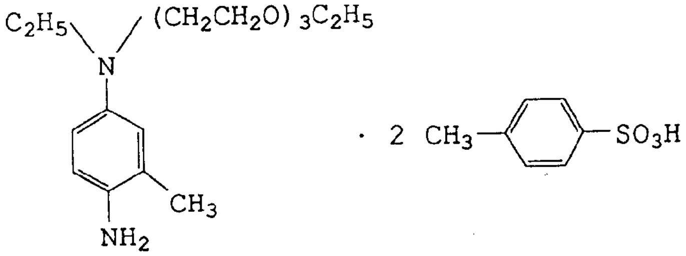

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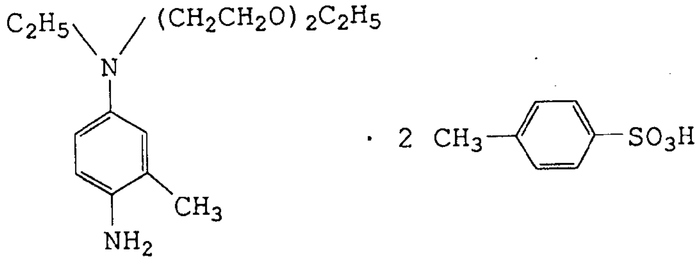

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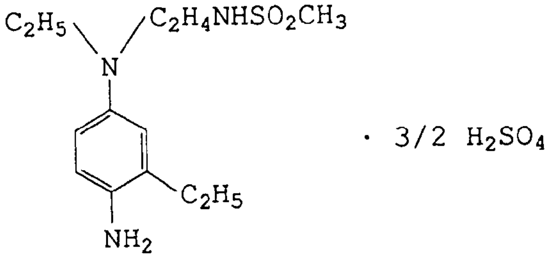
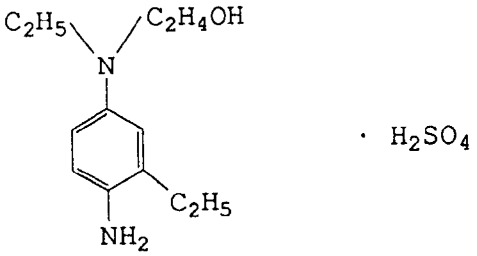


(DA-16)



Of the above exemplary color developing agents, what are preferably used in the present invention are the compounds denoted as Exemplary Compounds No. (DA-1), (DA-2), (DA-3), (DA-4), (DA-6), (DA-7) and (DA-15). Compounds (DA-1), (DA-2) and (DA-3) are particularly preferred.

The color developing agent may preferably be added in an amount of not less than 0.5×10^{-2} mol per liter of a color developing solution. It may more preferably be added in an amount ranging from 1.0×10^{-2} mol to 1.0×10^{-1} mol, and most preferably from 1.5×10^{-2} mol to 7.0×10^{-2} mol.

The above color developing agent is usually used in the form of a salt such as a hydrochloride, a sulfate, a p-toluenesulfonate or a phosphate.

The color developing solution used in the step of color developing may contain an alkali agent usually used in developing solutions, as exemplified by sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborate or borax. It may also contain various additives as exemplified by benzyl alcohol or a halogenated alkali, potassium bromide or potassium chloride, a development regulator as exemplified by citrazinic acid, and a preservative as exemplified by hydroxylamine, a hydroxylamine derivative (e.g., diethylhydroxylamine), a hydrazine derivative (e.g., hydrazinodiacetic acid) or a sulfite.

The color developing solution may still also appropriately contain various kinds of antifoaming agent and surface active agent, and an organic solvent such as methanol, dimethylformamide or dimethylsulfoxide.

The color developing solution may usually have a pH of not less than 7, and preferably about 9 to about 13.

The color developing solution may optionally contain tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, aromatic secondary alcohol, hydroxamic acid, pentose or hexose, pyrogallol-1,3-dimethyl ether or the like as an antioxidant.

In the color developing solution, various kinds of chelating agent can be used in combination as a metal ion blocking agent. Such a chelating agent may include aminopolycarboxylic acids such as ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, aminopolyphosphonic acids such as aminotri(methylenephosphonic acid), oxycarboxylic acids such as citric acid or gluconic acid, phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid, and polyphosphoric acids such as hexametaphosphoric acid.

In continuous processing, the color developing solution may be replenished, in the case of color negative films, preferably in an amount of not more than 15.0 ml, more preferably 2.5 ml to 9.0 ml, and still more preferably 3.0 ml to 7.0 ml, per 100 cm^2 of a light-sensitive material.

In the case of color photographic papers, this solution may preferably be replenished in an amount of not more than 3.0 ml, and more preferably 0.2 ml to 2.0 ml.

The bleaching agent used in the present invention in the processing solution having a bleaching ability may include the ferric complex salts of the organic acid represented by Formula A or B previously described, and ferric complex salts of the exemplary compounds shown later as A'-1 to 16,

The ferric complex salts of the aminopolycarboxylic acid represented by Formula A or B, though having an excellent silver bleaching performance, may give ill influences on the deposition of crystals. Such ill influences, however can be effectively prevented by the present invention constituted as herein disclosed. The constitution of the present invention can be effective for preventing the aforesaid deposition of crystals.

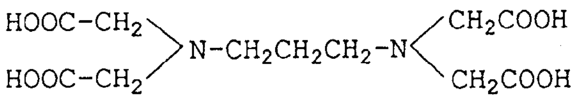
The compound represented by Formula A will be described below in detail.

In the present invention, the ferric complex salt of the organic acid represented by Formula A-1 previously described is particularly preferred as the bleaching solution.

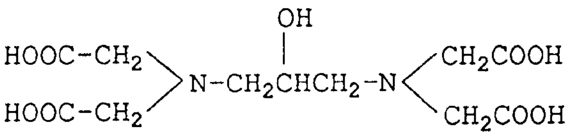
In carrying out the present invention, ammonium ions should be in a content of not more than 50 %, preferably not more than 30 %, and particularly preferably not more than 10 %, as the cation component in the bleaching solution. This makes the effect of the present invention more remarkable and, as additional effect, also effective for decreasing bleach fog or lowering the possibility of environmental pollution.

Preferred examples of the compound represented by Formula A previously described are shown below.

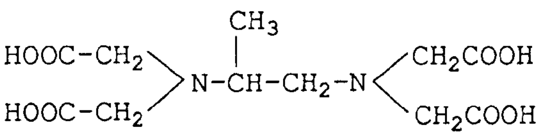
(A-1)



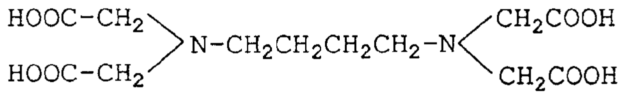
(A-2)



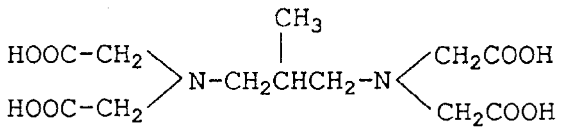
(A-3)



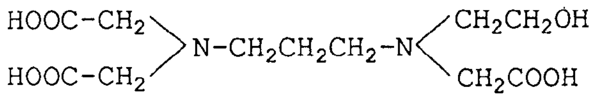
(A-4)



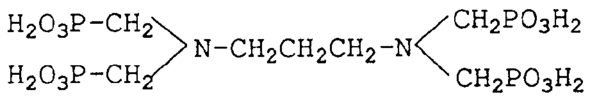
(A-5)



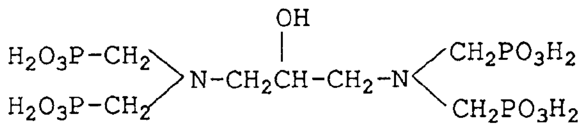
(A-6)



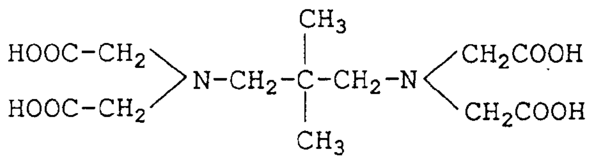
(A-7)



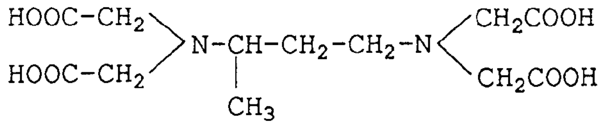
(A-8)



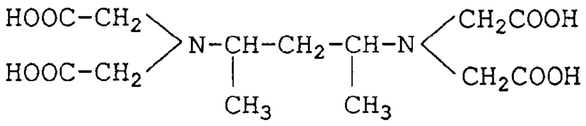
(A-9)



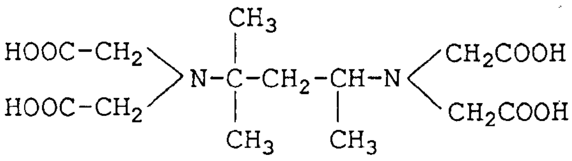
(A-10)



(A-11)



(A-12)



The ferric complex salts of these compounds (A-1) to (A-12) can be arbitrarily used in the form of sodium salts, potassium salts or ammonium salts of these ferric complex salts.

In view of the effect as aimed in the present invention and the solubility, ammonium salts of these ferric complex salts are preferably used.

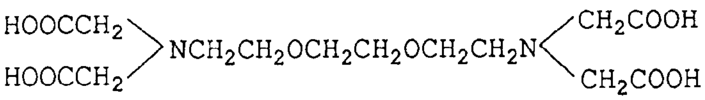
The compound (A-1) is particularly preferred.

The compound represented by Formula B will be described below in detail.

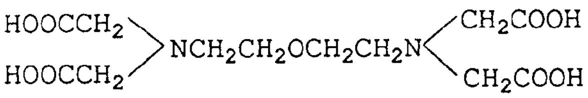
A_1 to A_4 are the same as those defined in Formula A and n represent an integer of 1 to 8. B_1 and B_2 may be the same or different and each represent a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms, as exemplified by ethylene, propylene, butylene or pentamethylene. The substituent therefor may include a hydroxyl group, and a lower alkyl group having 1 to 3 carbon atoms such as a methyl group, an ethyl group or a propyl group.

Preferred examples of the compound represented by Formula B previously described are shown below.

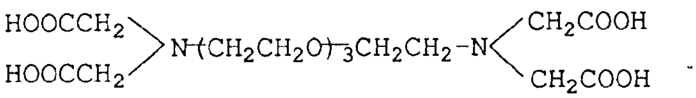
(B-1)



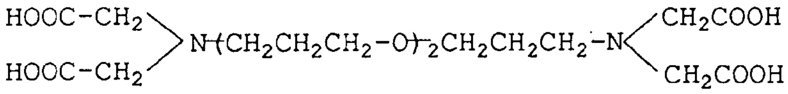
(B-2)



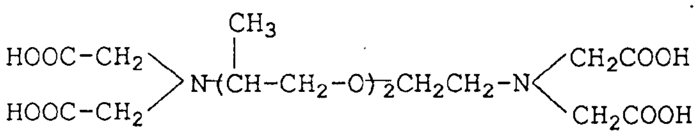
(B-3)



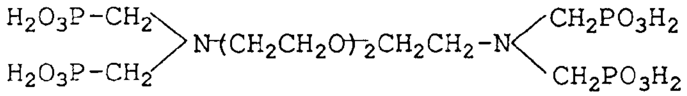
(B-4)



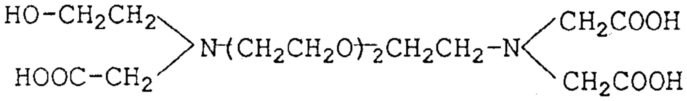
(B-5)



(B-6)



(B-7)



The ferric complex salts of these compounds (B-1) to (B-7) can be arbitrarily used in the form of sodium salts, potassium salts or ammonium salts of these ferric complex salts. In the present invention, in view of a sufficiently high oxidation power of the bleaching solution described above and the fact that the bleach fog tends to occur in the case of the ammonium salts, the ammonium salt should be in an amount of not more than 50 mol %, preferably not more than 20 mol %, and particularly preferably not more than 10 mol %. This is a preferred embodiment in carrying out the present invention.

Of the above examples of the compound represented by Formula B, the compounds (B-1), (B-2) and (B-7) are particularly preferably used. The compound (B-1) is more particularly preferably used.

The organic acid ferric complex salt may preferably be contained in an amount ranging from 0.1 mol to 2.0 mol, and more preferably from 0.15 mol to 1.5 mol, per liter of the processing solution having a bleaching ability.

In the processing solution having a bleaching ability, a preferred bleaching agent other than the compound represented by Formula A or B can be exemplified by ferric complex salts (e.g., ammonium, sodium, potassium or triethanolamine salts) of the following compounds.

Examples thereof are by no means limited to these.

[A'-1] Ethylenediaminetetraacetic acid
[A'-2] Trans-1,2-cyclohexanediaminetetraacetic acid
[A'-3] Dihydroxyethylglycidic acid
[A'-4] Ethylenediaminetetrakismethylenephosphonic acid
[A'-5] Nitrilotrismethylenephosphonic acid
[A'-6] Diethylenetriaminepentakismethylenephosphonic acid
[A'-7] Diethylenetriaminepentaacetic acid
[A'-8] Diethylenediamineorthohydroxydiphenylacetic acid
[A'-9] Hydroxyethylenediaminetriacetic acid
[A'-10] Ethylenediaminedipropionic acid
[A'-11] Ethylenediaminediacetic acid
[A'-12] Hydroxyethyliminodiacetic acid
[A'-13] Nitrilotriacetic acid
[A'-14] Nitrilotripropionic acid
[A'-15] Triethylenetetraminehexaacetic acid
[A'-16] Ethylenediaminetetrapropionic acid

In the processing solution having a bleaching ability, the ferric complex salt of the compound represented by Formula A or B previously described can be used in combination with one or more kinds of ferric complex salt of any of the above compounds A'-1 to 16.

When the organic acid ferric complex salt is used in combination of two or more kinds, the ferric complex salt of the compound of Formula A or B may preferably comprise not less than 70 % (as a molar basis), more preferably not less than 80 %, particularly preferably not less than 90 %, and more preferably not less than 95

%, from the viewpoint of bringing about a better effect of the present invention.

The organic iron (III) complex salt may be used in the form of the complex salt itself, or an iron (III) salt as exemplified by ferric sulfate, ferric chloride, ferric acetate, ferric ammonium sulfate or ferric phosphate and an aminopolycarboxylic acid or a salt thereof may be used together to form an iron (III) ion complex salt in a solution. In the instance where it is used in the form of the complex salt, one kind of complex salt may be used or two or more kinds of complex salt may be used. In the instance where a ferric salt and an aminopolycarboxylic acid are used to form a complex salt in a solution, one or more kinds of ferric salt may be used. One or more kinds of aminopolycarboxylic acid may also be used. In all instances, the aminopolycarboxylic acid may be used in excess, beyond the amount necessary for the formation of the iron (III) ion complex salt.

In the bleach-fixing solution or bleaching solution containing the iron (III) ion complex salt described above, a metal ion complex salt comprising cobalt, copper, nickel, zinc or the like other than iron may be present.

In the processing solution having a bleaching ability, at least one of the imidazoles or derivatives thereof as disclosed in Japanese Patent O.P.I. Publication No. 295258/1989 or the compounds represented by Formula I to IX and exemplary compounds thereof as disclosed in the specification of the same publication may be contained as a bleach accelerator. This can be effective for rapid processing.

Besides the above bleach accelerators, it is also possible to use the exemplary compounds disclosed in Japanese Patent O.P.I. Publication No. 123459/1987, pages 51 to 115 of its specification, the exemplary compounds disclosed in Japanese Patent O.P.I. Publication No. 17445/1985, pages 51 to 115 of its specification, and the compounds disclosed in Japanese Patent O.P.I: Publications No. 95630/1978 and No. 28426/1978.

These bleach accelerators may be used alone or in combination of two or more kinds, and may preferably be added in an amount ranging from approximately 0.001 g to 100 g, more preferably 0.05 g to 50 g, and particularly preferably 0.05 g to 15 g.

In the case when the bleach accelerator is added, it may be added and dissolved as it is. Alternatively, as commonly done, it may be added after it has been dissolved in water, alkali, organic acid or the like, and may also be added optionally after it has been dissolved therein using an organic solvent such as methanol, ethanol or acetone.

