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(54)
Bleach-fixing solution having good processing performance and method for processing light-sensitive material using the same.

(57) Disclosed is a bleach-fixing solution comprising a processing solution for bleach-fixing a light-sensitive silver halide photographic material for photographing, wherein said solution has the pH ranging between 3.0 and 6.8, contains a ferric complex salt having a ligand comprising a compound represented by General Formula (I), and further contain at least one of;

i) at least one compound selected from the compounds represented respecytively by General Formula (II) and General Formula (III);

ii) a polymer having a unit of pyrrolidone nucleus in the molecular structure; and iii) a ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII). The General Formulas (I) to (VII) are described in the specification.

Disclosed is also a method for processing a light-sensitive material by using the bleach-fixing solution.

By use of the bleach-fixing solution of this invention, rapid processing of the light-sensitive material is enabled without a generation of ammonia gas, because the bleach-fixing solution can delay the occurence of the precipitation even during storage with time to attain a stable bleach-fixing performance, and it can improve the bleach stain at a non-image portion of a light-sensitive material when the processing with low replenishment is carried out.

Bleach-fixing solution having good rapid processing performance and method for processing light-sensitive material using the same

BACKGROUND OF THE INVENTION

This invention relates to a bleach-fixing solution, and particularly to a bleach-fixing solution that can achieve rapid processing when applied in a light-sensitive material for photographing.

At present, the desilvering of light-sensitive materials for photographing in which a highly sensitive silver iodobromide-rich emulsion is used is carried out separately in a bleaching step and a fixing step.

In an attempt to achieve a simple and rapid desilvering of the above light-sensitive materials for photographing, the present inventors have made studies on a bleach-fixing system in which the bleaching and fixing are carried out in a monobath.

In the course of that studies, as it has been conventionally considered advantageous for the above bleach-fixing solution to be used in a higher pH range from viewpoints of the shelf stability of a solution and the inferior color reproduction that may occur on a resulting dye image, researches were made for a bleaching agent that can have a good desilvering ability in such a high pH range. As a result, the present inventors have proposed that, among various aminopolycarboxylic acid iron complexes, a diethylenetriaminepentaacetic acid ferric complex salt (hereinafter "DTPA·Fe complex salt") can satisfy the desilvering speed, the color reproduction of a resulting color image and the shelf stability with time, of a bleach-fixing solution (Japanese Unexamined Patent Publications No. 134238/1985, No. 130738/1985, No. 136744/1985, etc.).

The above DTPA·Fe complex salt can satisfy the above properties when used in the higher pH range, specifically, at about pH 7 to 9. However, ammonia gas may be readily generated when used in such a pH range, so that there has been a problem undesirable from a viewpoint of the work environment if the developing is carried out in a small room. In addition, with lapse of time when a light-sensitive material is processed over a long period of time, it has become clearer that there may occur a lowering of the desilvering ability and an inferiority in the color reproduction that are considered to be caused by the accumulation of ferrous ions in a bleach-fixing solution.

As a result of detailed studies on the above disadvantages, it was found that the accumulation of ferrous ions largely depends on the pH of the bleach-fixing solution, and, at the pH more than a certain value, this is a problem that may commonly occur in the aminopolycarboxylic acid iron complex salts usually used as a bleaching agent, with lapse of time when processing is carried out.

SUMMARY OF THE INVENTION

The present inventors have continued further studies to find, as a result, that the lowering of the desilvering ability and the inferiority in the color reproduction that are considered to be caused by the above-mentioned accumulation of ferrous ions can be solved at the same time and the problem of the generation of ammonia gas can be solved by using a bleach-fixing solution having the pH in a particular lower range and containing a particular aminopolycarboxylic ferric complex salt.

The present inventors have also made further studies to find the facts as shown below, thus accomplishing this invention.

It became clear that, when the bleach-fixing solution is put into practical use, a particular preservative may be used in not less than a particular amount, whereby the shelf stability with time of the bleach-fixing solution can be advantageously prevented from being deteriorated at the time of continuous processing without adversely affecting the effect of improving the above problems.

It was also found that although conventional bleach-fixing solution using sulfite in a lower concentration have caused precipitation in a relatively shorter time by storage, at least one of the compounds selected from the compounds represented respectively by General Formulas (II) and (III) of this invention as described below may be used, so that the precipitation can be made not to be readily caused and the shelf stability can be improved.

Some compounds of the compounds represented respectively by General Formulas (II) and (III) of this invention are known to be used in a bleach-fixing solution containing an ethylenediaminetetraacetic acid iron (III) complex (hereinafter "EDTA·Fe) as a bleaching agent, as disclosed, for example, in Japanese Publication No. 38895/1979. However, it was revealed that such compounds may gradually release sulfite ions when used in the bleach-fixing solution containing the above EDTA•Fe, so that aldehydes or ketones may be accumulated and the desilvering speed may be gradually lowered.

In contrast thereto, it was revealed that a particular aminopolycarboxylic acid iron complex salt may be used in a bleach-fixing solution used in a particular lower pH range, whereby the shelf stability can be particularly remarkably improved without lowering the good desilvering and color reproduction performances possessed by the bleach-fixing solution.

It was also found that a particular polyvinyl pyrrolidone may be used when the bleach-fixing solution is put into practical use, whereby it becomes possible to delay the occurrence of the precipitation of silver sulfide during storage with time, without adversely affecting the effect of improving the aforesaid problems, and also it becomes possible to improve the bleach stain at a non-image portion that may be readily generated when the bleach-fixing solution is used in the processing with low replenishment. This invention has thus been accomplished.

Accordingly, a first object of this invention is to provide a bleach-fixing solution made feasible for rapid processing of a light-sensitive photographic material for photographing.

A second object of this invention is to provide a bleach-fixing solution free from generation of ammonia gas and desirable from the viewpoint of work environment.

A third object of this invention is further to provide a bleach-fixing solution that can delay the occurrence of the precipitation even during storage with time to attain a stable bleach-fixing performance.

A fourth object of this invention is to provide a bleach-fixing solution that can improve the bleach stain at a non-image portion of a light-sensitive material when the processing with low replenishment is carried out.

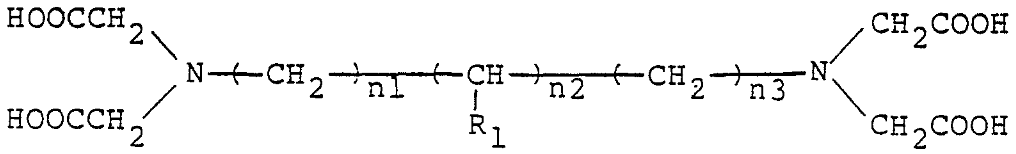
The above objects of this invention cab be achieved by a bleach-fixing solution for processing a light-sensitive silver halide photographic material for photographing, wherein said solution has the pH ranging between 3.0 and 6.8, contains a ferric complex salt having a ligand comprising a compound represented by General Formula (I) shown below, and further contains at least one of;

i) at least one compound selected from the compounds represented respectively by General Formula (II) and General Formula (III) shown below;

ii) a polymer having a unit of a pyrrolidone nucleus in the molecular structure; and

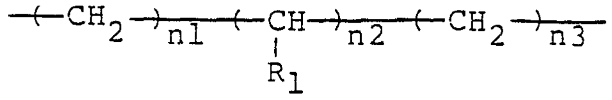
iii) a ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII),

General Formula (I):



$$(HOOCCH_2)_2N-(CH_2)_{n1}-(\underset{R_1}{CH})_{n2}-(CH_2)_{n3}-N(CH_2COOH)_2$$

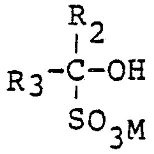
wherein R_1 represents a hydrogen atom or an alkyl group having 1 to 3 carbon atoms; and n_1, n_2 and n_3 each represent an integer of 0 to 3, provided that the sum of n_1, n_2 and n_3 is an integer of 2 to 4 and the total sum of the carbon atoms in



$$-(CH_2)_{n1}-(\underset{R_1}{CH})_{n2}-(CH_2)_{n3}-$$

is 3 or more,

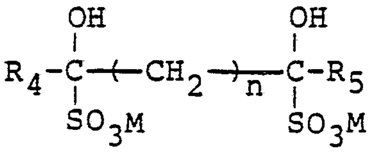
General Formula (II):



$$R_3-\underset{SO_3M}{\overset{R_2}{C}}-OH$$

wherein R_2 and R_3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; and M represents an alkali metal atom or an ammonium group,

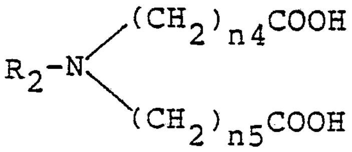
General Formula (III):



$$R_4-\underset{SO_3M}{\overset{OH}{C}}-(CH_2)_n-\underset{SO_3M}{\overset{OH}{C}}-R_5$$

wherein R_4 and R_5 each represent a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; M represents an alkali metal atom or an ammonium group; and n represents an integer of 0 to 6,

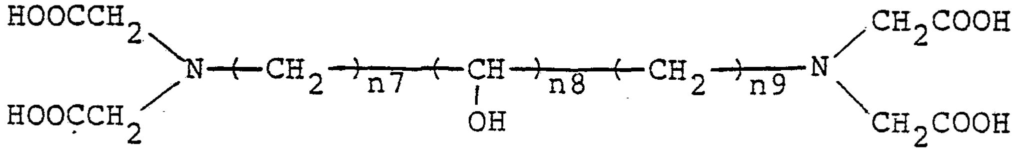
General Formula (IV):



$$R_2-N\begin{array}{l}(CH_2)_{n4}COOH\\(CH_2)_{n5}COOH\end{array}$$

wherein R_2 represents an alkyl group having 1 to 5 carbon atoms, a hydroxyl-substituted alkyl group having 1 to 5 carbon atoms, or $-(CH_2)_{n6}COOH$; and n_4, n_5 and n_6 each represents an integer of 1 or 2,

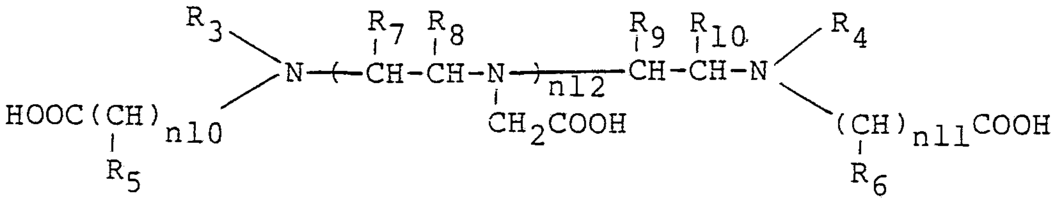
General Formula (V):



$$\begin{array}{l}HOOCCH_2\\HOOCCH_2\end{array}N-(CH_2)_{n7}-(\underset{OH}{CH})_{n8}-(CH_2)_{n9}-N\begin{array}{l}CH_2COOH\\CH_2COOH\end{array}$$

wherein n_7 and n_9 each represent an integer of 0 to 3, and n_8 represents an integer of 1 to 3, provided that the sum of n_7, n_8 and n_9 is 2 or more,

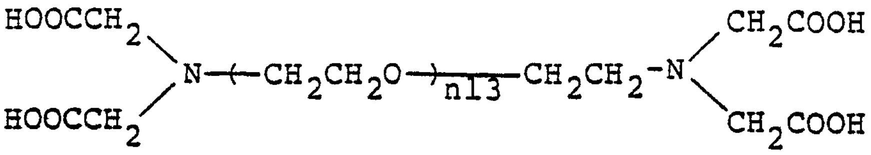
General Formula (VI):



$$\begin{array}{r}R_3\\HOOC(\underset{R_5}{CH})_{n10}\end{array}N-(\overset{R_7}{CH}-\overset{R_8}{CH}-\underset{CH_2COOH}{N})_{n12}-\overset{R_9}{CH}-\overset{R_{10}}{CH}-N\begin{array}{l}R_4\\(\underset{R_6}{CH})_{n11}COOH\end{array}$$

wherein R_3 and R_4 each represent a hydrogen atom, a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, or a carboxyl-substituted alkyl group having 1 or 2 carbon atoms; R_5 and R_6 each represent a hydrogen atom or a hydroxyl-substituted phenyl group; R_7, R_8, R_9 and R_{10} each represent a hydrogen atom or a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, provided that R_7, R_8, R_9 and R_{10} each may combine to form a ring having 5 to 8 carbon atoms; n_{10} and n_{11} each represent an integer of 1 to 3; and n_{12} represents an integer of 0 to 4,

General Formula (VII):



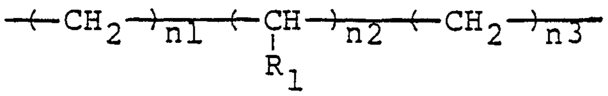
$$(HOOCCH_2)_2N\text{-}(CH_2CH_2O)_{n13}\text{-}CH_2CH_2\text{-}N(CH_2COOH)_2$$

wherein n_{13} represents an integer of 1 to 8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the bleach-fixing solution of this invention, the ferric complex salt having a ligand comprising the compound represented by General Formula (I) is used.

In General Formula (I), R_1 may preferably be a hydrogen atom. Also, the total sum of the carbon atom number in



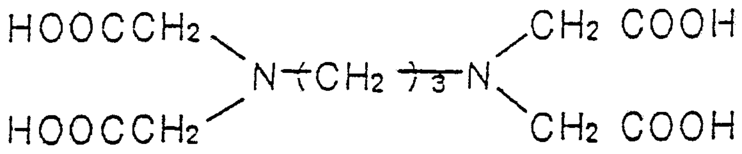
$$-(CH_2)_{n1}-(\underset{\underset{R_1}{|}}{CH})_{n2}-(CH_2)_{n3}-$$

may most preferably be 3.

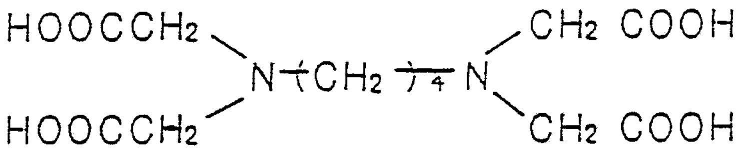
Preferred specific examples of the compound represented by General Formula (I) are shown below.

Exemplary Compounds:

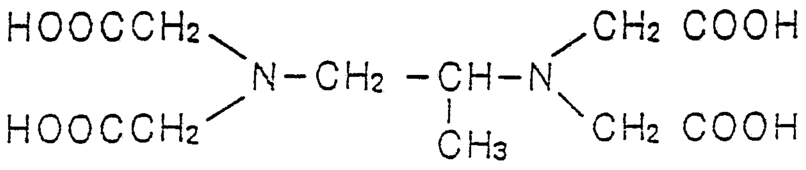
I-1



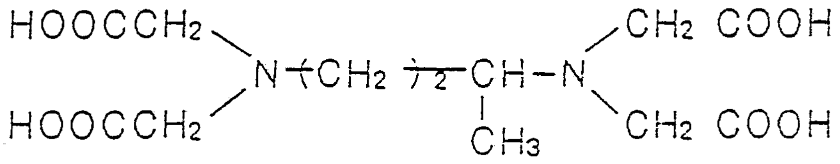
I-2



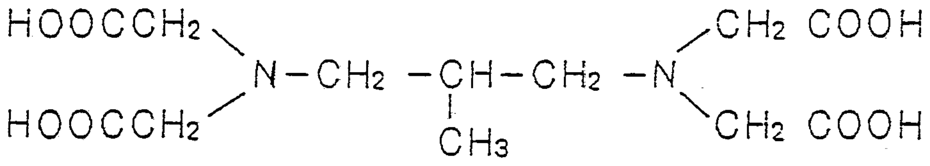
I-3



I-4



I-5



The ferric complex salt having a ligand comprising the compound represented by the above General Formula (I) may be used also in the form of a free acid (hydrogen salt), or may also be used in the form of a counter salt including alkali metal salts such as a sodium salt, a potassium salt and a lithium salt or an ammonium salt, or water soluble amines, for example, triethanolamine, etc. Preferably used are a potassium salt, a sodium salt and an ammonium salt. At least one of these ferric complex salts of this invention may be used, but two or more of these can also be used in combination. It is also possible to use them in combination with any ferric complex salts outside this invention.