The bleaching solution according to the present invention should be used at a temperature of 20°C to 50°C, and preferably 25°C to 45°C.

The pH of the bleaching solution may preferably be not more than 6.0, and more preferably be controlled to be not less than 1.0 and not more than 5.5.

The pH of the bleaching solution is the pH of the processing bath solution used in the processing of light-sensitive silver halide photographic materials, and can be clearly distinguished from the pH of what is called a replenisher or replenishing solution.

When the bleaching solution is used, a halide such as ammonium bromide, potassium bromide or sodium bromide is usually added to the solution. Various kinds of fluorescent brightening agent, antifoaming agent or surface active agent may also be incorporated therein.

The bleaching solution according to the present invention may preferably be replenished in an amount of not more than 500 ml, more preferably 20 ml to 400 ml, and most preferably 40 ml to 350 ml, per 1 m^2 of the light-sensitive silver halide color photographic material. The effect of the present invention becomes more remarkable as the solution is replenished in a smaller amount.

In the present invention, air or oxygen may optionally be blown in processing baths and processing solution replenisher holding tanks so that the activity of the processing solution having a bleaching ability can be increased. Alternatively, a suitable oxidant as exemplified by hydrogen peroxide, a bromate or a persulfate may be appropriately added. It is also possible to use a member having a high oxygen permeability.

As for a fixing agent used in the processing solution having a fixing ability (i.e., a bleach-fixing solution or a fixing solution), it may preferably include a thiosulfate and a thiocyanate.

In the fixing solution or bleach-fixing solution of the present invention, the thiocyanate may preferably be contained in an amount of not less than 0.1 mol/lit., and particularly preferably not less than 0.5 mol/lit., in order to prevent crystals from being deposited at the aperture through which light-sensitive materials are transported from a fixing bath or bleach-fixing bath to a stabilizing bath and at the transport aperture between stabilizing baths. In particular, this effect can be more remarkable as the aperture area of the transport aperture is made smaller.

In the bleach-fixing solution or fixing solution of the present invention, ammonium ions as the cation component should be controlled to be in a content of not more than 50 %, preferably not more than 30 %, and particularly preferably not more than 10 %, from the viewpoint of lowering the possibility of environmental pollution. In such an instance, the thiocyanate may be used as a fixing component, whereby the fixing performance can be prevented from becoming inferior.

In addition to such a fixing agent, the bleach-fixing solution or fixing solution may also contain one or more kinds of pH adjuster comprising various kinds of compound such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate or ammonium hydroxide.

The bleach-fixing solution or fixing solution should further contain a large quantity of a re-halogenating agent such as an alkali halide or ammonium halide, as exemplified by potassium bromide, sodium bromide, sodium chloride or ammonium bromide. It is also possible to appropriately add compounds which are known to be usually added to processing solutions having a fixing ability, as exemplified by alkylamines and polyethylene oxides.

Silver may be recovered from the bleach-fixing solution or fixing solution by known methods. For example, the electrolytic method as disclosed in French Patent No. 2,299,667, the precipitation method as disclosed in Japanese Patent O.P.I. Publication No. 73037/1977 and German Patent No. 23 31 220, the ion-exchange method as disclosed in Japanese Patent O.P.I. Publication No. 17114/1976, German Patent No. 25 48 237 and KOKAI GIHO No. 90-473, and the metallic replacement method as disclosed in British Patent No. 1,353,805 can be effectively used.

These silver recovering methods are particularly preferred when silver is recovered by in-line treatment using the electrolytic method or an anion-exchange resin, since the rapid-processing adaptability can be thereby more improved. Alternatively, silver may be recovered from overflow waste liquor and then regenerated for its use.

The bleach-fixing solution or fixing solution may preferably be replenished in an amount of not more than 900 ml, more preferably 20 ml to 750 ml, and particularly preferably 50 ml to 620 ml, per 1 m^2 of the light-sensitive material.

The compound represented by Formula FA as disclosed in Japanese Patent O.P.I. Publication No. 295258/1989, page 56 of its specification, together with its exemplary compounds may be added to the fixing solution, whereby an additional effect can be obtained such that sludge may much less occur when light-sensitive materials are processed in a small quantity over a long period of time using the bleach-fixing solution or fixing solution.

The compounds represented by Formula FA as described in that specification can be synthesized by usual methods as disclosed in U.S. Patents No. 3,335,161 and No. 3,260,718. The compounds represented by Formula FA may be used alone or in combination of two or more kinds.

These compounds represented by Formula FA may be added in an amount of 0.1 g to 200 g per liter of the processing solution, within the range of which good results can be obtained.

A sulfite and/or a sulfite-releasing compound may be used in the bleach-fixing solution or fixing solution. As specific examples of these compounds, they may include potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. They may also include the compound represented by Formula B-1 or B-2 as disclosed in Japanese Patent O.P.I. Publication No. 295258/1989, page 60 of its specification.

When these sulfite and/or sulfite-releasing compound are used, these must be in an amount of at least 0.05 mol in terms of sulfite ion per liter of the bleach-fixing solution or fixing solution, and may preferably be in the range of 0.08 mol/lit. to 0.65 mol/lit., particularly preferably in the range of 0.10 mol/lit. to 0.50 mol/lit., and more particularly preferably in the range of 0.12 mol/lit. to 0.40 mol/lit.

The processing using the bleaching solution, the bleach-fixing solution and the fixing, solution each may be carried out for any desired time. The processing may each preferably be carried out for not more than 3 minutes 30 seconds, more preferably in the range of 10 seconds to 3 minutes 20 seconds, and particularly preferably 20 seconds to 3 minutes.

In the present invention, it is preferred as an embodiment of the present invention to bring the bleaching solution, the bleach-fixing solution and the fixing solution under forced liquid stirring. This is because not only the effect as aimed in the present invention can be better attained but also the adaptability to rapid processing should be taken into account. Herein what is meant by the forced liquid stirring is not the usual diffusion movement in a solution but the stirring forcedly carried out with a stirring means additionally applied. As a means for the forced stirring, it is possible to employ the means as disclosed in Japanese Patent O.P.I. Publication No. 222259/1989 and No. 206343/1989.

In the present invention, the solution cross-over time between baths, e.g., from a fixing bath to a stabilizing bath should be not longer than 10 seconds, and preferably not longer than 7 seconds. This is effective for the prevention of bleach fog, which is an effect different from that of the present invention. A method in which a duck hill valve or the like is provided so as to lessen the processing solution a light-sensitive material may carry in is also a preferred embodiment in carrying out the present invention.

Silver halide grains used in the light-sensitive silver halide color photographic material (hereinafter abbreviated "light-sensitive material" as occasion calls) may be any of silver chloride, silver chlorobromide, silver iodobromide and silver chloroiodobromide. Silver iodobromide is preferably used from the viewpoint of attaining the effect of the present invention.

An average content of silver iodide in the whole silver halide emulsions in the light-sensitive material may preferably be 0.1 mol % to 15 mol %, preferably 0.5 mol % to 12 mol %, and particularly preferably 1 mol % to 10 mol %.

An average grain size of the hole silver halide emulsions in the light-sensitive material may preferably be not larger than 2.0 μm, and more preferably 0.1 μm to 1.0 μm.

In instances in which a silver halide emulsion contains grains wherein average value of grain diameter/grain thickness is less than 5, its grain size distribution should preferably be monodisperse in view of desilvering performance.

A monodisperse silver halide emulsion refers to an emulsion in which the weight of silver halide grains included within the grain size range of ± 20 % around the average grain size $\bar{r}$ holds not less than 60 %, preferably not less than 70 %, and more preferably not less than 80 %, based on the total weight of silver halide grains.

Here, the average grain size $\bar{r}$ is defined to be a grain size ri determined when ni x ri^3, the product of frequencies ni and ri^3 of grains having a grain size ri, comes to be maximum. (The effective number is three figures, and a minimum figure number is round off.)

The grain size herein referred to is based on the diameters of grains in the case of spherical silver halide grains, and, in the case of grains with shapes other than the spherical shape, the diameters obtained when a projected image of the grain is calculated into a circular image having the same area.

The grain size can be obtained, for example, by photographing the grain under 10,000 to 50,000 magnification by means of an electron microscope, and actually measuring the diameters or projected areas of grains on the print. (Number of grains to be measured should be not less than 1,000 at random.)

A highly monodisperse emulsion, particularly preferred in the present invention, has a degree of monodispersion of not more than 20 %, and more preferably not more than 15 %, when it is defined by the expression:

$$\frac{\text{Grain size standard deviation}}{\text{Average grain size}} \times 100 = \text{Breadth of distribution (\%)}$$

The crystal of the silver halide grains described above may be regular crystals or twinned crystals, or may be of any other form. Those having any ratio of [1.0.0] face to [1.1.1] face can be used. With regard to the crystal structure, these silver halide grains may have a structure which is uniform from the interior to the outer surface, or a layer structure wherein the inside and the outer surface are of different nature (i.e, a core/shell type). These silver halide grains may be of the type wherein a latent image is mainly formed on the surface, or the type wherein it is formed in the interior of grains. Tabular silver halide grains (see Japanese Patent O.P.I. Publications No. 113934/1983 and No. 47959/1986) can also be used.

The silver halide grains may be those obtained by any preparation method such as the acid method, the neutral method or the ammonia method.

They may also be those prepared by a method in which seed grains are formed by the acid method, which are then made to grow by the ammonia method capable of achieving a higher grow rate, until they come to have a given size. When the silver halide grains are grown, it is preferred to control the pH, pAg, etc. in a reaction vessel and to successively and simultaneously add and mix silver ions and halide ions in the amounts corresponding to the rate of growth of silver halide grains, as in the manner disclosed, for example, in Japanese Patent O.P.I. Publication No. 48521/1979.

The silver halide grains are preferably prepared in the manner described above. In the present specification, compositions containing such silver halide grains are called silver halide emulsions.

Such silver halide emulsions may be chemically sensitized using active gelatin; a sulfur sensitizer as exemplified by allylthiocarbamide, thiourea or cystine; a selenium sensitizer; a reduction sensitizer as exemplified by stannous chloride, thiourea dioxide or polyamine; a noble metal sensitizer as exemplified by a gold sensitizer specifically including potassium aurothiocyanate, potassium chloroaurate and 2-aurothio-3-methylbenzothiazolium chloride, or exemplified by a sensitizer comprised of a water-soluble salt of ruthenium, palladium, platinum, rhodium or iridium, specifically including ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladate (some of these act as sensitizers or fog restrainers depending on whether they are used in a large amount or small amount); which may be used alone, or in combination as exemplified by a combination of the gold sensitizer and the sulfur sensitizer or a combination of the gold sensitizer and the selenium sensitizer.

The silver halide emulsion may be subjected to chemical ripening with addition of a sulfur-containing compound. At least one of at least one hydroxytetrazaindene and a nitrogen-containing heterocyclic compound having a mercapto group may be incorporated before this chemical ripening, during the ripening or after the ripening.

Silver halide may be optically sensitized by adding a sensitizing dye in an amount of, for example, 5×10^{-8} mol to 3×10^{-3} mol per mol of silver halide so that it can be made sensitive to each desired sensitivity wavelength region. As the sensitizing dye, various sensitizing dyes can be used, and also they can be used alone or in combination of two or more kinds.

The light-sensitive material may preferably contain couplers, a yellow coupler, a magenta coupler and a cyan coupler, respectively in a red-sensitive silver halide emulsion layer, a blue-sensitive silver halide emulsion layer and a green-sensitive silver halide emulsion layer, i.e., compounds capable of forming a dye upon reaction with an oxidized product of a calor developing agent.

The yellow coupler that can be used may include closed-chain ketomethylene compounds and also what is called two-equivalent couplers such as a coupling-position -o-aryl substitution coupler, a coupling-position -o-acyl substitution coupler, a coupling-position hydantoin compound substitution coupler, a coupling-position urazole compound substitution coupler, a coupling-position succinimide compound substitution coupler, a coupling-position fluorine substitution coupler, a coupling-position chlorine or bromine substitution coupler, and a coupling-position -o-sulfonyl substitution coupler. Examples of usable yellow couplers may be those disclosed in U.S. Patents No. 2,875,057, No. 3,265,506, No. 3,408,194, No. 3,551,155, No. 3,582,322, No. 3,725,072, No. 3,891,445, No. 3,933,501, No. 4,022,620, No. 4,326,024 and No. 4,401,752, West German Patent No. 15 47 868, West German Patent Application Publications No. 22 19 917, No. 22 61 361 and No. 24 14 006, British Patents No. 1,425,020 and No. 1,476,760, Japanese Patent Examined Publication No. 10783/1976, Japanese Patent O.P.I. Publications No. 26133/1972, No. 73147/1973, No. 102636/1976, No. 6341/1975, No. 123342/1975, No. 130442/1975, No. 21827/1976, No. 876509/1975, No. 82424/1977, No. 115219/1977, No. 95346/1983 and No. 180542/1989, etc.

The magenta coupler that can be used may include compounds of a pyrazolone type, a pyrazolotriazole type, a pyrazolinobenzimidazole type or an indazolone type. These magenta couplers may include not only four-equivalent couplers but also two-equivalent couplers as in the case of the yellow coupler. Examples of usable magenta couplers may be those disclosed in U.S. Patents No. 2,600,788, No. 2,983,608, No. 3,062,653, No. 3,127,269, No. 3,311,476, No. 3,419,391, No. 3,519,429, No. 3,558,319, No. 3,582,322, No. 3,615,506, No. 3,834,908, No. 3,891,445, No. 4,310,619, No. 4,351,897, No. 4,500,630 and No. 4,540,654, West German Patent No. 18 10 464, West German Patent Application Publications (OLS) No. 24 08 665, No. 24 17 945 and No. 24 24 467, Japanese Patent Examined Publication No. 6031/1965, Japanese Patent O.P.I Publications No. 20826/1976, No. 58922/1977, No. 129538/1974, No. 74027/1974, No. 159336/1975, No. 42121/1977, No. 74028/1974, No. 60233/1975, No. 26541/1976, No. 55122/1978 and No. 43659/1985, European Patent No. 73636, etc.

The cyan coupler that can be used may include hydrophobic and non-diffusion type naphthol and phenol couplers, and may preferably include as typical examples, oxygen atom releasable two-equivalent naphthol couplers. A coupler capable of forming a cyan dye durable to humidity and temperature is also preferably used. Typical examples thereof are the phenol type cyan coupler having on the meta-position of the phenol nucleus an alkyl group such as an ethyl group or a group with more carbon atoms, as disclosed in U.S. Patent No. 3,772,002, a 2,5-diacylamino-substituted phenol type cyan coupler, a phenol type cyan coupler having a phenylureido group on the 2-position and also having an acylamino group on the 5-position, and the 5-amidonaphthol type cyan coupler as disclosed in European Patent Publication No. 161626A.

In the light-sensitive material to be processed by the method of the present invention, it is possible to use a coupler capable of imagewise releasing a nucleating agent or a development accelerator, or a precursor thereof, at the time of development. Examples of such a compound are disclosed in British Patent No. 2,097,140 and No. 2,131,188. Besides, it is possible to use the coupler capable of releasing a DIR redox compound as disclosed in Japanese Patent O.P.I. Publication No. 185950/1985 and the coupler capable of releasing a dye recurring after split-off as disclosed in European Patent Publication No. 173302A.

In silver halide emulsion layers and other photographic component layers, couplers such as colored magenta or colored cyan couplers and polymer couplers may be used in combination. The colored magenta or colored cyan couplers and the polymer couplers can be seen from the disclosure in Japanese Patent Application No. 193611/1984, filed by the present applicant (see Japanese Patent O.P.I. Publication No. 72235/1986), and the disclosure in Japanese Patent Application No. 172151/1984, filed by the present applicant (see Japanese Patent O.P.I. Publication No. 5014/1986), respectively.

In the present invention, it is particularly preferred in view of the effect as aimed in the present invention, in particular, the rapid-processing performance, to use in combination with the light-sensitive material of the present invention the magenta coupler represented by Formula M-1 as described on page 29 of the specification in Japanese Patent O.P.I. Publication No. 106655/1985 (including as specific exemplary magenta couplers, the compounds No. 1 to No. 77 described on pages 26 to 34 of the specification in Japanese Patent O.P.I.