Among the ferric complex salts of this invention as exemplified in the above, preferred are ferric complex salts in which any of exemplary compounds (I-1), (I-2) and (I-3) is used as the ligand. Still among these exemplary compounds (I-1), (I-2) and (I-3), it is particularly preferred to use (I-1) or (I-2) from a viewpoint of the solubility, and, taking account of various points such as the effect aimed at in this invention, it is most preferred in this invention to use (I-1).

The ferric complex salt can be used in any amount in the bleach-fixing solution of this invention so long as it is in an amount sufficient for obtaining the effect of this invention. However, overly high concentration of the ferric complex salt may cause the deterioration of shelf stability of the bleach-fixing solution, and, on the other hand, overly low concentration of the ferric complex salt may cause the deterioration of desilvering performance and color reproduction performance. Accordingly, it may be usually used preferably in the range of 0.02 to 1.30 mol/lit., more preferably 0.10 to 1.20 mol/lit. Particularly, the effect of this invention can be preferably exhibited when used in the range of 0.20 to 0.80 mol/lit.

The bleach-fixing solution of this invention may be appropriately in the pH range of pH 3.0 to 6.8, because sulfite gas may be generated at less than pH 3.0 and the effect of this invention may be insufficient if the pH is higher than 6.8. It can be used at any pH so long as it is used in this pH range, but is preferably used at pH 4.0 to 6.7, particularly preferably pH 5.0 to 6.5, taking account of the solubility of various iron salts at low temperature the odor of the sulfite gas generated from sulfite ions in addition to desilvering performance and color reproduction.

The bleach-fixing solution of this invention may preferably contain a variety of sulfites therein, and these sulfites may include ammonium sulfite, sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite, sodium metabisulfite, etc.

Embodiment i) of this invention will be described below.

As embodiment i), at least one compound selected from the compounds represented respectively by General Formulas (II) and (III) (hereinafter referred to as the bisulfite addition compound of this invention) may be used as a preservative in the bleach-fixing solution of this invention.

In General Formula (II), the alkyl group having 1 to 8 carbon atoms, represented respectively by R_2 and R_3, may preferably include an alkyl group having 1 to 4 carbon atoms.

One of the preferred compounds included in the carbonyl bisulfite addition compound represented by General Formula (II) is a compound wherein R_2 is a hydrogen atom and R_3 is an alkyl group having 1 to 4 carbon atoms, and another of them is a compound wherein R_2 and R_3 each are an alkyl group having 1 to 4 carbon atoms.

In General Formula (III), the alkyl group having 1 to 8 carbon atoms, represented respectively by R_4 and R_5, may preferably include an alkyl group having 1 or 2 carbon atoms.

The symbol n, which represents an integer of 0 to 6, may preferably be an integer of 1 to 4.

One of the preferred compounds included in the carbonyl bis-bisulfite addition compound represented by General Formula (III) is a compound wherein R_4 and R_5 each are a hydrogen atom and n is an integer of 1 to 4. Another of them is a compound wherein R_4 and R_5 each are an alkyl group having 1 or 2 carbon atoms and n is an integer of 1 to 4.

Specific examples of the bisulfite addition compound of this invention are shown below, but by no means limited to these.

Exemplary bisulfite addition compounds:

II-1	Sodium acetaldehyde bisulfite
II-2	Sodium propionaldehyde bisulfite
II-3	Sodium butylaldehyde bisulfite
II-4	Sodium acetone bisulfite
II-5	Sodium butanone bisulfite
II-6	Sodium pentanone bisulfite
III-1	Sodium succinaldehyde bisbisulfite
III-2	Sodium glutalaldehyde bisbisulfite
III-3	Sodium β-methylglutalaldehyde bisbisulfite
III-4	Sodium maleic dialdehyde bisbisulfite
III-5	Sodium 2,4-pentanedione bisbisulfite

The above bisulfite addition compound of this invention may be used by using one kind thereof alone or two or more thereof in combination, and can be used in an amount of 0.01 mol to 2 mols, preferably 0.02 to 1 mol, and more preferably 0.05 to 0.5 mole, per liter of the bleach-fixing solution of this invention.

Embodiment ii) of this invention will be described below.

It has been conventionally known in, for example, Japanese Patent Publication No. 38937/1975, etc. that polyvinyl pyrrolidone is used in a bleach-fixing solution for the purpose of maintaining the bleaching power in a long term storage. However, in the prior arts including these, there has been a disadvantage that the ethylenediaminetetraacetic acid ferric complex salt conventionally having been frequently used as a bleaching agent of bleach-fixing solutions tends to cause, when used in the acidic range, a trouble of the color reproduction inferiority particularly with regard to light-sensitive materials for highly sensitive photographing which contains silver in a large amount. However, in this invention, where a particular aminopolycarboxylic acid ferric complex salt and polyvinyl pyrrolidone are used in combination in the bleach-fixing solution having the pH of 3 to 6.8, it was found that there is surprisingly no disadvantage of the color reproduction inferiority, and the precipitation of silver sulfide characteristically occurring in bleach-fixing solutions can be prevented from being occurred, and also the effect aimed at in this invention as mentioned above can be exhibited, thus accomplishing this invention.

The polymer having a unit of a pyrrolidone nucleus in the molecular structure (hereinafter called "vinyl pyrrolidone polymer of this invention") will be described below.

The vinyl pyrrolidone polymer of this invention may comprise either a homopolymer of vinyl pyrrolidone alone or a copolymer thereof with additional copolymerizable monomer(s), but it is required to be water-soluble as a polymer.

The above additional monomer copolymerizable with vinyl pyrrolidone may typically include, for example, vinyl esters, acrylates, methacrylates, acrylic acids, methacrylic acid, styrene, etc. The vinyl esters may include, for example, vinyl acetate, vinyl propionate, vinyl butyrate. The acrylic esters may include, for example, methyl ester, ethyl ester, butyl ester, 2-ethyl hexyl ester, etc. In the case of the copolymer of these, the copolymerization ratio may preferably be selected in the range of 5 to 100 mol % based on the vinyl pyrrolidone.

There is no particular limitation in the average molecular weight of the vinyl pyrrolidone polymer of this invention, but it may preferably in the range of 500 to 800,000, more preferably 2,000 to 400,000.

The determination of the average molecular weight of the polymer can be carried out according to a usual method, for example, according to the following:

Precisely 1,000 g of a polymer sample is weighed and introduced in a 100 ml messflask, to which distilled water is added to prepare a 1 % aqueous solution, and the viscosity of the aqueous solution and that of the water serving as a solvent are measured, respectively. There was utilized a Ubbelohde's capillary viscometer for the measurement of the viscosity. The viscometer holding the solution to be measured was hanged in a thermostat and kept to stand at 20°C ± 0.01°C for 30 minutes to measure the time required for the solution to pass between the gauges. An average value for several times was taken and a relative viscosity was calculated from the relation represented by the following formula:

$$\eta rel = \frac{\text{Flow time of the solution}}{\text{Flow time of the solvent}}$$

Based on the relative viscosity, the value K is determined according to Fikentscher's viscosity formula (see Physikalische U. Technologische Prüfungsverfahren fur Lacke und ihre Rohstoffe, 1953 Edit.), and the average molecular weight is determined from the value K according to a usual method.

Typical examples of the vinyl pyrrolidone polymer of this invention are shown below, but by no means limited to these.