Publication No. 106655/1985), the cyan couplers represented by Formula C-I or C-II also described on pages 34 (including as specific exemplary cyan couplers, the compounds C′-1 to C′-82 and C″-1 to C″-36 described on pages 37 to 42 of the specification in same the publication), the high-speed yellow couplers also described on page 20 (including as specific exemplary yellow couplers, the compounds Y′-1 to Y′-39 described on pages 21 to 26 of the specification in the same publication and the compounds Y-1 to Y-31 described on pages 280 to 283 of the specification in Japanese Patent O.P.I. Publication No. 180542/1989).

In instances in which light-sensitive materials with a high silver chloride content are used, it is preferred to use a nitrogen-containing heterocyclic mercapto compound combination.

Such a nitrogen-containing heterocyclic mercapto compound can be exemplified by the compounds I′-1 to I′-87 described on pages 42 to 45 of the specification in Japanese Patent O.P.I. Publication No. 106655/1988.

Other various photographic additives can be incorporated in the light-sensitive material. For example, it is possible to use the antifoggants, stabilizers, ultraviolet absorbents, anti-color-stain agents, fluorescent brightening agents, color-image fading preventive agents, antistatic agents, hardening agents, surface active agents, plasticizers and wetting agents as disclosed in Research Disclosure No. 17643.

In the light-sensitive material, a hydrophilic colloid, which is used for preparing emulsions, may preferably gelatin, and may also include any of proteins such as derived gelatin, a graft polymer of gelatin with other polymer, albumin and casein, cellulose derivatives such as hydroxyethyl cellulose and carboxymethyl cellulose, starch derivatives, and synthetic hydrophilic macromolecules of homopolymers or copolymers such as polyvinyl alcohol, polyvinyl imidazole and polyacrylamide.

A support, used for the light-sensitive material, may include films made of polyesters such as cellulose acetate, cellulose nitrate and polyethylene terephthalate, polyamide films, polycarbonate films, polystyrene films, baryta paper, polyethylene-coated paper, polypropylene synthetic paper, and transparent supports comprised of a reflective layer in combination, as exemplified by glass plate. Other usual transparent supports are also available. These supports may be appropriately selected according to the purpose for which the light-sensitive material is used.

The silver halide emulsion layers and other photographic component layers can be provided using various coating processes such as dip coating, air-knife coating, curtain coating and hopper coating. It is also possible to use a process by which two or more layers are simultaneously coated, according to the method disclosed in U.S. Patents No. 2,761,791 and No. 2,941,898.

The position at which each emulsion layer is provided can be arbitrarily determined. For example, in the case of color negative photographic materials for full-color photography, emulsion layers may preferably be arranged in order of a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a blue-sensitive silver halide emulsion layer from the support. These light-sensitive silver halide emulsion layers may each be comprised of two or more layers.

In the light-sensitive material to be processed by the method of the present invention, it is optional to provide an intermediate layer with a suitable thickness according to the purpose. Various layers such as a filter layer, a anti-curl layer, a protective layer and an antihalation layer may also be used as component layers in appropriate combination. In these component layers, the hydrophilic colloid that can be used in the emulsion layers as described above can be similarly used as a binder. In those layers, the various photographic additives that can be incorporated in the emulsion layers as described above can also be incorporated.

The method of processing the light-sensitive material according to the present invention can be applied to any light-sensitive materials such as color negative films, color papers, color positive films, slide color reversal films, motion picture color reversal films, TV color reversal films and reversal color papers, so long as the light-sensitive materials are light-sensitive materials processed by what is called the coupler-in-emulsion processing system in which couplers are contained in light-sensitive materials.

In the light-sensitive silver halide color photographic material used in the present invention, the silver halide emulsions as disclosed in Research Disclosure No. 308119 (hereinafter "RD308119") can be used. Items described and paragraphs thereof are shown in the following table.

Items	Page of RD308119	
Iodine formation	993	Par. I-A
Preparation method	993	Par. I-A and
	994	Par. E
Crystal habit:		
Normal crystal	993	Par. I-A
Twinned crystal	"	"
Epitaxial growth	"	"
Halogen composition:		
Uniform	993	Par. I-B
Not uniform	"	"
Halogen conversion	994	Par. I-C
Halogen substitution	"	"
Metal content	994	Par. I-D
Monodispersion	995	Par. I-F
Addition of solvent	"	"
Latent image forming position:		
Surface	995	Par. I-G
Interior	"	"
Light-sensitive material:		
Negative	995	Par. I-H
Positive (containing internal fog grains)	"	"
Use of emulsion by mixture	995	Par. I-J
Desalting	995	Par. II-A

In the present invention, silver halide emulsions having been subjected physical ripening, chemical ripening and spectral sensitization are used. Additives used in such steps are described in Research Disclosures No. 17643, No. 18716 and No. 308119 (hereinafter "RD17643", "RD18716" and "RD308119", respectively).

Items described and paragraphs thereof are shown in the following table.

Items	Page of RD308119,		RD17643,	RD18716
Chemical sensitizer	996	Par. III-A	23	648
Spectral sensitizer	996	Par. IV-A-A,B,C,D,E,H,I,J	23-24	648-649
Supersensitizer	996	Par. IV-A-E,J	23-24	648-649
Antifoggant	998	Par. VI	24-25	649
Stabilizer	998	Par. VI	24-25	649

Known photographic additives that can be used in the present invention are also described in the above Research Disclosures. Items described and paragraphs thereof are shown in the following table.

Items	Page of RD308119,		RD17643,	RD18716
Color contamination preventive agent	1002	Par. VII-I	25	650
Color image stabilizer	1001	Par. VII-J	25	
Brightening agent	998	V	24	
Ultraviolet absorbent	1003	Par. VIIIC XIIIC	25-26	
Light absorbing agent	1003	Par. VIII	25-26	
Light scattering agent	1003	Par. VIII		
Filter dye	1003	Par. VIII	25-26	
Binder	1003	Par. IX	26	651
Antistatic agent	1006	Par. XIII	27	650
Hardening agent	1004	Par. X	26	651
Plasticizer	1006	Par. XII	27	650
Lubricant	1006	Par. XII	27	650
Surfactant, coating aid	1005	Par. XI	26-27	650
Matting agent	1007	Par. VI		
Developing agent	1011	Par. XX-B		

(contained in light-sensitive materials)

Various couplers can be used in the present invention. Examples thereof are described in the above Research Disclosures. Related items described and paragraph thereof are shown in the following table.

Items	Page of RD308119,		RD17643, RD18716
Yellow coupler	1001	Par. VII-D	Par. VII-C-G
Magenta coupler	1001	Par. VII-D	Par. VII-C-G
Cyan coupler	1001	Par. VII-D	Par. VII-C-G
DIR coupler	1001	Par. VII-F	Par. VII-F
BAR coupler	1002	Par. VII-F	
Other useful residual group releasing coupler	1001	Par. VII-F	
Alkali-soluble coupler	1001	Par. VII-E	

The additives used in the present invention can be added by the dispersion method as described in RD308119, Paragraph XIV.

In the present invention, the supports as described in the aforesaid RD17643, page 28, RD18716, pages 647-648 and RD308119, Paragraph XIX can be used.

The light-sensitive material can be provided with the auxiliary layers such as filter layers and intermediate layers as described in RD308119, Paragraph VII-K.

The light-sensitive material used in the present invention can be comprised of various layers of conventional layer order, inverse layer order or unit structure as described in the aforesaid RD308119, Paragraph VII-K.

In the present invention, the effect of the present invention can be better attained when a vinylsulfone type hardening agent is used in the light-sensitive material.

The vinylsulfone type hardening agent refers to a compound having a vinyl group bonded to a sulfonyl group, or a group capable of forming such a vinyl group. It may preferably be a compound having at least two vinyl groups bonded to sulfonyl groups, or groups capable of forming such vinyl groups. For example, a compound represented by the following Formula VS-1 may preferably be used in the present invention.

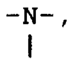
Formula VS-1

$$L\text{-}(SO_2\text{-}X)_m$$

In the above Formula VS-1, L represents a connecting group with a valence of m, and X represents $-CH=CH_2$ or $-CH_2CH_2Y$, wherein Y represents a group capable of being split off in the form of HY, as exemplified by a halogen atom, a sulfonyloxy group, a sulfoxy group (including a salt thereof) or a residual group of tertiary amine.

The symbol m represents an integer of 2 to 10. When m is two or more, the $-SO_2-X$ moieties may be the same or different from each other.

The connecting group with a valence of m is a group with a valence of m formed by the combination of one or a plurality of, for example, aliphatic hydrocarbon group(s) as exemplified by alkylene, alkylidene or alkylidine, or a group formed by the union of any of these; aromatic hydrocarbon group(s) as exemplified by arylene, or a group formed by the union of any of these; or bond(s) represented by -O-, -NR′- (R′ represents a hydrogen atom or preferably an alkyl group having 1 to 15 carbon atoms), -S-,



$$-\underset{|}{N}-,$$

-CO, SO-, $-SO_2-$ or $-SO_3-$. When two or more -NR′- are contained, the R′s thereof may combine to form a ring. The connecting group L may also include those having a substituent such as a hydroxyl group, an alkoxyl group, a carbamoyl group, a sulfamoyl group, an alkyl group or an aryl group.

Examples of X may preferably be $-CH=CH_2$ or $-CH_2CH_2Cl$.

Typical examples of the vinylsulfone type hardening agent are shown below.

VS-1 $H_2C=CHSO_2CH_2SO_2CH=CH_2$

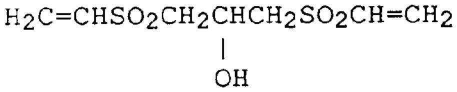
VS-2 $H_2C=CHSO_2(CH_2)_2SO_2CH=CH_2$

VS-3 $H_2C{=}CHSO_2(CH_2)_3SO_2CH{=}CH_2$

VS-4 $H_2C{=}CHSO_2CH_2OCH_2SO_2CH{=}CH_2$

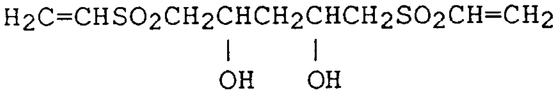
VS-5 $H_2C{=}CHSO_2(CH_2)_2O(CH_2)_2SO_2CH{=}CH_2$

VS-6



$H_2C{=}CHSO_2CH_2\underset{\mathrm{OH}}{\underset{|}{CH}}CH_2SO_2CH{=}CH_2$

VS-7



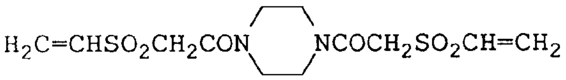
$H_2C{=}CHSO_2CH_2\underset{\mathrm{OH}}{\underset{|}{CH}}CH_2\underset{\mathrm{OH}}{\underset{|}{CH}}CH_2SO_2CH{=}CH_2$

VS-8 $H_2C{=}CHSO_2CH_2CONHCH_2NHCOCH_2SO_2CH{=}CH_2$

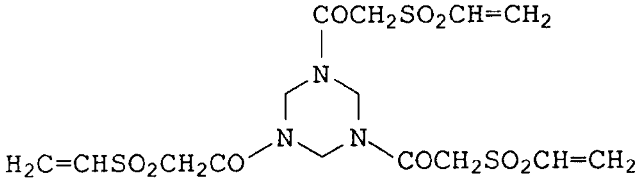
VS-9 $H_2C{=}CHSO_2CH_2CONH(CH_2)_2NHCOCH_2SO_2CH{=}CH_2$

VS-10 $H_2C{=}CHSO_2CH_2CONHCH_2CH_2CH_2NHCOCH_2SO_2CH{=}CH_2$

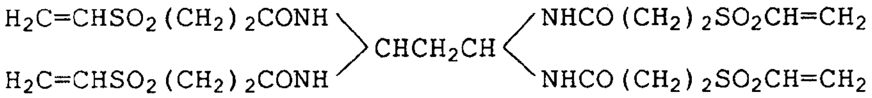
VS-11



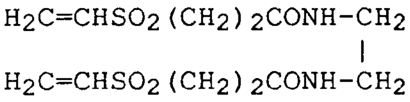
VS-12



VS-13

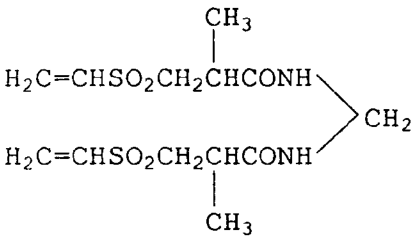


VS-14

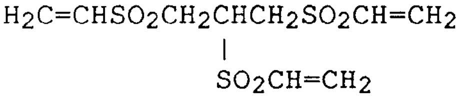


$$\begin{array}{l}H_2C{=}CHSO_2(CH_2)_2CONH{-}CH_2\\ \qquad\qquad\qquad\qquad\qquad\quad |\\ H_2C{=}CHSO_2(CH_2)_2CONH{-}CH_2\end{array}$$

VS-15

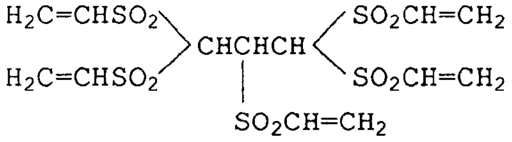


VS-16

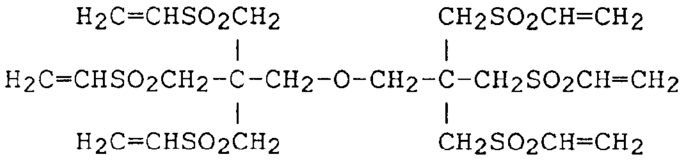


$H_2C{=}CHSO_2CH_2\underset{SO_2CH{=}CH_2}{\underset{|}{CH}}CH_2SO_2CH{=}CH_2$

VS-17

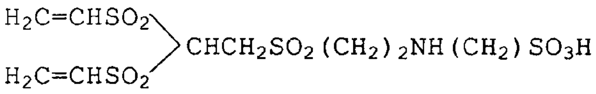


VS-18



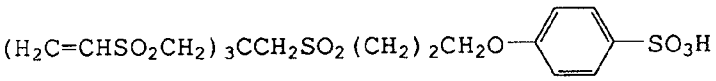
$$\begin{array}{ccc} H_2C{=}CHSO_2CH_2 & & CH_2SO_2CH{=}CH_2 \\ | & & | \\ H_2C{=}CHSO_2CH_2{-}C & {-}CH_2{-}O{-}CH_2{-} & C{-}CH_2SO_2CH{=}CH_2 \\ | & & | \\ H_2C{=}CHSO_2CH_2 & & CH_2SO_2CH{=}CH_2 \end{array}$$