Exemplary compounds:

(1) Polyvinyl pyrrolidone (average molecular weight: about 40,000)

(2) Polyvinyl pyrrolidone (average molecular weight: about 9,000)

(3) Polyvinyl pyrrolidone (average molecular weight: about 16,000)

(4) Vinyl pyrrolidone/vinyl acetate copolymer
(copolymerization molar ratio: 7:3)
(average molecular weight: 4,000)

(5) Vinyl pyrrolidone/methyl acrylate copolymer
(copolymerization molar ratio: 7:3)
(average molecular weight: 1,000)

(6) Vinyl pyrrolidone/ethyl acrylate copolymer
(copolymerization molar ratio: 7:3)
(average molecular weight: 25,000)

(7) Vinyl pyrrolidone/butyl acrylate copolymer
(copolymerization molar ratio: 7:3)
(average molecular weight: 7,000)

(8) Vinyl pyrrolidone/2-ethyl hexyl acrylate copolymer
(copolymerization molar ratio: 7:3)
(average molecular weight: 18,000)

(9) Vinyl pyrrolidone/styrene copolymer
(copolymerization molar ratio: 1:3)
(average molecular weight: 20,000)

The amount for the addition of the above vinyl pyrrolidone polymer of this invention may vary depending on the type of the polymer, the polymerization degree and so forth, but approximately may preferably in the range of 0.1 to 100 g, more preferably 0.2 to 50 g, still more preferably 0.3 to 20 g, and particularly preferably 0.5 to 10 g, per liter of the bleach-fixing solution of this invention.

The vinyl pyrrolidone polymer of this invention may be added in the bleach-fixing solution by, for example, adding it directly as it is in the form of powder, or may be added by dissolving it in a solvent such as water.

In embodiment ii) of this invention, the above vinyl pyrrolidone polymer of this invention may be more preferably used for the purpose of better improving the shelf stability of the bleach-fixing solution, when a sulfite or a sulfite-releasable compound (for example, carbonyl bisulfite addition compounds disclosed in Japanese Patent Publication No. 38895/1979) is used in combination with it.

In this embodiment ii), the sulfite or the sulfite-releasable compound may preferably be contained in an amount of 1×10^{-3} mol or more per liter of the bleach-fixing solution of this invention. It may be used more preferably in an amount of not less than 0.02 mol and not more than 2.0 mols, still more preferably not less than 0.05 mol and not more than 1.3 mols, and most preferably not less than 0.09 mol and not more than 0.9 mol.

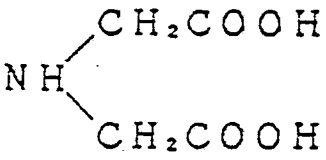
The above sulfite may include ammonium sulfite, sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite, sodium metabisulfite, etc.

Embodiment iii) of this invention will be described below.

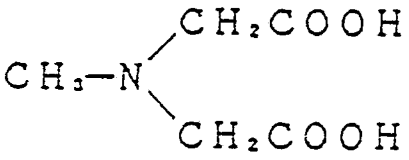
Preferred examples of the compounds represented respectively by General Formulas (IV) to (VII), used in embodiment iii) are shown below.

Exemplary Compounds:

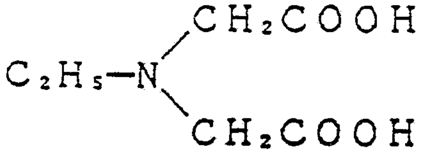
IV-1



IV-2



IV-3



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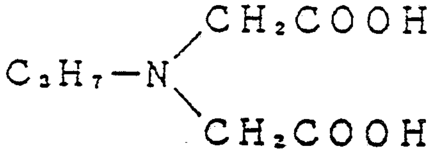

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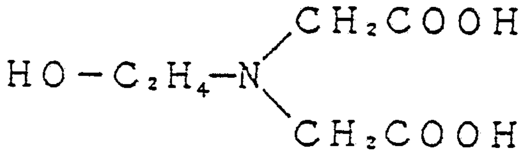

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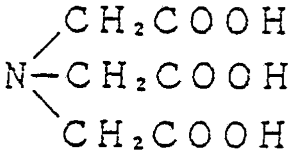

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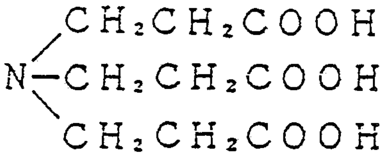

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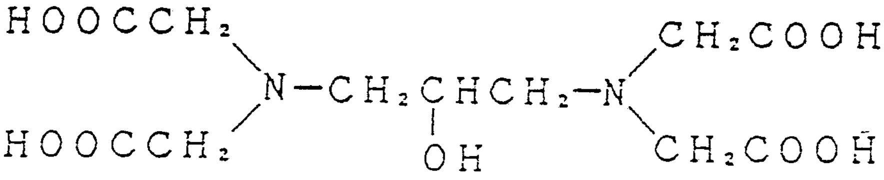
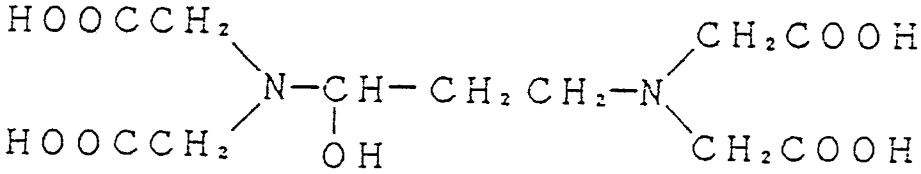


V-2



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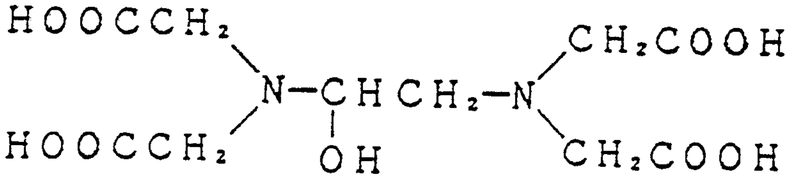

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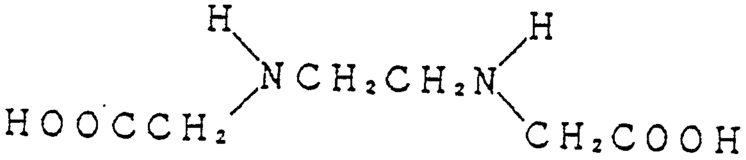

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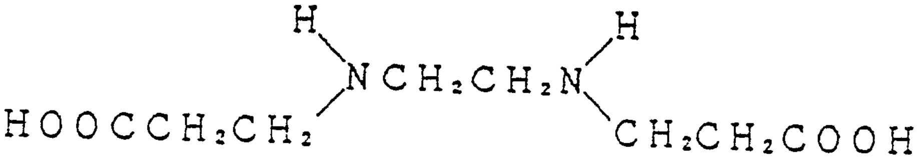
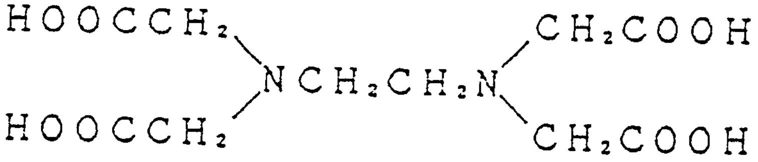


VI-3



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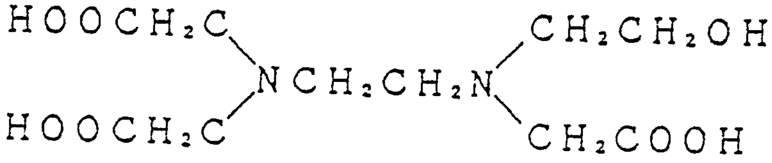