VS-19



VS-20 $[(H_2C{=}CHSO_2)_3CCH_2SO_2(CH_2)_2SCH_2]_2CO$

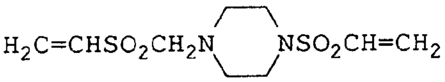
VS-21



VS-22

$(H_2C{=}CHSO_2CH_2)_4C$

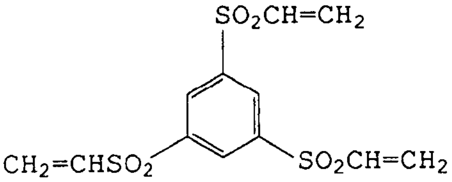
VS-23



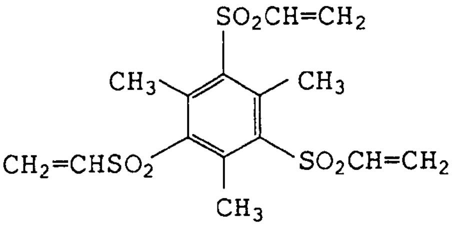
VS-24

$(H_2C{=}CHSO_2CH_2)_3CC_2H_5$

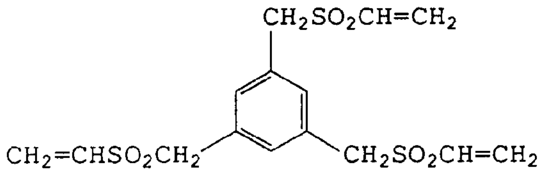
VS-25



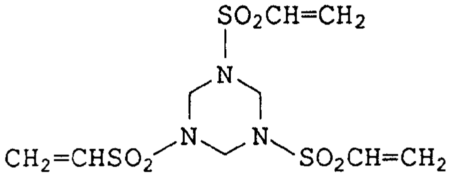
VS-26



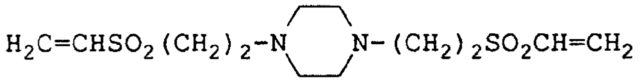
VS-27



VS-28



VS-29



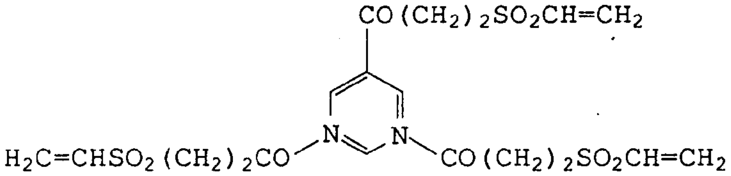
VS-30

$H_2C=CHSO_2(CH_2)_2SO_2(CH_2)_2SO_2CH=CH_2$

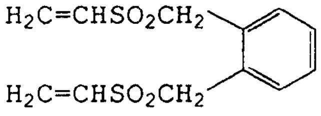
VS-31

$H_2C=CHSO_2(CH_2)_2O(CH_2)_2NHONH(CH_2)_2O\text{-}(CH_2)_2SO_2CH=CH_2$

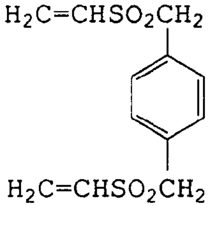
VS-32



VS-33



VS-34



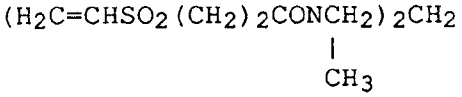
VS-35

$(H_2C=CHSO_2NH)_2CH_2$

VS-36

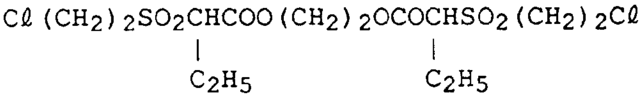
$H_2C=CHSO_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2SO_2CH=CH_2$

VS-37



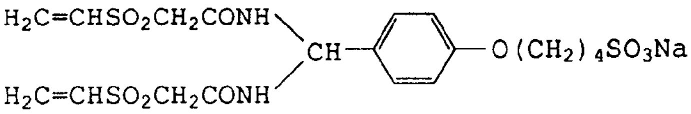
$(H_2C{=}CHSO_2(CH_2)_2CO\underset{CH_3}{\underset{|}{N}}CH_2)_2CH_2$

VS-38

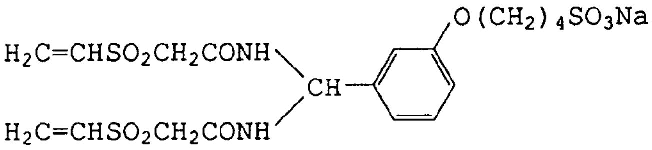


$C\ell(CH_2)_2SO_2\underset{C_2H_5}{\underset{|}{C}}HCOO(CH_2)_2OCO\underset{C_2H_5}{\underset{|}{C}}HSO_2(CH_2)_2C\ell$

VS-39



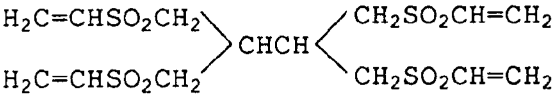
VS-40



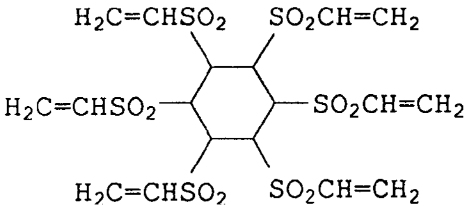
VS-41

$C_8H_{17}C(CH_2SO_2CH{=}CH_2)_3$

VS-42



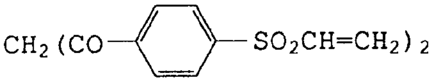
VS-43



VS-44

$CH_2(CONHCH_2SO_2CH{=}CH_2)_2$

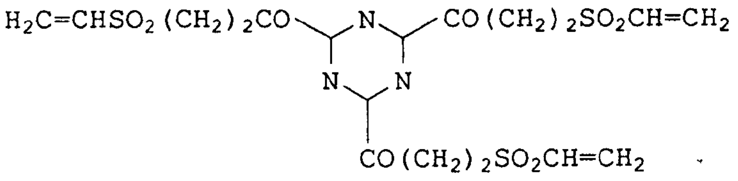
VS-45



VS-46

$C[CO(CH_2)_2SO_2CH{=}CH_2]_4$

VS-47



VS-48 $NH[(CH_2)_2SO_2CH=CH_2]_2$

VS-49 $CH_3C(CH_2OCH_2SO_2CH=CH_2)_3$

VS-50 $C(CH_2OCH_2SO_2CH=CH_2)_4$

VS-51 $N[(CH_2)_2OCH_2SO_2CH=CH_2]_3$

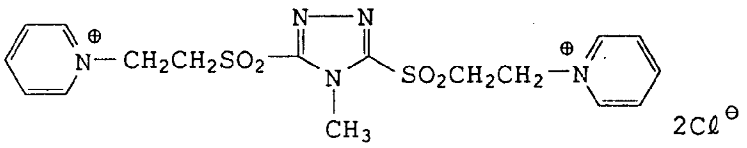
VS-52 $(CH_2=CHSO_2CH_2)_3CCHSO_2(CH_2)_2C\ell$

VS-53 $H_2C=CHSO_2CH=CH_2$

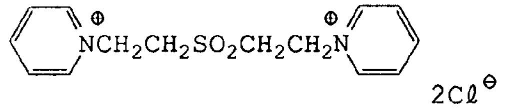
VS-54 $H_2C=CHSO_2CH_2(CH_2SO_2CH_2CH_2OSO_3^{\ominus}Na^{\oplus})_3$

VS-55 $CH_3SO_3(CH_2)_2SO_2(CH_2)_2OSO_2CH_3$

VS-56



VS-57



The vinylsulfone type hardening agent used in the present invention may include, for example, the aromatic compounds as disclosed in German Patent No. 1,100,942, U.S. Patent No. 3,490,911, etc., the alkyl compounds bonded with a hetero atom, as disclosed in Japanese Patent Examined Publications No. 29622/1969, No. 25373/1972, No. 24259/1972, etc., the sulfonamide or ester compounds as disclosed in Japanese Patent Examined Publication No. 8736/1972, the 1,3,5-tris[β-(vinylsulfonyl)-propionyl]hexahydro-S-triazine as disclosed in Japanese Patent O.P.I. Publication No. 24435/1974, etc., the alkyl compounds as disclosed in Japanese Patent Examined Publication No. 35807/1975, Japanese Patent O.P.I. Publication No. 44164/1976, etc., and the compounds as disclosed in Japanese Patent O.P.I. Publication No. 18944/1984, etc.

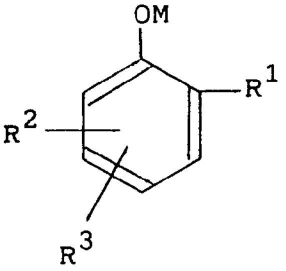
These vinylsulfone type hardening agents may be dissolved in water or an organic solvent when used, and may be used in an amount of 0.005 % by weight to 20 % by weight, and preferably 0.02 % by weight to 10 % by weight, based on a binder (e.g., gelatin).

When they are added to photographic layers, a batch system or an in-line addition system is employed.

When these hardening agents are added to photographic layers, there are no particular limitations on the layer(s) to which they are added. For example, any of them may be added to the uppermost one layer, the lowermost one layer or all the layers.

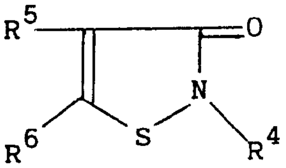
In the present invention, the light-sensitive silver halide color photographic material may preferably contain at least one of compounds represented by the following Formulas B-1 to B-3.

Formula B-1

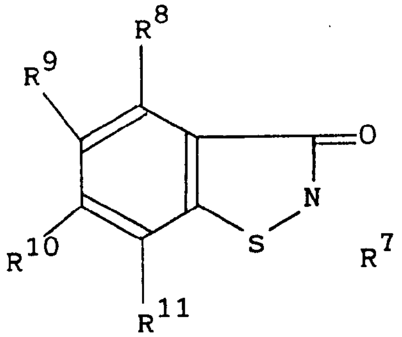


wherein R^1 represents an alkyl group, an cycloalkyl group, an aryl group, a hydroxyl group, an alkoxycarbonyl group, an amino group a carboxylic acid group (including a salt thereof) or a sulfonic acid group (including a salt thereof); R^2 and R^3 each represent a hydrogen atom, a halogen atom, an amino group, a nitro group, a hydroxyl group, an alkoxycarbonyl group, a carboxylic acid group (including a salt thereof) or a sulfonic acid group (including a salt thereof); and M represents a hydrogen atom, an alkali metal or an ammonium group.

Formula B-2



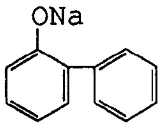
Formula B-3



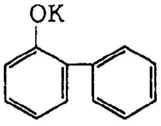
wherein R^4 represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a halogenated alkyl group, $-R^{12}-OR^{13}$, $-CONHR^{14}$ (where R^{12} represents an alkyl group and R^{13} and R^{14} each represent a hydrogen atom, an alkyl group or an arylalkyl group) or an arylalkyl group; R^5 and R^6 each represent a hydrogen atom, a halogen atom, a halogenated alkyl group or an alkyl group; R^7 represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a halogenated alkyl group, an arylalkyl group, $-R^{15}-OR^{16}$ or $-CONHR^{17}$ (where R^{15} represents an alkylene group, and R^{16} and R^{17} each represent a hydrogen atom or an alkyl group); R^8, R^9, R^{10} and R^{11} each represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkyl group, an amino group or a nitro group.

As examples of the compound represented by Formula B-1, the compound may include the following exemplary compounds.

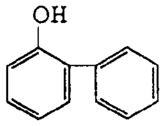
(B-1-1)



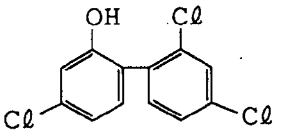
(B-1-2)



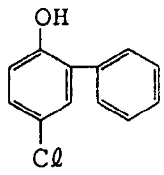
(B-1-3)



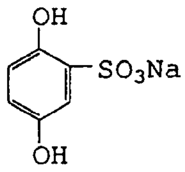
(B-1-4)



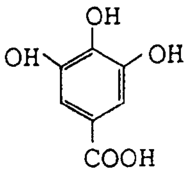
(B-1-5)



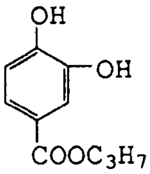
(B-1-6)



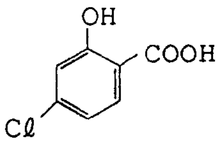
(B-1-7)



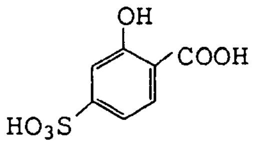
(B-1-8)



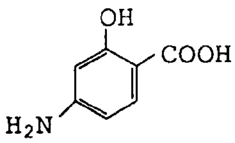
(B-1-9)



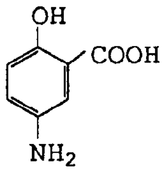
(B-1-10)



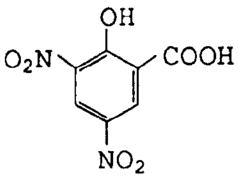
(B-1-11)



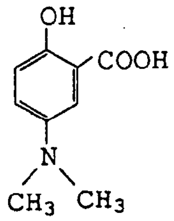
(B-1-12)



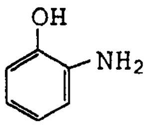
(B-1-13)



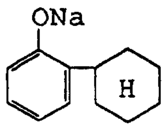
(B-1-14)



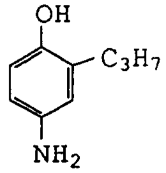
(B-1-15)



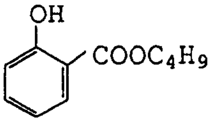
(B-1-16)



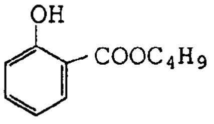
(B-1-17)



(B-1-18)



(B-1-19)



Some of the above compound represented by Formula B-1 are known as antiseptics of oranges or the like and are on the market. Thus, they are readily available to those skilled in the art.

Preferred compounds among the above exemplary compounds are B-1-1, B-1-2, B-1-3, B-1-4 and B-1-5.

The compound represented by Formula B-1 may preferably be used in an amount of 0.03 g to 50 g, more preferably 0.12 g to 10 g, and particularly preferably 0.15 g to 5 g, per liter of the stabilizing solution of the present invention.

Specific exemplary compounds of the compounds represented by Formulas B-2 and B-3 are shown below. Examples are by no means limited to these.

B-2-1	2-Methyl-4-isothiazolin-3-one
B-2-2	5-Chloro-2-methyl-4-isothiazolin-3-one
B-2-3	2-Methyl-5-phenyl-4-isothiazolin-3-one
B-2-4	4-Bromo-5-chloro-2-methyl-4-isothiazolin-3-one
B-2-5	2-Hydroxymethyl-4-isothiazolin-3-one
B-2-6	2-(2-Ethoxyethyl)-4-isothiazolin-3-one
B-2-7	2-(N-methyl-carbamoyl-4-isothiazolin-3-one
B-2-8	5-Bromomethyl-2-(N-dichlrophenyl-carbamoyl)-4-isothiazolin-3-one
B-2-9	5-Chloro-2-(2-phenylethyl)-4-isothiazolin-3-one
B-2-10	4-Methyl-2-(3,4-dichlorophenyl)-4-isothiazolin-3-one
B-3-1	1,2-Benzisothiazolin-3-one
B-3-2	2-(2-Bromoethyl)-1,2-benzisothiazolin-3-one
B-3-3	2-Methyl-1,2-benzisothiazolin-3-one
B-3-4	2-Ethyl-5-nitro-1,2-benzisothiazolin-3-one
B-3-5	2-Benzyl-1,2-benzisothiazolin-3-one
B-3-6	5-Chloro-1,2-benzisothiazolin-3-one

With regard to these exemplary compounds, methods for their synthesis and examples of application thereof to other fields are disclosed in U.S. Patents No. 2,767,172, No. 2,767,173, No. 2,767,174 and No. 2,870,015, British Patent No. 848,130, French Patent No. 1,555,416, etc. Some of them are also on the market, and available under trade names of Topcide 300 (Permachem Asia Ltd.), Topcide 600 (Permachem Asia Ltd.), or Finecide J-700 (Tokyo Fine Chemical Co., Ltd.) and Proxel GXL (I.C.I. Organics, Inc.).

These compounds represented by Formulas B-1 to B-3 may each be used in an amount ranging from 0.1 mg to 500 mg, and preferably from 0.5 mg to 100 mg. per 1 m^2 of the light-sensitive material. These compounds represented by Formulas B-1 to B-3 may also be used in combination of two or more kinds.

The present invention can be applied to light-sensitive color photographic materials for general use or for use in motion pictures or the like, such as color papers, color negative films, color reversal films, color reversal papers, direct positive color papers; movie color films and television color films.

EXAMPLES

Specific examples of the present invention will be described below. Embodiments for carrying out the present invention are by no means limited to these.

Example 1

A light-sensitive silver halide photographic material having been exposed was processed using a slit type automatic processor 1 as shown in Fig. 1 (a cross-sectional view). As shown in Fig. 1, a processing tank 2 is comprised of a processing housing 4 and fitted therein a lid 8 hanging a comb-shaped upper lid 6, to form a processing path 15 with a narrow clearance (a slit-like cross section). The lid 8 is provided with a handle 10. The upper lid 6 comprises a plurality of upper lid members 12 having a rectangular cross section and made of vinyl chloride, which are substantially vertically disposed. Carrying reels 16 for the light-sensitive silver halide photographic material (N) are disposed at the upper and lower ends of these upper lid members.