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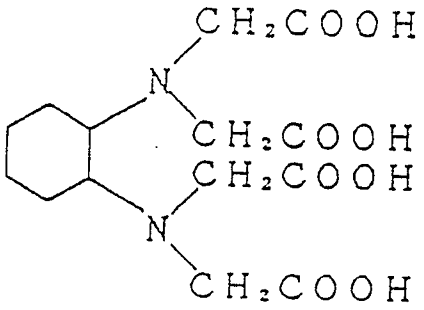
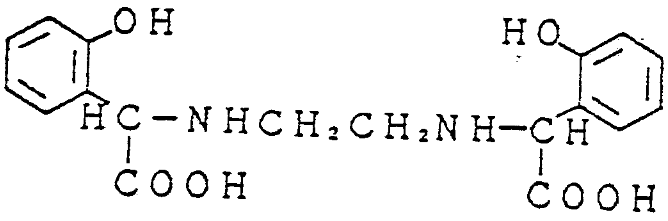


VI－6



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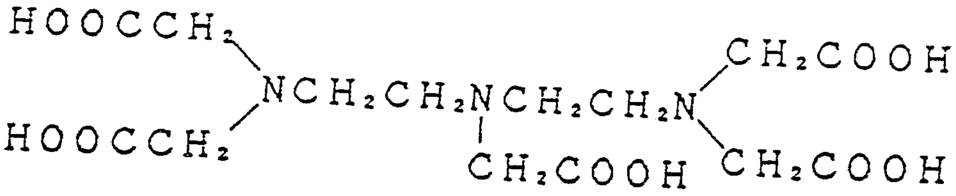
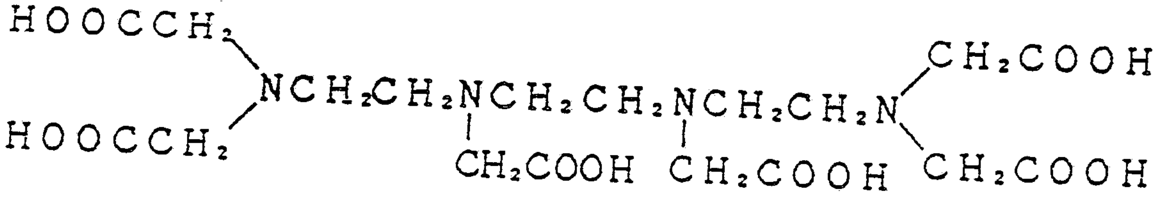
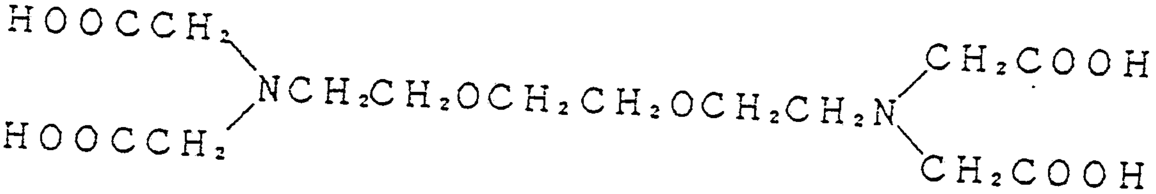


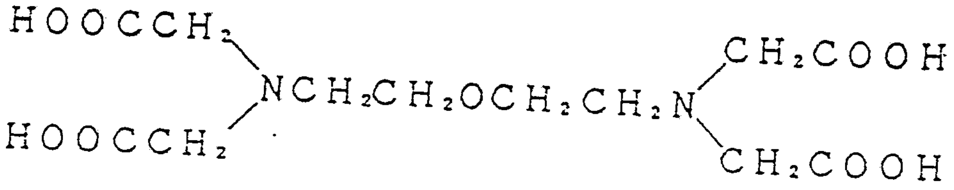
VI－8



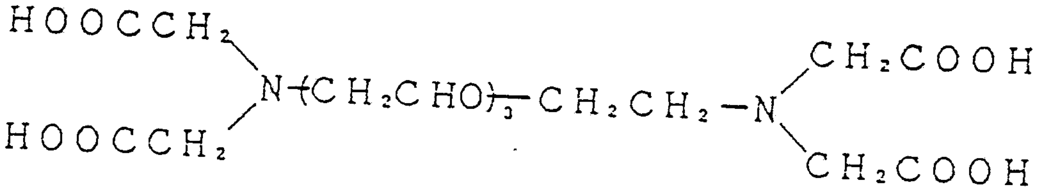
VII－1



VII－II



VII－III



The ferric complex salt having a ligand comprising at least one of the compounds represented respectively by General Formulas (IV) to (VII) may be used also in the form of a free acid (hydrogen salt), or may also be used in the form of a counter salt including alkali metal salts such as a sodium salt, a potassium salt and a lithium salt or an ammonium salt, or water soluble amine salts, for example, triethanolamine salt, etc. Preferably used are a potassium salt, a sodium salt and an ammonium salt.

In the bleach-fixing solution of the present embodiment, where the ferric complex salt having a ligand comprising the compound represented by General Formula (I) and ferric complex salt having a ligand comprising at least one of the compounds represented respectively by General Formulas (IV) to (VII) of this invention are used, the latter ferric complex salt may preferably be in the range of 1 mol % to 95 mol %, more preferably 5 mol % to 90 mol %, and most preferably 10 mol % to 80 mol %, based on the total amount of these.

In this invention, most effective from a viewpoint of overall performances for the desilvering, color reproduction and shelf stability is the combination of the compound represented by General Formula (I) with the compound VI-3 or VI-7. Particularly effective is the combination of I-1 with VI-7 or the combination of I-2 with VI-7.

The ferric complex salt having a ligand comprising the compound represented by General Formula (I) and that having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII) of this invention can be used in any amount in the bleach-fixing solution of this invention so long as it is in an amount sufficient for obtaining the effect of this invention. However, overly high concentration of the ferric complex salt may cause the deterioration of shelf stability of the bleach-fixing solution, and, on the other hand, overly low concentration of the ferric complex salt may cause the deterioration of desilvering performance and color reproduction performance. Accordingly, it may be usually used preferably in the range of 0.02 to 1.30 mol/lit., more preferably 0.10 to 1.20 mol/lit., in the total amount of them. Particularly, the effect of this invention can be preferably exhibited when used in the range of 0.20 to 0.80 mol/lit.

In the present embodiment, there can be found a feature in that the ferric complex salt having a ligand comprising the compound represented by General Formula (I) and ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII) of this invention are used in combination, so that the shelf stability can be improved while maintaining the good desilvering and color reproduction performances inherent in the bleach-fixing solution of this invention.

In general, it is known to use several kinds of bleaching agents in combination in order to improve various performances. For example, Research Disclosure No. 24023 (April, 1984) discloses a technique in which several kinds of bleaching agents are added by mixing them in a bleaching solution for the purpose of improving the color reproduction inferiority, stain and air oxidation rate.

However, the fact has been unknown at all that the shelf stability of the bleach-fixing solution of this invention can be remarkably improved by adding the ferric complex salt having a ligand comprising at least one of the compounds represented respectively by General Formulas

(IV) to (VII) to ferric complex salt having a ligand comprising the compound represented by General Formula (I). Also, this is a surprising fact that can not be obvious, considering that there can be no effect of improving the shelf stability even with use of the bleach-fixing solution having the composition of this invention if the pH is outside the range of this invention, and that there can be no effect of improving the shelf stability even with the pH inside the range of this invention if the combination comprises bleaching agents other than those of this invention.

The bleach-fixing solution of the present embodiment may preferably contain a sulfite and/or a sulfite-releasable compound in order to further improve the shelf stability. Such compounds may include ammonium sulfite, sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite, sodium metabisulfite, formaldehyde bisulfite addition compounds, etc.

These compounds may be used in an amount of 0.001 mol to 2.0 mols, preferably 0.001 mol to 1.3 mols, most preferably 0.01 mol to 0.9 mol, per liter of the bleach-fixing solution of this invention.