Inside the processing housing, tank wall members 14 that form the processing path 15 in combination with the upper lid members 12 are disposed. Thus, the upper lid members 12 and the tank wall members 14 constitute the processing path in a wavy or serpentine continuous form and the light-sensitive material carrying reels 16 are each disposed at the part where the processing path bents at its each top and bottom. In the processor shown in Fig. 1, four light-sensitive material carrying reeels are provided at its upper part, and five reels at its lower part.

In the following description, CD denotes color developing (or a color developing bath); BL, bleaching (or a bleaching bath); and STB, stabilizing (or a stabilizing bath).

The processing path 15 is provided with replenishing openings 5, 9, 13, 32 and 34 and overflows 3, 7, 11, 31 and 33. Processing solutions are replenished from the replenishing openings and discharged from the overflows.

Each replenishing opening is provided at a little higher position than each overflow. A light-sensitive material feed reel 17 and a take-up reel 18 are disposed at the left upper part and right upper part, respectively, of the processing path 15. Ahead the take-up reel 18, the processing path is connected with a drying zone 19. At the right upper part of the drying zone 19, another light-sensitive material take-up roll 21 is disposed. In order to maintain the processing solutions to a given temperature, hot water is put in the processing housing 4. The light-sensitive material N is then fed through the light-sensitive material feed reel 17 to the processing path 15, and photographically processed while it is, transported by means of the plural light-sensitive material carrying reels 16. The light-sensitive material processed is passed over the take-up reel 18, and then taken out after drying.

Each aperture area of the STB was adjusted by controlling the space between the upper lid member 12 and the tank wall member 14 so as to give the aperture area as shown in Table 1 shown later.

A multi-layer color negative film processed in Example 1 was prepared in the following way.

In the following, the amounts of the components added in the light-sensitive silver halide photographic material are indicated as gram number per 1 m^2 unless particularly noted. Those of silver halides and colloidal silver are indicated in terms of silver. Meanwhile, those of sensitizing dyes are indicated as molar number per mole of silver halide in the same layer.

- Light-sensitive Material Sample -

First layer: Anti-halation layer

Black colloidal silver	0.2
UV absorbent (UV-1)	0.23
High-boiling solvent (Oil-1)	0.18
Gelatin	1.4

Second layer: First intermediate layer

Gelatin	1.3

Third layer: Low-speed red-sensitive emulsion layer

Silver iodobromide emulsion	1.0
(average grains size: 0.4 μm; AgI: 2.0 mol%)	
Sensitizing dye (SD-1)	1.8×10^{-5} mol/mol·Ag
Sensitizing dye (SD-2)	2.8×10^{-4} mol/mol·Ag
Sensitizing dye (SD-3)	3.0×10^{-4} mol/mol·Ag
Cyan coupler (C-1)	0.70
Colored cyan coupler (CC-1)	0.066
DIR compound (D-1)	0.03
DIR compound (D-3)	0.01
High-boiling solvent (Oil-1)	0.64
Gelatin	1.2

Fourth layer: Mid-speed red-sensitive emulsion layer

Silver iodobromide emulsion	0.8
(average grains size: 0.7 μm; AgI: 8.0 mol%)	
Sensitizing dye (SD-1)	2.1×10^{-5} mol/mol·Ag
Sensitizing dye (SD-2)	1.9×10^{-4} mol/mol·Ag
Sensitizing dye (SD-3)	1.9×10^{-4} mol/mol·Ag
Cyan coupler (C-1)	0.28
Colored cyan coupler (CC-1)	0.027
DIR compound (D-1)	0.01
High-boiling solvent (Oil-1)	0.26
Gelatin	0.6

Fifth layer: High-speed red-sensitive emulsion layer

Silver iodobromide emulsion	1.70
(average grains size: 0.8 µm; AgI: 8.0 mol%)	
Sensitizing dye (SD-1)	1.9×10^{-5} mol/mol·Ag
Sensitizing dye (SD-2)	1.7×10^{-4} mol/mol·Ag
Sensitizing dye (SD-3)	1.7×10^{-4} mol/mol·Ag
Cyan coupler (C-1)	0.05
Cyan coupler (C-2)	0.10
Colored cyan coupler (CC-1)	0.02
DIR compound (D-1)	0.025
High-boiling solvent (Oil-1)	0.17
Gelatin	1.2

Sixth layer: Second intermediate layer

Gelatin 0.8

Seventh layer: Low-speed green-sensitive emulsion layer

Silver iodobromide emulsion	1.1
(average grains size: 0.4 µm; AgI: 2.0 mol%)	
Sensitizing dye (SD-4)	6.8×10^{-5} mol/mol·Ag
Sensitizing dye (SD-5)	6.2×10^{-4} mol/mol·Ag
Magenta coupler (M-1)	0.54
Magenta coupler (M-2)	0.19
Colored magenta coupler (CM-1)	0.06
DIR compound (D-2)	0.017
DIR compound (D-3)	0.01
High-boiling solvent (Oil-2)	0.81
Gelatin	1.8

Eighth layer: Mid-speed green-sensitive emulsion layer

Silver iodobromide emulsion	0.7
(average grains size: 0.7 µm; AgI: 8.0 mol%)	
Sensitizing dye (SD-6)	1.9×10^{-4} mol/mol·Ag
Sensitizing dye (SD-7)	1.2×10^{-4} mol/mol·Ag
Sensitizing dye (SD-8)	1.5×10^{-5} mol/mol·Ag
Magenta coupler (M-1)	0.07
Magenta coupler (M-2)	0.03
Colored magenta coupler (CM-1)	0.04
DIR compound (D-2)	0.018
High-boiling solvent (Oil-2)	0.30
Gelatin	0.8

Ninth layer: High-speed green-sensitive emulsion layer

Silver iodobromide emulsion	1.7
(average grains size: 1.0 µm; AgI: 8.0 mol%)	
Sensitizing dye (SD-6)	1.2×10^{-4} mol/mol·Ag
Sensitizing dye (SD-7)	1.0×10^{-4} mol/mol·Ag
Sensitizing dye (SD-8)	3.4×10^{-6} mol/mol·Ag
Magenta coupler (M-1)	0.09
Magenta coupler (M-3)	0.04
Colored magenta coupler (CM-1)	0.04
High-boiling solvent (Oil-2)	0.31
Gelatin	1.2

Tenth layer: Yellow filter layer

Yellow colloidal silver	0.05
Anti-color-stain agent (SC-1)	0.1
High-boiling solvent (Oil-2)	0.13
Gelatin	0.7
Formalin scavenger (HS-1)	0.09
Formalin scavenger (HS-2)	0.07

Eleventh layer: Low-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grains size: 0.4 µm; AgI: 2.0 mol%)	
Silver iodobromide emulsion (average grains size: 0.7 µm; AgI: 8.0 mol%)	(in total) 0.5
Sensitizing dye (SD-9)	5.2×10^{-4} mol/mol·Ag
Sensitizing dye (SD-10)	1.9×10^{-5} mol/mol·Ag
Yellow coupler (Y-1)	0.65
Yellow coupler (Y-2)	0.24
DIR compound (D-1)	0.03
High-boiling solvent (Oil-2)	0.18
Gelatin	1.3
Formalin scavenger (HS-1)	0.08

Twelfth layer: High-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grains size: 1.0 µm; AgI: 8.0 mol%)	1.0
Sensitizing dye (SD-9)	1.8×10^{-4} mol/mol·Ag
Sensitizing dye (SD-10)	7.9×10^{-5} mol/mol·Ag
Yellow coupler (Y-1)	0.15
Yellow coupler (Y-2)	0.05
High-boiling solvent (Oil-2)	0.074
Gelatin	1.30
Formalin scavenger (HS-1)	0.05
Formalin scavenger (HS-2)	0.12

Thirteenth layer: First protective layer

Fine-grain silver iodobromide emulsion (average grains size: 0.08 μm; AgI: 1 mol%)	0.4
UV absorbent (UV-1)	0.07
UV absorbent (UV-2)	0.10
High-boiling solvent (Oil-1)	0.07
High-boiling solvent (Oil-3)	0.07
Formalin scavenger (HS-1)	0.13
Formalin scavenger (HS-2)	0.37
Gelatin	1.3

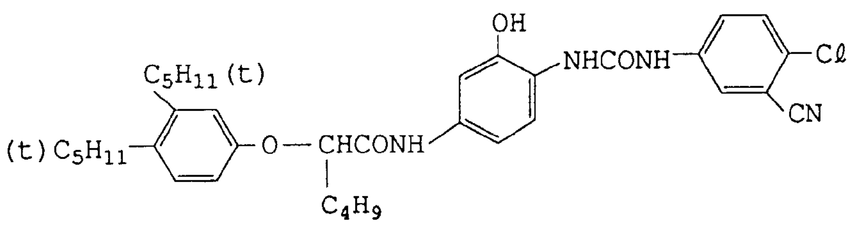
Fourteenth layer: Second protective layer

Alkali-soluble matting agent (average particle diameter: 2 μm)	0.13
Polymethyl methacrylate (average particle diameter: 3 μm)	0.02
Lubricant (WAX-1)	0.04
Gelatin	1.3

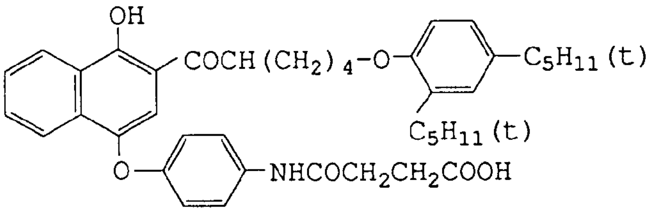
In addition to the above composition, a coating aid Su-1, a dispersing agent Su-2, a viscosity regulator, hardening agents H-1 and H-2, a stabilizer ST-1, antifoggants AF-1 and two kinds of AF-2 with Mw of 10,000 and Mw of 1,100,000 were added to each layer.

The emulsions used in the above sample was a monodisperse emulsion of the type wherein less silver iodide is contained in its grain surfaces, and was subjected to optimum gold and sulfur sensitization according to a conventional method. The average grain size is indicated as grain size calculated as a cube.

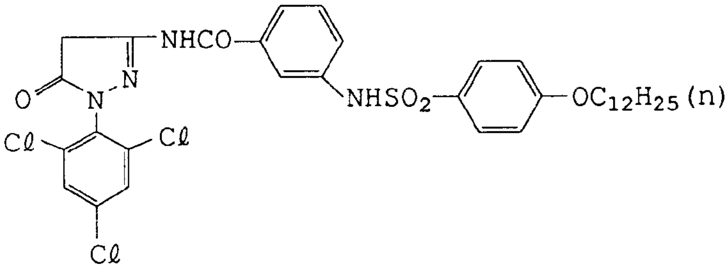
C-1



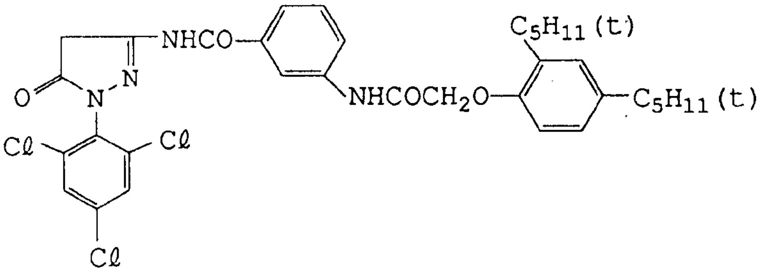
C-2


OH
COCH(CH2)4-O
C5H11(t)
C5H11(t)
O
NHCOCH2CH2COOH

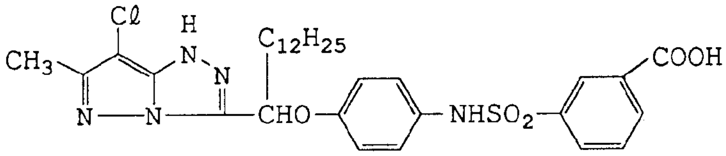
M-1


NHCO
O
N
N
NHSO2
OC12H25(n)
Cℓ
Cℓ
Cℓ

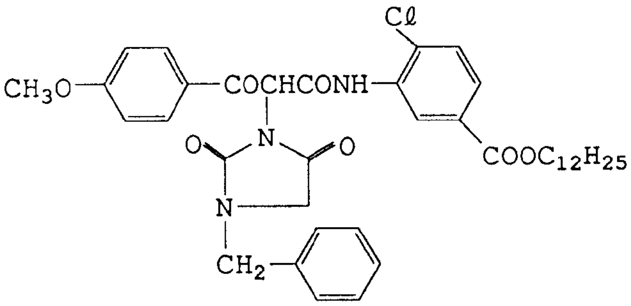
M-2


NHCO
C5H11(t)
O
N
N
NHCOCH2O
C5H11(t)
Cℓ
Cℓ
Cℓ

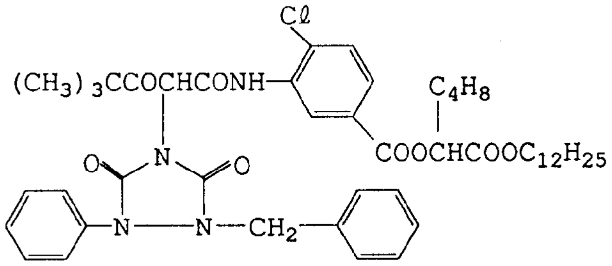
M-3


Cℓ
H
C12H25
COOH
CH3
N
N
N
N
CHO
NHSO2

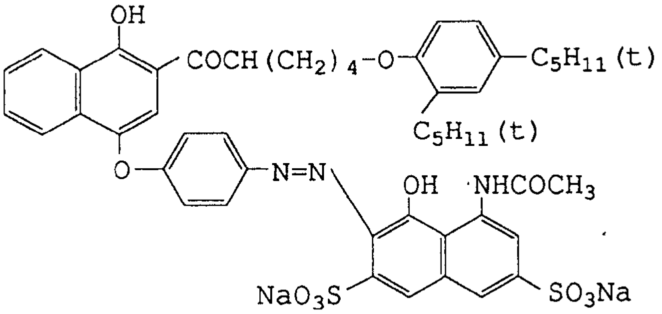
Y-1


Cℓ
CH3O
COCHCONH
O
N
O
COOC12H25
N
CH2

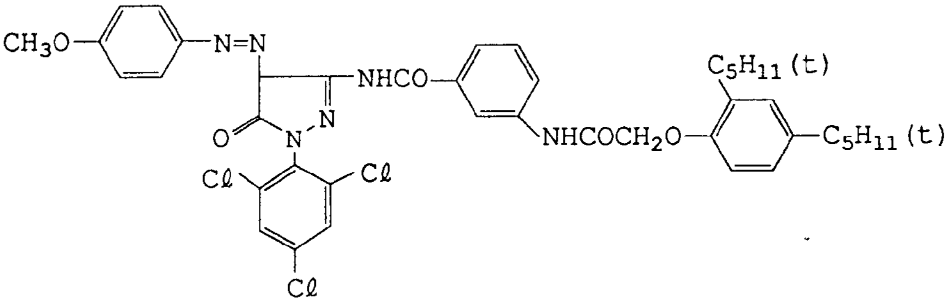
Y-2



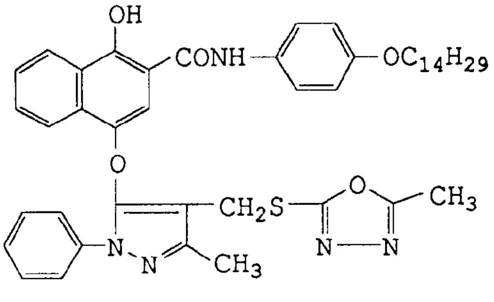
CC-1



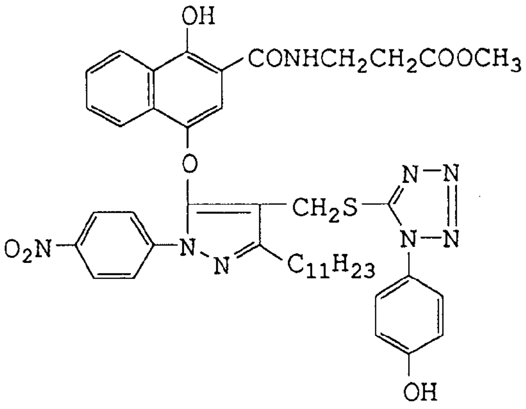
CM-1



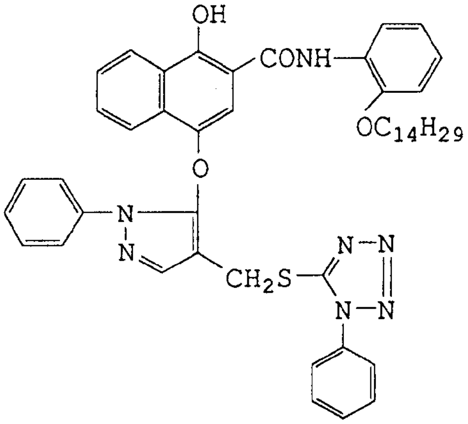
D-1



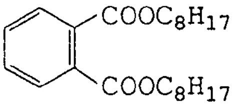
D-2



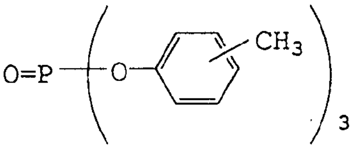
D-3



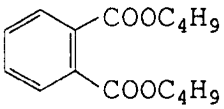
Oil-1



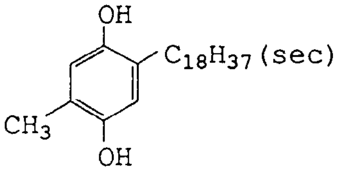
Oil-2



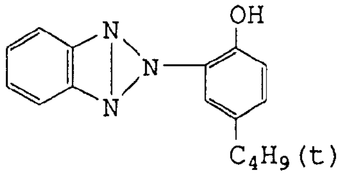
Oil-3



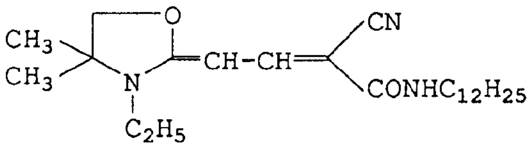
SC-1



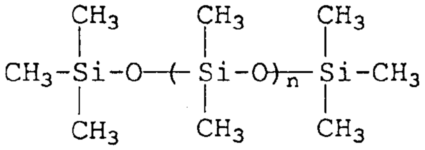
UV-1



UV-2



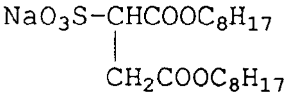
WAX-1



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

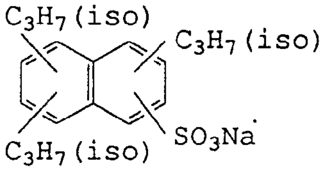
Mw=3,000 (weight-average molecular weight)

Su-1

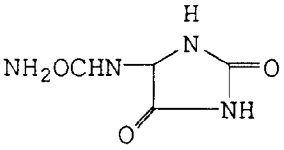


$$NaO_3S-\underset{CH_2COOC_8H_{17}}{CH}COOC_8H_{17}$$

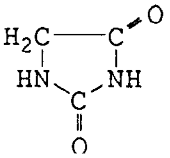
Su-2



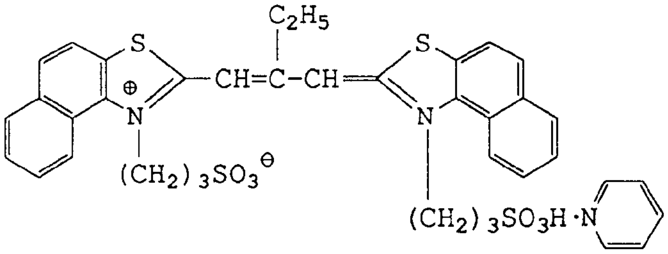
HS-1



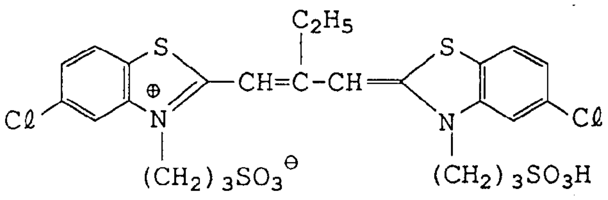
HS-2



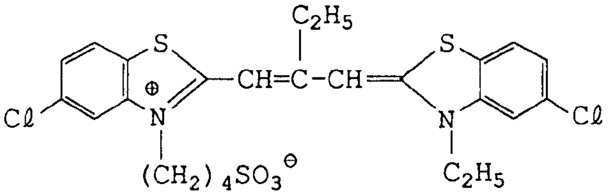
SD-1



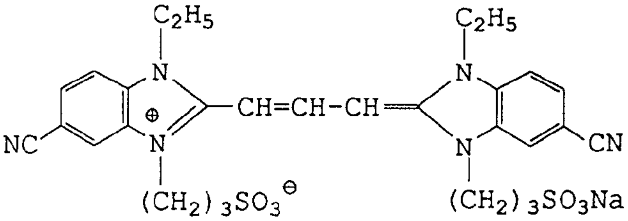
SD-2



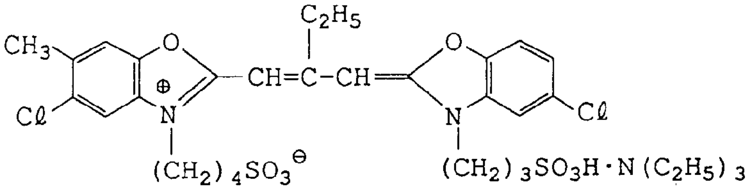
SD-3



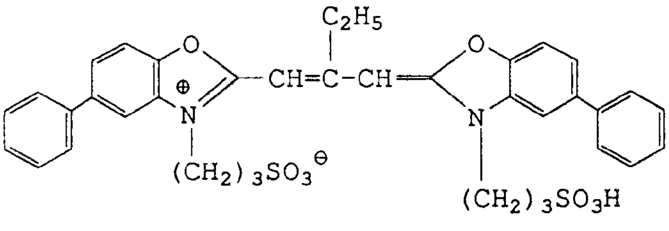
SD-4



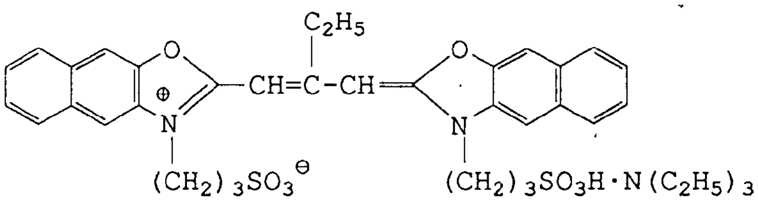
SD-5



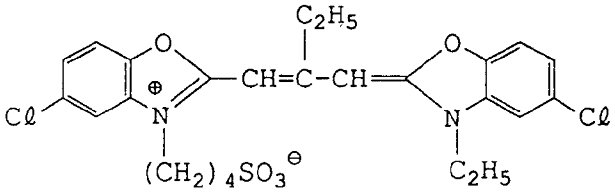
SD-6



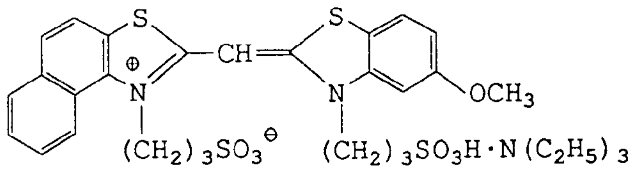
SD-7



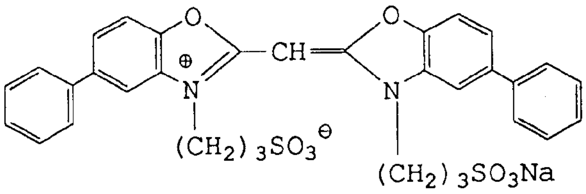
SD-8



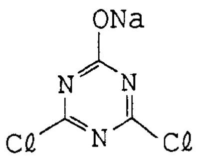
SD-9



SD-10



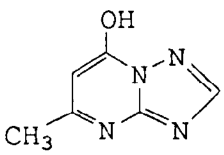
H-1



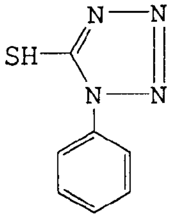
H-2

$(CH_2{=}CHSO_2CH_2)_2O$

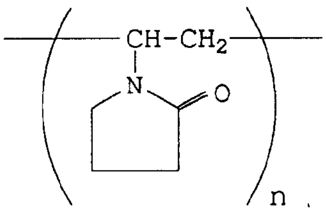
ST-1



AF-1



AF-2



n: (polymerization degree)

The film sample thus prepared was subjected to practical exposure using a camera, and running tests were carried out under the following conditions.

Processing step	Processing Time	Processing temperature	Amount of replenishing
Color developing	3 min 15 sec	38°C	775 ml
Bleaching	45 sec	38°C	155 ml
Fixing	1 min 30 sec	38°C	500 ml
Stabilizing	50 sec	38°C	775 ml
Drying	1 min	40-70°C	-

(The amount of replenishing is indicated as a value per 1 m^2 of light-sensitive material)

The stabilizing was carried out in a two-bath countercurrent and by a system in which the stabilizing solution is replenished to the final bath and its overflow is flowed in the pre-bath. In addition, part (275 ml/m^2) of the overflow from the stabilizing bath subsequent to the fixing bath was flowed into the fixing bath.

A color developing solution used was composed of the following:

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.2 g

Potassium iodide	0.6 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate	4.6 g
Diethylenetriaminepentaacetic acid	3.0 g
Potassium hydroxide	1.2 g

Made up to 1 liter by adding water, and adjusted to pH 10.01 using potassium hydroxide or 20 % sulfuric acid.

A color developing replenishing solution used was composed of the following:

Potassium carbonate	40 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	7 g
Sodium bromide	0.5 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate	6.0 g
Diethylenetriaminepentaacetic acid	3.0 g
Potassium hydroxide	2 g

Made up to 1 liter by adding water, and adjusted to pH 10.12 using potassium hydroxide or 20 % sulfuric acid.

A bleaching solution used was composed of the following:

Ferric ammonium 1,3-propylenediaminetetraacetate

(Exemplary Compound A-1)	0.32 mol
Disodium ethylenediaminetetraacetate	10 g
Ammonium bromide	100 g
Glacial acetic acid	40 g
Ammonium nitrate	40 g

Made up to 1 liter by adding water, and adjusted to pH 4.4 using ammonia water.

A bleaching replenishing solution was composed of the following:

Ferric ammonium 1,3-propylenediaminetetraacetate

(Exemplary Compound A-1)	0.35 mol
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	120 g
Ammonium nitrate	50 g
Glacial acetic acid	40 g

Made up to 1 liter by adding water, and adjusted to pH 3.4 using ammonia water.

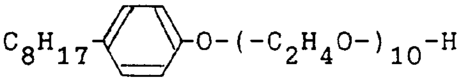
A fixing solution and fixing replenishing solution used were composed of the following:

Ammonium thiosulfate	250 g
Anhydrous sodium bisulfite	20 g
Sodium metabisulfite	4.0 g
Disodium ethylenediaminetetraacetate	1.0 g

Made up to 1 liter by adding water, and adjusted to pH 6.5 using glacial acetic acid and ammonia water.

A stabilizing solution and stabilizing replenishing solution use were composed of the following:

Surface active agent 0.1 g



Formalin and the compound of the present invention as shown in Table 1

Made up to 1 liter by adding water, and adjusted to pH 7.0 using potassium hydroxide or sulfuric acid.

Running processing was carried out at 0.3 R (which means that the proportion of the amount of replenishing solutions with respect to the capacity of baths is 30 %) per day over a period of 20 days. Deposition of crystals at the transport apertures at the cross-over from the fixing bath to stabilizing bath and the cross-over from the first stabilizing bath to second stabilizing bath, the occurrence of scratches on the light-sensitive material processed, the appearance of solutions after processing, and the decrease in green densities at the maximum density portions of the processed samples after storage of two weeks at a temperature of 50°C and a humidity of 75%RH were examined and evaluated. Results obtained are shown in Table 1.

Evaluation was made according to the following criteria.

Storage stability of solutions

AA:	No precipitates are seen even after storage for more than 2 weeks.
A:	Precipitates appeared in 2 weeks.
B:	Precipitates appeared in 1 to 2 weeks
C:	Precipitates appeared in 3 to 5 days
D:	Precipitates appeared in 2 days.

Deposition of crystals

AA:	No deposition at transport apertures.
A:	Slight deposition at transport apertures.
B:	Deposition occurs at transport apertures, but light-sensitive materials can be transported.
C:	Deposition occurs at transport apertures to cause jamming occasionally during transport.
D:	Deposition occurs in a large quantity at transport apertures to cause jamming frequently during transport.

Occurrence of scratches

AA:	No scratch at all.
A:	Small scratches are occasionally seen.
B:	Small scratches are seen.
C:	Clear scratches are occasionally seen and small scratches are frequently seen.
D:	Clear scratches are seen in a large number.

Table 1

Test No.	Aperture area (cm^2/Ω)	Formaldehyde or compound of the invention	(1)	(2)	(3)	Green density difference *1
1-1	1.0	Formaldehyde 5.0×10^{-2} mol/Ω	D	D	D	-0.10
1-2	1.0	" 1.0×10^{-3} "	B	B	B	-0.15
1-3	1.0	" 0 "	AA	AA	AA	-0.25
1-4	10	" 1.0×10^{-3} "	A	A	D	-0.17
1-5	5.0	" 1.0×10^{-3} "	B	B	C	-0.15
1-6	0.5	" 1.0×10^{-3} "	C	C	A	-0.14
1-7	10	F-1-1 0.3 g/Ω	AA	AA	C	-0.12
1-8	5.0	" "	AA	AA	A	-0.11
1-9	2.5	" "	AA	AA	A-AA	-0.11
1-10	1.0	" "	AA	AA	AA	-0.11
1-11	0.5	" "	A	A	AA	-0.10
1-12	10	F-2-1 0.3 g/Ω	AA	AA	C	-0.13
1-13	5.0	" "	AA	AA	A	-0.12
1-14	2.5	" "	AA	AA	A-AA	-0.11
1-15	1.0	" "	AA	AA	AA	-0.11
1-16	0.5	" "	A	A	AA	-0.10

Table 1 (cont'd)

Test No.	Aperture area	Formaldehyde or compound of the invention		(1)	(2)	(3)	Green density difference *1
	(cm^2/Ω)						
1-17	10	A-1-1	0.3 g/Ω	A	AA	C	-0.10
1-18	5.0	"	"	A	AA	A	-0.10
1-19	2.5	"	"	A	AA	A-AA	-0.10
1-20	1.0	"	"	A	AA	AA	-0.09
1-21	0.5	"	"	A	A	AA	-0.09
1-22	1.0	F-1-5	0.3 g/Ω	AA	AA	AA	-0.14
1-23	"	F-1-16	"	A	A	A	-0.16
1-24	"	F-2-2	"	AA	AA	AA	-0.13
1-25	"	F-3-1	"	A	A	A	-0.17
1-26	"	F-4-1	"	A	A	A	-0.15
1-27	"	F-5-1	"	A	A	A	-0.18
1-28	"	F-6-1	"	A	A	A	-0.18
1-29	"	F-7-1	"	A	A	A	-0.17
1-30	"	F-8-1	"	A	A	A	-0.17
1-31	"	F-9-1	"	A	A	A	-0.16
1-32	"	F-10-1	"	A	A	A	-0.17

(1): Deposition of crystals

(2): Occurrence of scratches

(3): Storage stability of stabilizing solution

*1: (Transmission density after storage) - (Transmission density on the very day)

As is clear from the results shown in Table 1, use of the stabilizing solution containing formaldehyde brings about the problems that crystals are more deposited and scratches more greatly occur as the aperture area is made smaller. Although such problems can be eliminated to a certain extent as the concentration of formaldehyde is lowered, there is a disadvantage of a great decrease in green density after storage of images.

On the other hand, it is seen that use of the compound of the present invention brings about the advantages that the effect becomes more remarkable as the aperture area is made smaller, and moreover the storage stability of the stabilizing solution can be improved and the transmission green density after storage can be prevented from decreasing to a certain extent.