The silver halide fixing agent to be contained in the bleach-fixing solution of this invention may include a compound capable of forming a water-soluble complex salt through the reaction with the silver halide used in usual fixing, typically including, for example, thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate, thioureas, thioethers, highly concentrated bromides, iodides, etc. These fixing agents can be used in an amount of not less than 5 g/lit., preferably not less than

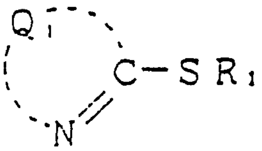
50 g/lit., or more preferably not less than 70 g/lit. and in the amount of the range they can be dissolved.

The bleach-fixing solution of this invention may contain various additives. Preferably contained as the additives are alkali halides or ammonium halides, for example, potassium bromide, sodium bromide, sodium chloride, ammonium bromide, potassium iodide, sodium iodide, ammonium iodide, etc.

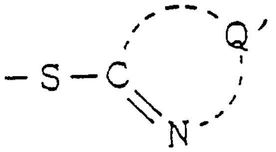
The bleach-fixing solution of this invention may contain, alone or in combination of two or more of, pH buffering agents including boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate, ammonium hydroxide, etc. It may further contain every kind of brightening agents, anti-foaming agents, surface active agents and mildewproofing agents. It may also appropriately contain organic chelating agents such as acetyl acetone, phosphonocarboxylic acid, polyphosphoric acid, organic phosphonic acid, oxycarboxylic acid, polycarboxylic acid, dicarboxylic acid and aminopolycarboxylic acid, stabilizers such as nitroalcohol and nitrate, solubilizing agents such as alkanolamine, anti-stain agents such as organic amine, other additives, and organic solvents such as methanol, dimethylformamide and dimethylsulfoxide.

A bleach accelerator may preferably be used in the bleach-fixing solution of this invention. For example, there can be used the compounds described in Japanese Unexamined Patent Publication No. 19851/1987, and, to exhibit the effect of this invention with good results, the compounds represented respectively by General Formulas (A-I) to (A-Iv) shown below.

General Formula (A-I):

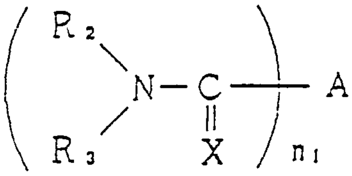


In the formula, Q_1 represents a group of atoms necessary for the formation of a nitrogen-containing heterocyclic ring (including those condensed with a saturated or unsaturated ring of 5 or 6 members); R_1 represents a hydrogen atom, an alkali metal atom,



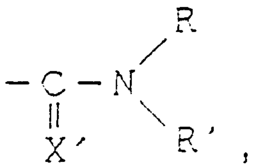
or an alkyl group, provided that Q' have the same meaning as defined for Q_1.

General Formula (A-II):

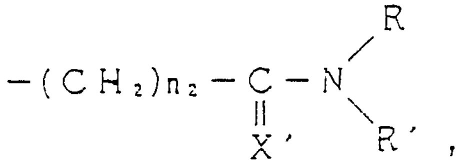


$$\left(\begin{matrix} R_2 \\ R_3 \end{matrix} \!\!> N - \underset{\underset{X}{\|}}{C} \right)_{n_1} \!\!- A$$

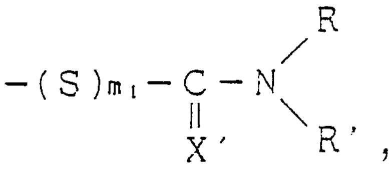
In the formula, R_2 and R_3 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyl group, a carboxyl group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group or an alkenyl group. A represents a group of;



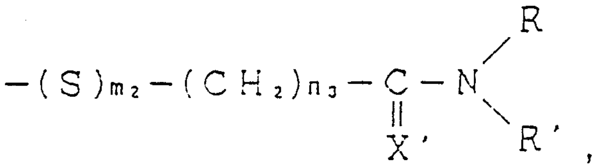
$$-\underset{\underset{X'}{\|}}{C}-N\!<\!\begin{matrix} R \\ R' \end{matrix},$$



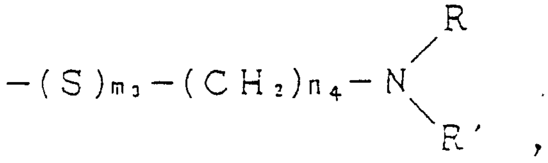
$$-(CH_2)_{n_2}-\underset{\underset{X'}{\|}}{C}-N\!<\!\begin{matrix} R \\ R' \end{matrix},$$



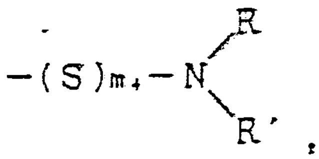
$$-(S)_{m_1}-\underset{\underset{X'}{\|}}{C}-N\!<\!\begin{matrix} R \\ R' \end{matrix},$$



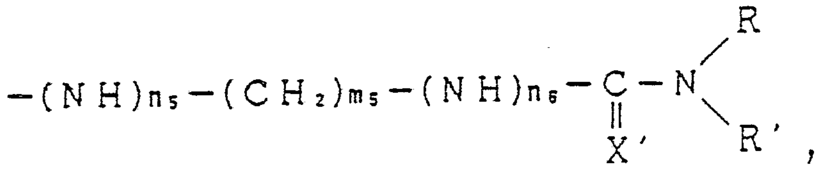
$$-(S)_{m_2}-(CH_2)_{n_3}-\underset{\underset{X'}{\|}}{C}-N\!<\!\begin{matrix} R \\ R' \end{matrix},$$



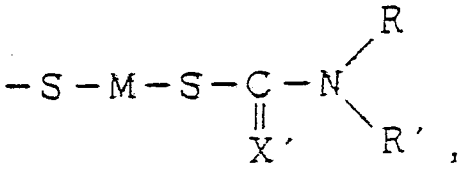
$$-(S)_{m_3}-(CH_2)_{n_4}-N\!<\!\begin{matrix} R \\ R' \end{matrix},$$



$$-(S)_{m_4}-N\begin{matrix}R\\R'\end{matrix},$$



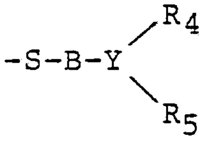
$$-(NH)_{n_5}-(CH_2)_{m_5}-(NH)_{n_6}-\underset{\underset{X'}{\|}}{C}-N\begin{matrix}R\\R'\end{matrix},$$



$$-S-M-S-\underset{\underset{X'}{\|}}{C}-N\begin{matrix}R\\R'\end{matrix},$$

$-SZ$

or a heterocyclic residual group with a valence of n_1 (including those condensed with an unsaturated ring of 5 or 6 members); and X represents =S, =O or =NR". Here, R and R' each have the same meaning as R_2 and R_3, X' have the same meaning as X; Z represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic group, an alkyl group or

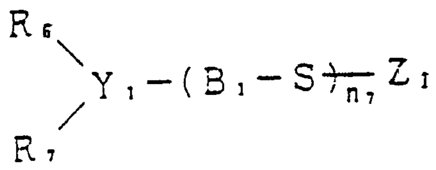


$-S-B-Y\begin{matrix}R_4\\R_5\end{matrix}$; M represents a divalent metal atom;

R" represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic residual group (including those condensed with an unsaturated ring of 5 or 6 members) or an amino group; and n_1 to n_6 and m_1 to m_5 each represent an integer of 1 to 6. B represents an alkylene group having 1 to 6 carbon atoms; Y represents $-N<$ or $-CH<$, R_4 and R_5 each have the same meaning as R_2 and R_3, provided that R_4 and R_5 each may represent -B-SZ, or R_2 and R_3, and R_4 and R_5 each may combine to form a ring.

The compound represented by the above formula may include compounds of enol form and salts thereof.

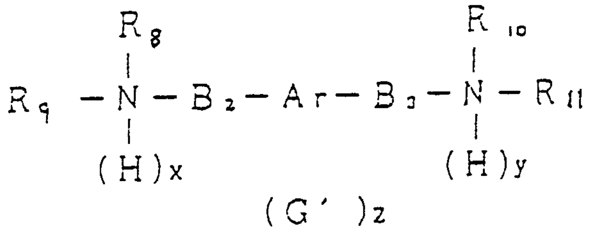
General Formula (A-III):



$$\begin{matrix} R_6 \\ R_7 \end{matrix} \rangle Y_1 - (B_1 - S)_{n_7} Z_1$$

In the formula, R_6 and R_7 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyl group, a carboxyl group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group, an alkenyl group or $-B_1-S-Z_1$, provided that R_6 and R_7 may combine to form a ring. Y_1 represents $>N-$ or $>CH-$; B_1 represents an alkylene group having 1 to 6 carbon atoms; Z_1 represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic residual group, or $-S-B_1-Y_1\langle\begin{matrix} R_6 \\ R_7 \end{matrix}$; and n_7 represents an integer of 1 to 6.

General Formula (IV):



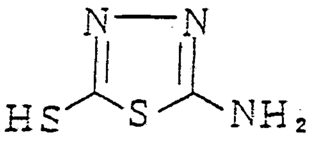
$$R_9 - \underset{(H)_x}{\overset{R_8}{N}} - B_2 - Ar - B_3 - \underset{(H)_y}{\overset{R_{10}}{N}} - R_{11} \quad (G')_z$$

In the formula, Ar represents a divalent arylene group or a divalent organic group comprising the combination of an aryl group with an oxygen atom and/or an alkylene group; B_2 and B_3 each represent a lower alkylene group; R_8, R_9, R_{10} and R_{11} each represent a hydroxyl-substituted lower alkyl group; and x and y each represent 0 or 1. G' represents an anion; and z represents 0, 1 or 2.

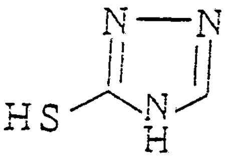
Specific examples of the bleaching accelerators preferably usable in this invention are shown below.

Exemplary compounds:

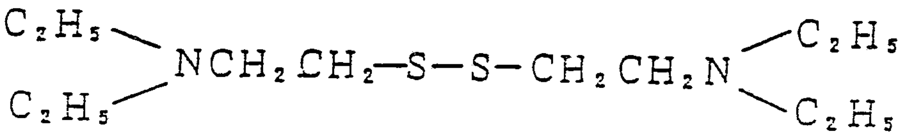
(A - 1)



(A - 2)

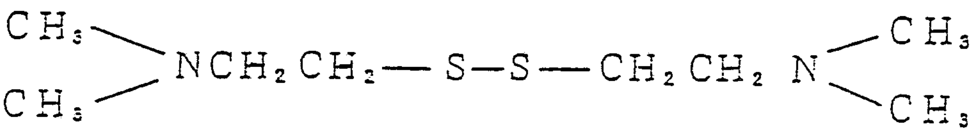


(A - 3)



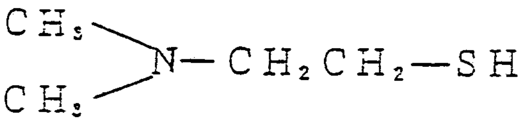
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}NCH_2CH_2-S-S-CH_2CH_2N{<}\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$$

(A - 4)



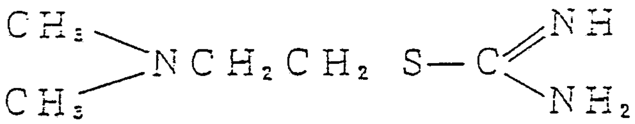
$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}NCH_2CH_2-S-S-CH_2CH_2N{<}\begin{matrix}CH_3\\CH_3\end{matrix}$$

(A - 5)



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}N-CH_2CH_2-SH$$

(A - 6)

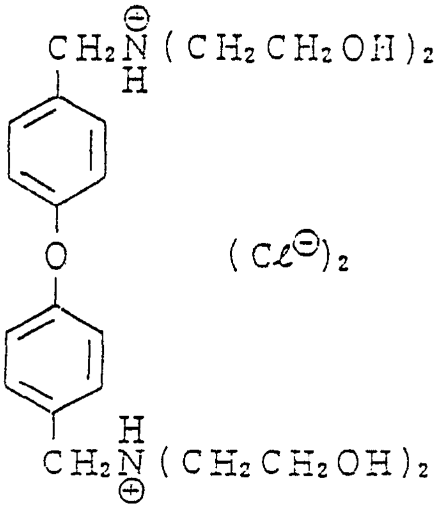


$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}NCH_2CH_2S-C\begin{matrix}{=}NH\\-NH_2\end{matrix}$$

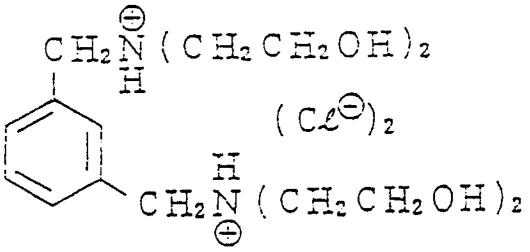
(A - 7)

$H_2N{-}CSNHNHCS{-}NH_2$

(A - 8)



(A - 9)



The bleaching accelerator may preferably added in an amount ranging from about 0.01 to 100 g, more preferably 0.05 to 50 g, and particularly preferably 0.05 to 15 g, per liter of the bleach-fixing solution of this invention.

Recent years, a low replenishment processing is carried out for the purposes of decreasing an environmental load and decreasing the cost for processing solutions. The bleach-fixing solution of this invention can preferably be also applied in the low replenishment processing. Here, it is expected that iodide ions are accumulated in the bleach-fixing solution of this invention. Although the accumulation of iodide ions is conventionally known to bring about a lowering of the desilvering speed, it became clear that not only the bleach-fixing solution of this invention may cause substantially no lowering of the desilvering performance even by the accumulation of iodide ions, but also it may hardly cause surprisingly any density increase at a non-image portion (the so-called fogging) also when a light-sensitive material is dipped in the bleach-fixing solution without taking the step of rinsing such as washing with water after color developing processing.

In this occasion, the iodide ions may preferably be contained in the bleach-fixing solution in an amount of not less than 0.0005 mol/lit. More preferably, it may preferably contained in the bleach-fixing solution in an amount of not less than 0.001 mol/lit.

The processing time when using the bleach-fixing solution of this invention may be not longer than 3 minutes and 30 seconds without any problem, but may preferably be not longer than 3 minutes, more preferably in 2 minutes and 30 seconds.

The bleach-fixing solution of this invention may be used at a temperature of 80°C or less, desirably 55°C or less, and most preferably 45°C or less. It can also desirably be used while suppressing evaporation or the like.

The bleach-fixing solution of this invention can be applied in any light-sensitive silver halide photographic materials so long as they are light-sensitive photographic materials for photographing. Specifically, they may preferably be light-sensitive materials employing a highly sensitive silver iodobromide emulsion having a silver iodide content of not less than 0.5 mol %, more preferably not less than 1 mol % per liter.

The bleach-fixing solution of this invention may be used as a processing solution for bleach-fixing immediately after the color developing of the above light-sensitive silver halide photographic material for photographing, or, alternatively, used as a bleach-fixing solution after the color developing and after the processing such as washing, rinsing or stopping, or further may be used as a bleach-fixing solution after the pre-fixing was carried out after the color developing. The processing by use of the bleach-fixing solution of this invention may be also followed by washing with water, and thereafter may be followed by stabilizing. It can be also applied in the multi-step counter current stabilizing technique in which the washing step is omitted or the amount of water for the washing is extremely reduced as disclosed in Japanese Unexamined Patent Publication No. 8543/1982 or the processing technique in which a washing-substitutive processing solution is used as disclosed in Japanese Unexamined Patent Publication No. 14834/1983. If necessary, in addition to the steps such as color developing, bleach-fixing and washing, there can be also added various auxiliary steps such as hardening, neutralizing, black and white developing, reversing, and washing with a small amount of water.

The silver halide emulsion for photographing that can be applied in this invention can be chemically sensitized according to a conventional method, and can be optically sensitized to a desired wavelength region by using a sensitizing dye.