In particular, among the compounds of the present invention, the compounds A-1-1, F-1-1 and F-2-1 are seen to be greatly effective.

Example 2

Tests of No. 1-20 making use of the compound A-1-1 and Test No. 1-2 making use of formaldehyde in Example 1 were repeated except that the pH of the stabilizing solution was changed as shown in Table 2. Evaluation was made in the same manner as in Example 1.

Results obtained are shown in Table 2 (No. 1-2 and No. 1-20 in Example 1 correspond to Nos. 2-1 to 2-5 and No. 2-1 to 2-10, respectively).

Table 2

Test No.	Formaldehyde or compound of the invention	pH of stabilizing sol.	(1)	(2)	(3)	Green *1 density difference
2-1	Formaldehyde 1.0×10^{-3} mol/Ω	4.0	C	C	C	-0.15
2-2	"	5.0	C	C	C	-0.15
2-3	"	7.0	B	B	B	-0.15
2-4	"	9.0	B	B	B	-0.17
2-5	"	10.0	B	B	B	-0.18
2-6	A-1-1 0.3 g/Ω	4.0	B	B-A	B-A	-0.10
2-7	"	5.0	B	B-A	A	-0.10
2-8	"	7.0	A	AA	AA	-0.09
2-9	"	9.0	AA	AA	AA	-0.07
2-10	"	10.0	AA	AA	AA	-0.06

(1): Deposition of crystals

(2): Occurrence of scratches

(3): Storage stability of stabilizing solution

*1: (Transmission density after storage) - (Transmission density on the very day)

As is clear from Table 2, when the pH of the stabilizing solution is changed, no remarkable changes are seen in the characteristics of the stabilizing solutions containing formaldehyde. However, the effect on the storage stability of solutions and against the deposition of crystals and occurrence of scratches is seen to become more remarkable at pH 7.0 or more, particularly pH 9.0 or more, when the compound A-1-1 is used.

The same tendency was also seen when compounds F-1-1, F-1-10, F-2-1, F-3-1, F-3-4, F-4-1, F-6-1, F-7-15, F-9-6, F-10-4, F-10-13 and F-10-17.

Example 3

Tests of Nos. 1-6, 1-11, 1-16 and 1-21 (the aperture area is 0.5 each) and Nos. 1-2, 1-10, 1-15 and 1-20 (the aperture area is 1.0 each) in Example 1 were repeated except that the fixing solution and fixing replenishing solution were changed as shown below. Evaluation was made in the same manner as in Example 1.

Here, the running processing was carried out over a period of 1 month.

Results obtained are shown in Table 3 (No. 1-6, No. 1-11, No. 1-16 and No. 1-21 in Example 1 correspond to Nos. 3-1 to 3-3, Nos. 3-4 to 3-6, Nos. 3-7 to 3-9 and Nos. 3-10 to 3-12, respectively. No. 1-2, No. 1-10, No. 1-15 and No. 1-20 in Example 1 correspond to Nos. 3-13 to 3-15, Nos. 3-16 to 3-18, Nos. 3-19 to 3-21 and Nos. 3-22 to 3-24, respectively.)

- Fixing solution and fixing replenishing solution -

Ammonium thiosulfate	as shown in Table 3
Anhydrous sodium bisulfite	20 g
Ammonium thiocyanate	as shown in Table 3
Sodium metabisulfite	4.0 g
Disodium ethylenediaminetetraacetate	1.0 g

Made up to 1 liter by adding water, and adjusted to pH 7.0 using glacial acetic acid and ammonia water.

Table 3

Test No.	Formaldehyde or compound of the invention	AmTSF/ AmTCN (mol/Ω)	(1)	(2)	(3)	(4)
3-1	Formaldehyde $1.0x10^{-3}$ mol/Ω	1.7/None	C	C	A	-0.15
3-2	"	1.6/0.1	C-B	C-B	A	-0.15
3-3	"	1.1/0.6	B	B	A	-0.14
3-4	F-1-1 0.3 g/Ω	1.7/None	A	A	AA	-0.10
3-5	"	1.6/0.1	A-AA	A-AA	AA	-0.09
3-6	"	1.1/0.6	AA	AA	AA	-0.08
3-7	F-2-1 0.3 g/Ω	1.7/None	A	A	AA	-0.10
3-8	"	1.6/0.1	A-AA	AA	AA	-0.08
3-9	"	1.1/0.6	AA	AA	AA	-0.07
3-10	A-1-1 0.3 g/Ω	1.7/None	A	A	AA	-0.09
3-11	"	1.6/0.1	A-AA	A-AA	AA	-0.08
3-12	"	1.1/0.6	AA	AA	AA	-0.07

Table 3 (cont'd)

Test No.	Formaldehyde or compound of the invention	AmTSF/ AmTCN (mol/Ω)	(1)	(2)	(3)	(4)
3-13	Formaldehyde 1.0×10^{-3} mol/Ω	1.7/None	C	C	B	-
3-14	"	1.6/0.1	C	C	B	-
3-15	"	1.1/0.5	B	B	A	-
3-16	F-1-1 0.3 g/Ω	1.7/None	A	A	A	-
3-17	"	1.6/0.1	AA	AA	A	-
3-18	"	1.1/0.5	AA	AA	AA	-
3-19	F-2-1 0.3 g/Ω	1.7/None	A	A	A	-
3-20	"	1.6/0.1	AA	AA	A	-
3-21	"	1.1/0.5	AA	AA	AA	-
3-22	A-1-1 0.3 g/Ω	1.7/None	A	A	A	-
3-23	"	1.6/0.1	AA	AA	A	-
3-24	"	1.1/0.5	AA	AA	AA	-

AmTSF: Ammonium thiosulfate

AmTCN: Ammonium thiocyanate

(1): Deposition of crystals

(2): Occurrence of scratches

(3): Storage stability of stabilizing solution

(4): Green density difference = (Transmission density after storage) - (Transmission density on the very day)

As is clear from the results shown in Table 3, addition of thiocyanates is seen to bring about a decrease in the deposition of crystals and occurrence of scratches and also to bring about an improved storage stability of processing solutions.

Example 4

In Example 3, the amount of the ammonium serving as the cation in respect of the thiosulfates and thiocyantes was changed to 50 mol %, 10 mol % or 0 mol % and the ammonium was replaced with potassium. As a result, although Tests Nos. 3-1 to 3-3 and 3-13 to 3-15 making use of formaldehyde tended to show an increase in the deposition of crystals and a deterioration of the storage stability of solutions, Tests Nos. 3-4 to 3-12 and 3-16 to 3-24 making use of the compounds of the present invention showed little influence in the systems in which the thiocyanates were used.

Example 5

In Example 3, the total coating weight of silver in the light-sensitive material used in Example 1 was changed to 1.5, 2.0, 5.0 or 1.0 g per 1 m^2 in the same proportions for each layer. As a result, the deposition of crystals at the transport aperture at the cross-over from the fixing bath to stabilizing bath became serious when the silver weight is 2.0 or more. This tendency was remarkable when the thiosulfate was used as the fixing agent or the formaldehyde was used in the stabilizing solution, but the deposition of crystals became only a little observable even with an increase in the amount of silver, when the fixing solution making use of the thiocyanate and the stabilizing solution making use of the compound of the present invention are used. Thus there was a meaningful difference between the former and the latter.

Example 6

The same evaluation tests as in Example 1 were carried out using the light-sensitive silver halide color photographic material as used in Example 1, but using an automatic processor as shown in Fig. 2, comprised of processing tanks successively arranged. As a result, it was possible to obtain substantially the same results as in Example 1. It was also found possible to prevent jamming troubles. In the present Example, the evaluation tests were carried out in the state the aperture area was adjusted to 1 cm^2/lit.

In the automatic processor shown in Fig. 2, the aperture area refers to that of an air hole 22.

Example 7

The same evaluation tests as in Example 1 were carried out except that in the light-sensitive silver halide color photographic material as used in Example 1 the magenta couplers M-1 and M-2 were replaced with the magenta coupler as disclosed in Japanese Patent O.P.I. Publication No. 106655/1988, page 26 of its specification, specifically, each of the magenta couplers 1, 2, 4, 10, 20, 21, 31, 40, 60, 63, 64, 74, 76 and 81 disclosed in Japanese Patent O.P.I. Publication No. 106655/1988, pages 26 to 34 of its specification, the cyan coupler C-2 was replaced with each of the cyan couplers (C′-2), (C′-27), (C′-32), (C′-33), (C′-34), (C′-36), (C′-37), (C′-38), (C′-39), (C′-53), (C″-2), (C″-8) and (C″-9), and the automatic processor as shown in Fig. 2 was used. As a result, little differences were seen in the deposition of crystals, the occurrence of scratches and the storage stability of solutions. However, the decrease in transmission green density and transmission red density at maximum density areas after storage of images was as small as 0.05 to 0.09 in respect of the transmission green density and 0.04 to 0.08 in respect of the transmission red density, showing an improvement.

The automatic processor as shown in Fig. 2 can also be preferably used in the present invention. In Fig. 2, reference numeral 5 denotes delivery rollers; 6, delivery rollers; 7, opposed rollers; 8, a light-sensitive material; 9, processing tanks; 10, transport position; 11, floating lids; 12, liquid-sealing members serving also as squeegees; 13, liquid-drip trays; 14, liquid-level sensors; 15, a bath having a fixing ability; 16, a stabilizing bath; 17, jet pipes; 18, a circulating pump; 19, a circulating pipe; and 22, air holes.

Example 8

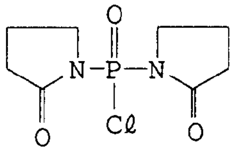
Tests were carried out in the same manner as Test No. 1-14 in Example 1 except that the hardening agent (H-2) contained in the film sample used in Test No. 1-14 was replaced with the hardening agents as shown in the following Table 4.

Results obtained are shown together in Table 4.

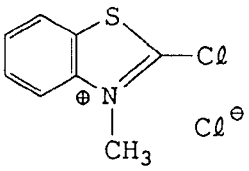
Table 4

Test No.	Hardening agent		Deposition of crystals	Stabilizing solution storage stability	Green density difference
4-1	Exemplary	(VS-2)	AA	A to AA	-0.11
4-2	"	(VS-4)	A to AA	AA	-0.11
4-3	"	(VS-6)	AA	AA	-0.09
4-4	"	(VS-9)	AA	A to AA	-0.10
4-5	"	(VS-10)	AA	AA	-0.11
4-6	"	(VS-12)	A to AA	A to AA	-0.11
4-7	"	(VS-22)	AA	AA	-0.09
4-8	"	(VS-33)	AA	AA	-0.10
4-9	"	(VS-54)	A to AA	AA	-0.10
4-10	RH-1 shown below		A	A	-0.13
4-11	RH-2 "		A	A	-0.14
4-12	RH-3 "		A	A	-0.13
4-13	RH-4 "		A	A	-0.12
4-14	RH-5 "		A	B to A	-0.15

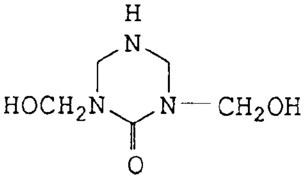
(RH-1)



(RH-2)



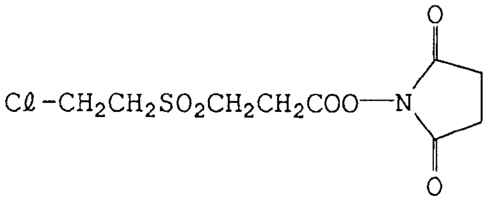
(RH-3)



(RH-4)

$[NaO_3SO(CH_2)_2O_2S\text{-}H_2C]_4C$

(RH-5)



As is clear from the above Table 4, the effect as aimed in the present invention can be better attained when any of the vinylsulfone type hardening agents is used in combination in the processing method of the present invention.

Example 9

Tests were carried out in the same manner as Test No. 1-19 in Example 1 except that test samples were prepared by adding to the film sample as used in Test No. 1-19 in Example 1 the compounds as shown in the following Table 5 in an amount of 10 mg/m^2 each.

Results obtained are shown together in Table 5.

Table 5

Test No.	Additive (10 mg/m^2)	Deposition of crystals	Stabilizing solution storage stability	Green density difference
5-1	None	A	A to AA	-0.10
5-2	Phenol	A	A to AA	-0.11
5-3	Dehydroacetic acid	A	A to AA	-0.12
5-4	Chlorodiphenyl	A	A	-0.11
5-5	Cresol	A	A to AA	-0.12
5-6	p-Aminobenzenesulfonamide	A	A to AA	-0.10
5-7	Thiazolylbenzimidazole	A	A to AA	-0.14
5-8	(B-1-1)	AA	AA	-0.07
5-9	(B-1-16)	A to AA	AA	-0.08
5-10	(B-1-18)	A to AA	AA	-0.07
5-11	(B-2-1)	AA	AA	-0.06
5-12	(B-2-2)	AA	AA	-0.07
5-13	(B-2-7)	A to AA	AA	-0.08
5-14	(B-2-10)	AA	AA	-0.07
5-15	(B-3-1)	AA	AA	-0.08
5-16	(B-3-6)	A	AA	-0.07

As is clear from the above Table 5, the effect of the present invention can be better attained when any of the compounds represented by Formula B-1 to B-3 previously described are used in combination in the processing method of the present invention.

As having been described above, the present invention can provide a method of processing a light-sensitive silver halide color photographic material, that enables stable processing without causing jamming or occurrence of scratches due to the deposition of crystals or the like even when the aperture area is made small, and also makes use of a stabilizing solution having a stable storage stability without regard to how many or few light-sensitive materials are processed.

Claims

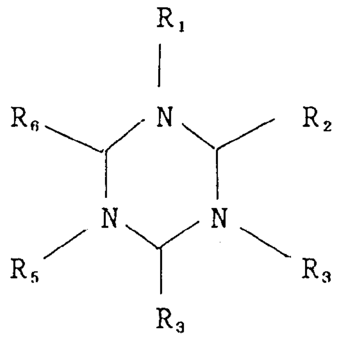
1. A method of processing a silver halide color photographic light-sensitive material comprising steps of:

developing, bleaching with a solution having a bleaching ability, fixing with a solution having a fixing ability, and stabilizing with a stabilizing solution wherein;

the stabilizing solution is essentially free from formaldehyde and contains a hexamethylenetetramine group and at least one compound from a group consists of formulae F-1 to f-10; and

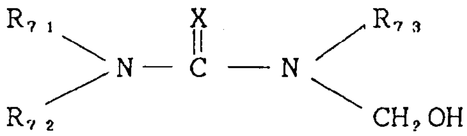
an air contact area of the stabilizing solution is less than 5 cm^2;

F-1

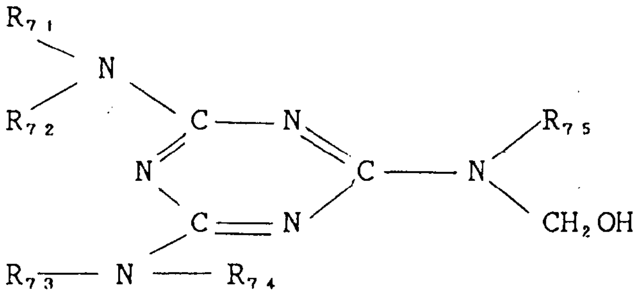


wherein R_1 through R_6 is a hydrogen atom or a mono-valent organic group,

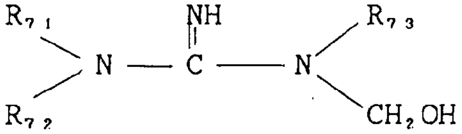
F-2



F-3

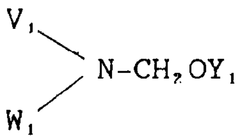


F-4



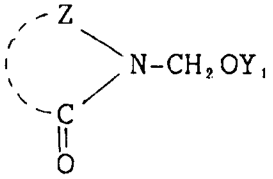
wherein R_{71} through R_{75} each represents hydrogen atom or a methylol group, X represens a hydrogen atom or a sulfur atom,

F-5

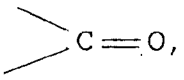


$$\begin{matrix} V_1 \\ W_1 \end{matrix} > N\text{-}CH_2OY_1$$

F-6

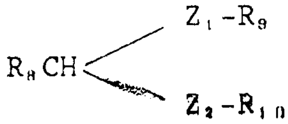


wherein V_1 and W_1 each represents a hydrogen atom, a lower alkyl group or an electrofilic group, and V_1 and W_1 may form a 5 or 6 membered nitrogen containing hetero cyclic group, Y, represents hydrogen atom or a group decomposed by a hydrolysis reaction, Z represents a nitrogen atom or a non-metalic atom capable to form a single ring or condensed nitrogen containing heterocyclic group with



$$>C=O,$$

F-7



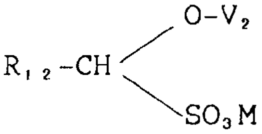
$$R_8CH < \begin{matrix} Z_1\text{-}R_9 \\ Z_2\text{-}R_{10} \end{matrix}$$

wherein R_8 represents a hydrogen atom or aliphatic group, R_9 and R_{10} each represents aliphatic group or aryl group and

R_9 and R_{10} may form a ring,

Z_1 and Z_2 each represents an oxigen atom, sulphur atom, or -N(R_{11})-, Z_1 and Z_2 never be both oxigen atoms, R_{11} is a hydrogen atom, hydroxy, aliphatic or an aryl group,

F-8

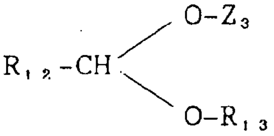


$$R_{12}\text{-}CH < \begin{matrix} O\text{-}V_2 \\ SO_3M \end{matrix}$$

F-9

$W_2\text{-}O\text{-}(CH_2O)_n\text{-}Y_2$

F-10



$$R_{12}\text{-}CH < \begin{matrix} O\text{-}Z_3 \\ O\text{-}R_{13} \end{matrix}$$

wherein R_{12} represents a hydrogen atom or an aliphatic group, V_2 represents a group decomposed by a hydrolysis, M represents a cation, W_2 and Y_2 each represents a hydrogen atom or a group decomposed by hydrolysis, n is an integer of 1 to 10, Z_3 and R_{13} each represents a hydrogen atom, aliphatic, or an aryl group or a group decomposed by a reaction of dehydrolysis, Z_3 and R_{13} may form a ring.

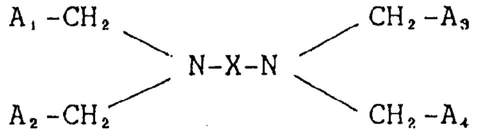
2. The method of claim 1, wherein the material contains silver more than 2.0 g. per m^2.

3. The method of claim 1 or 2, wherein the solution having the fixing ability contains a thiocyanic acid salt.

4. The method of claim 1, 2,or 3, wherein the solution having the fixing ability is a fixing solution.

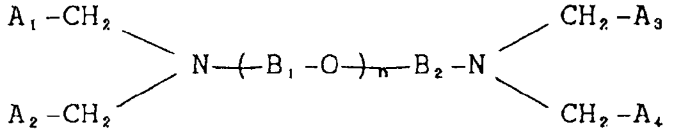
5. The method of claim 1, 2, 3 or 4, wherein one step advanced to the fixing process for fixing by the solution having the fixing ability is the bleaching process by the bleaching solution which contains a ferric complex salt of aminopolycarboxylic acid represented by formula A or B,

A



wherein A, through A, are different or identical and represent -CH_2OH, -COOM or -$PO_3M_1M_2$,
M, M_1, M_2 each represents a hydrogen atom, an alkalin metal or an ammonium ion,
X represents unsubstituted alkilene group of carbon number 3 to 6,

B



wherein A, through A, are synonymous as defined in formula A, n is an integer of 1 to 8,
B_1 and B_2 are different or identical, each represents substituted or un-substituted alkylene group of carbon number 1 to 5.

6. The method of claim 1, 2, 3, 4 or 5, wherein the stabilizing solution is a final processing solution and is free from an ammonium salt.

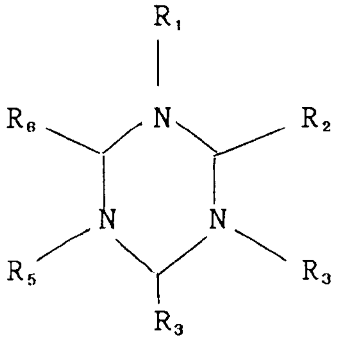
7. A method of processing a silver halide color photographic light-sensitive material containing silver more than 2.0 grams per square meter, comprising steps of:

a developing process for developing the material, a de-silvering process for de-silvering, a fixing process for fixing by a solution having a fixing ability, followed by a stabilizing process for stabilizing by a stabilizing solution which process being defined as a final process wherein;

the stabilizing solution is free from formaldehyde and an ammonium ion, and contains a hexamethylenetetramine group and at least one compound from a group consists of formulae F-1 to f-10; and

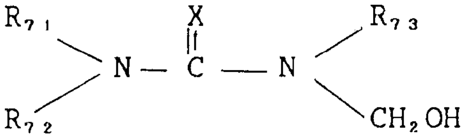
an air contact area of the stabilizing solution is less than 5 cm^2;

F-1

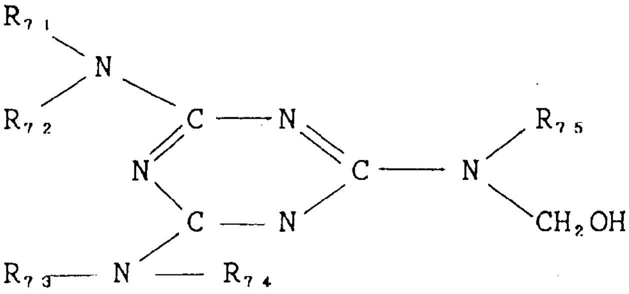


wherein R_1 through R_6 is a hydrogen atom or a mono-valent organic group,

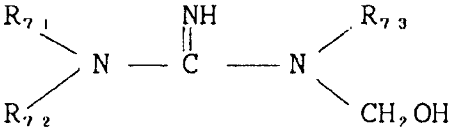
F-2



F-3

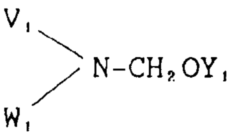


F-4

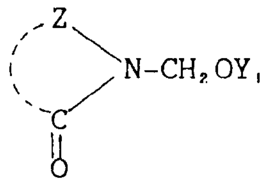


wherein R_{71} through R_{75} each represents hydrogen atom or a methylol group,

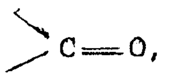
F-5



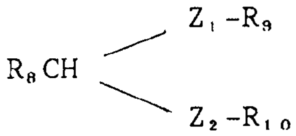
F-6



wherein V_1 and W_1 each represents a hydrogen atom, a lower alkyl group or an electrofilic group, and V_1 and W_1 may form a 5 or 6 membered nitrogen containing hetero cyclic group, Y_1 represents hydrogen atom or a group decomposed by a hydrolysis reaction, Z represents a nitrogen atom or a non-metalic atom capable to form a single ring or condensed nitrogen containing heterocyclic group with



F-7

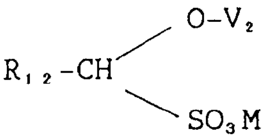


wherein R_8 represents a hydrogen atom or aliphatic group, R_9 and R_{10} each represents aliphatic group or aryl group and

R_9 and R_{10} may form a ring,

Z_1 and Z_2 each represents an oxigen atom, sulphur atom, or $-N(R_{11})-$, Z_1 and Z_2 never be both oxigen atoms, R_{11} is a hydrogen atom, hydroxy, aliphatic or an aryl group,

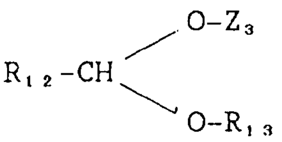
F-8



F-9

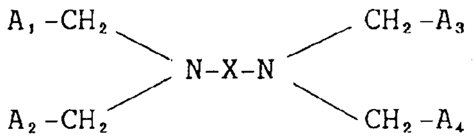
$$W_2-O-(CH_2O)_n-Y_2$$

F-10



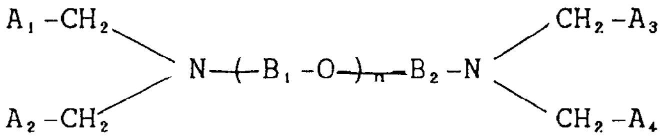
wherein R_{12} represents a hydrogen atom or an aliphatic group, V_2 represents a group decomposed by a hydrolysis, M represents a cation, W_2 and Y_2 each represents a hydrogen atom or a group decomposed by hydrolysis, n is an integer of 1 to 10, Z_3 and R_{13} each represents a hydrogen atom, aliphatic, or an aryl group or a group decomposed by a reaction of dehydrolysis, Z_3 and R_{13} may form a ring;

the bleaching process by the bleaching solution which contains a ferric complex salt of aminopolycarboxylic acid represented by formula A or B, A



wherein A, through A, are different or identical and represent -CH_2OH, -COOM or -$PO_3M_1M_2$, M, M_1, M_2 each represents a hydrogen atom, an alkalin metal or an ammonium ion, X represents unsubstituted alkilene group of carbon number 3 to 6,

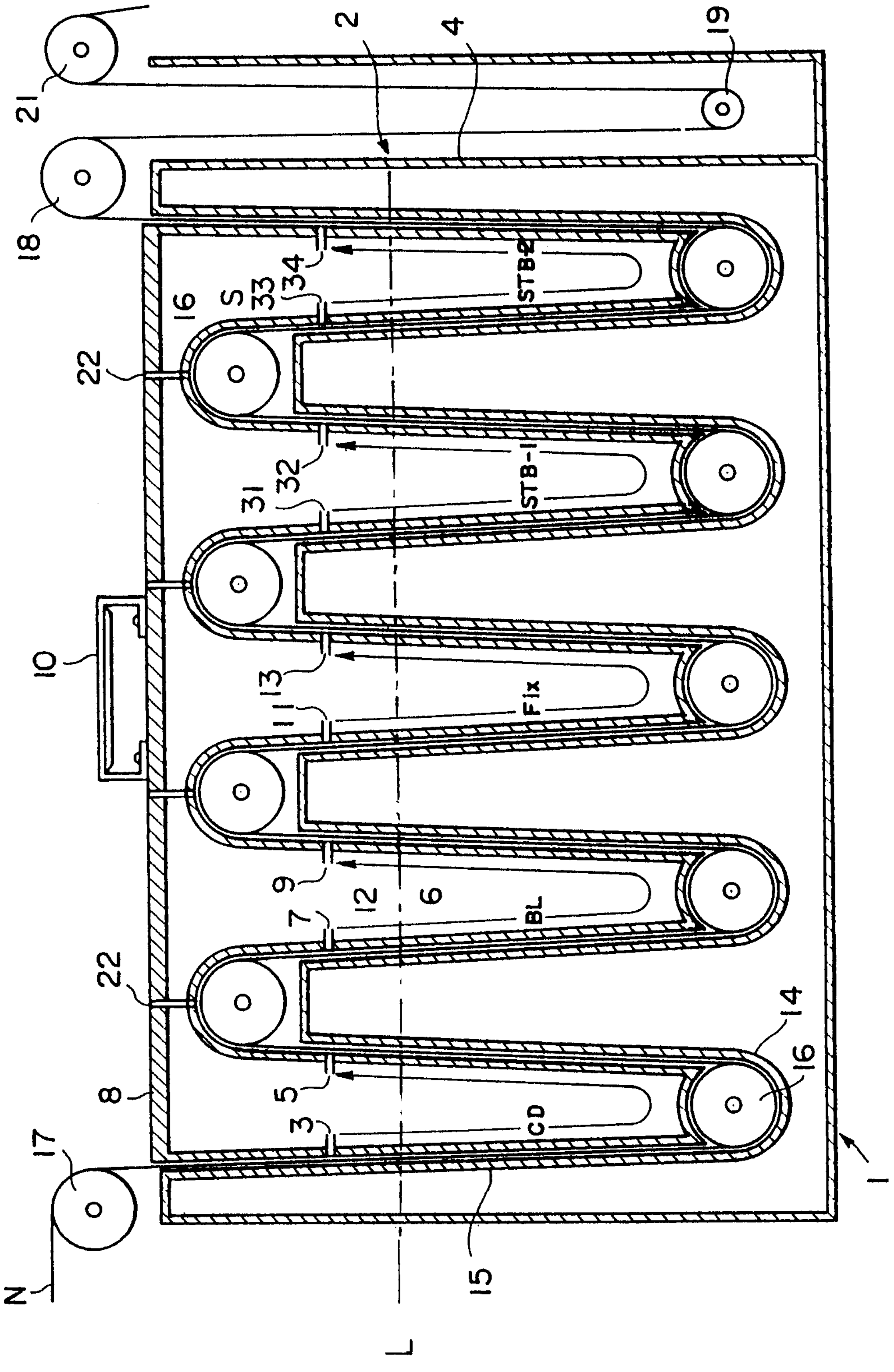
B



wherein A, through A_4 are synonymous as defined in formula A, n is an integer of 1 to 8, B_1 and B_2 are different or identical, each represents substituted or un-substituted alkylene group of carbon number 1 to 5;

the solution having the fixing ability contains a thiocyanic acid salt.

FIG. 1


21
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S
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STB-2
32
31
STB-1
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Fix
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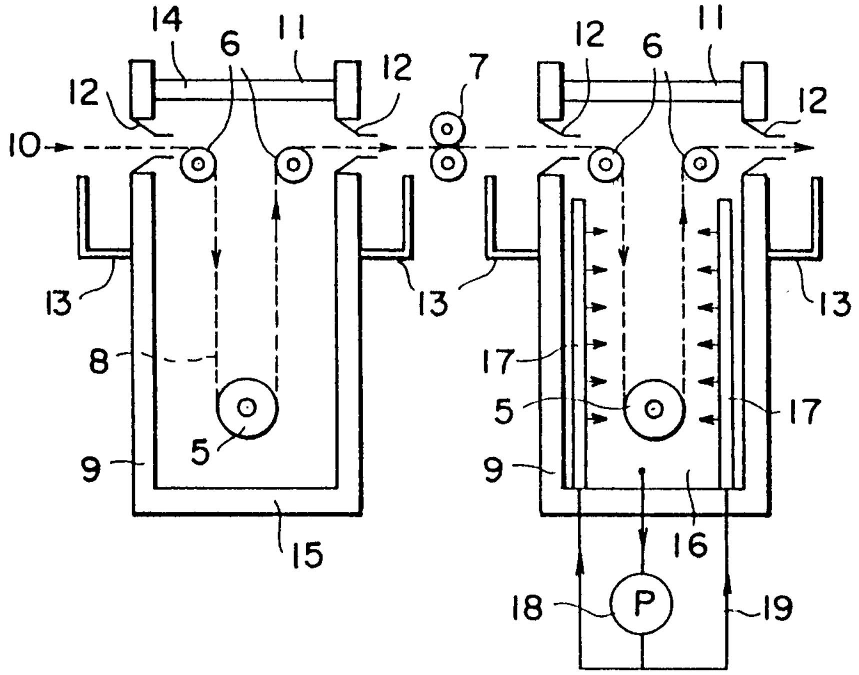

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8059

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 217 643 (KONISHIROKU) * page 16; examples 7,11 * * page 17, line 10 - line 15 * * page 27, line 4 - line 7 * * page 28, line 1 - line 10 * * page 29; table 4 * ---	1-7	G03C7/30 G03C7/42
Y	DE-A-3 520 292 (KONISHIROKU) * page 19, line 13 - line 15 * * page 20; examples 4,10 * * claim 1 * ---	1-7	
Y	WO-A-8 908 870 (KODAK) * page 4, line 1 - line 7 * * page 7, line 13 - page 8, line 12 * * page 12 * ---	1-7	
Y	US-A-4 927 746 (SCHWARTZ) * column 5, line 18 - line 48 * ---	1-7	
Y	US-A-2 579 436 (MACKEY) * column 2, line 24 - line 29 * * column 3, line 8 - line 22; claim 1 * ---	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 9 (P-811)(3357) 11 January 1989 & JP-A-63 216 050 (FUJI) 8 September 1988 * abstract * ---	1-7	
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 85 (P-834)(3433) 27 February 1989 & JP-A-63 266 452 (KONICA) 2 November 1988 * abstract * -----	1-7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 NOVEMBER 1991	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

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