An antifoggant, a stabilizer and so forth can be added in the silver halide emulsion. As a binder for the emulsion, gelatin can be used advantageously.

Emulsion layers and other hydrophilic colloid layers can be hardened, and also can contain a plasticizer, a dispersion of a water-soluble or slightly soluble synthetic polymer (i.e., latex).

Couplers can be used in the emulsion layers of a light-sensitive color photographic material.

There can be also used a compound capable of releasing photographically useful fragments such as development accelerators, bleaching accelerators, developers, silver halide solvents, color torning agents, hardening agents, fogging agents, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers through the coupling with a colored coupler, a competing coupler and an oxidized product of a developing agent.

The light-sensitive material can be provided with auxiliary layers such as a filter layer, a halation-preventive layer and an irradiation-preventive layer. These layers and/or emulsion layers may also contain a dye that may flow out from the light-sensitive material or may be bleached during development processing.

A matte agent, a lubricant, an image-stabilizing agent, a surface active agent, a color fog preventive agent, a development accelerator, a development retarder or a bleaching accelerator may be added in the light-sensitive material.

As a support, there can be used paper laminated with polyethylene or the like, a polyethylene terephthalate film, baryta paper, cellulose triacetate, etc.

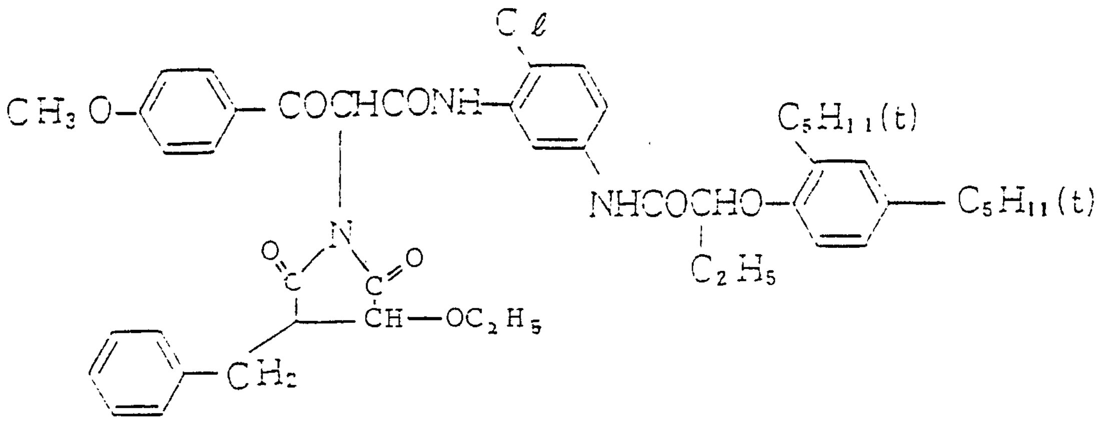
Details of this invention will be described below by Examples, but the embodiment of this invention are by no means limited by these.

Example 1

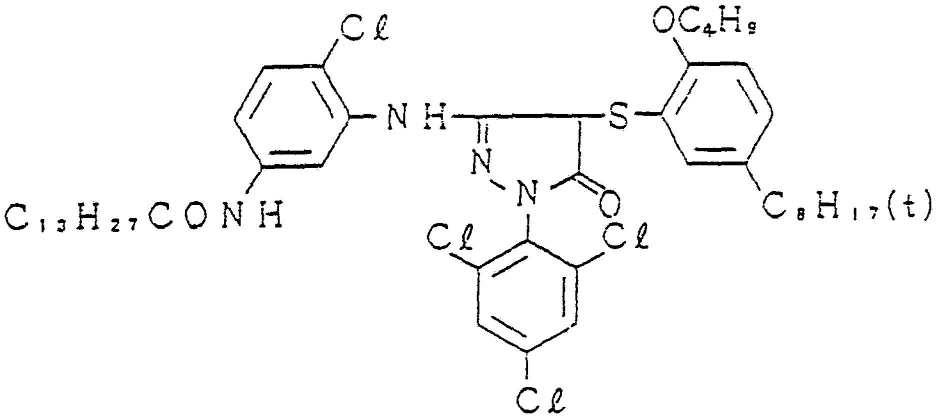
(Experiment 1)

On a triacetate film support, a halation-preventive layer and a gelatin layer were provided, and coated thereon were a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a filter layer containing yellow colloidal silver, and a blue-sensitive silver halide emulsion layer so as to give a total silver amount of 88 mg per 100 cm^2. The above emulsion layers comprised silver iodobromide having silver iodide mol % of about 4.3 %, and there were used the following (Y-1) as a yellow coupler in the blue-sensitive silver halide emulsion layer, the following (M-1) as a magenta coupler in the green-sensitive silver halide emulsion layer, and the following (C-1) as a cyan coupler in the red-sensitive silver halide emulsion layer. To the respective emulsion layers, a sensitizing dye, a hardening agent and a spreading agent were added. A light-sensitive silver halide color negative materials thus prepared was used as a sample.

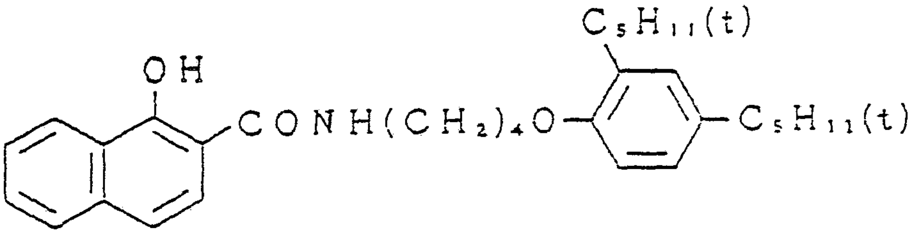
Yellow Coupler (Y-1):



Magenta Coupler (M-1):



Cyan Coupler (C-1):



Using samples obtained by cutting the above sample into pieces and subjected to wedge exposure according a conventional method, processing was carried out according to the following steps with use of a processing apparatus for pieces (hereinafter called "hand developing").

Processing step	Processing temp. (°C)	Number of tanks	Processing time
1. Color developing	37.8	1 tank	3 min 15 sec
2. Bleach-fixing	37.8	1 tank	4 min 20 sec
3. Washing	30 to 34	2 tanks	4 min 20 sec
4. Stabilizing	30 to 34	1 tank	2 min 10 sec
5. Drying			

As for the color developing solution, bleach-fixing solution and stabilizing solution, the solutions as shown below were used.

[Color developing solution]

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	5.0 g
Sodium bromide	1.2 g
Potassium iodide	2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
Sodium diethylenetriaminepentaacetate	2.0 g
N-ethyl-N-β-hydroxyethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Potassium hydroxide	1.2 g

Made up to 1 liter by adding water, and adjusted to pH 10.06 with use of sodium hydroxide or 20 % sulfuric acid.

[Bleach-fixing solution]

Ferric ammonium complex salt of organic acid as shown in Table 1	0.25 mol
Ammonium thiosulfate (a 70 % solution)	300 ml
Preservative shown in Table 1	Amount shown in Table 1
Silver powder	2.0 g

Made up to 1 liter in total amount by adding water, and adjusted the pH as shown in Table 1 with use of acetic acid and ammonia water.

[Stabilizing solution]

Formalin (a 37 % aqueous solution)	2 ml
Conidax (produced by Konishiroku Photo Industry Co., Ltd.)	5 ml

Made up to 1 liter by adding water.

Table 1

Bleach-fixing solution No.	Organic acid which forms ferric complex	pH	Preservative (amount, mol/lit.)
1-1 (Comparative)	Ethylene-diaminetetra-acetic acid (EDTA)	8.0	Exemplary compound No. II - 1 (0.20)
1-2 (Comparative)		7.0	
1-3 (Comparative)		6.8	
1-4 (Comparative)		6.7	
1-5 (Comparative)		6.5	
1-6 (Comparative)		5.0	
1-7 (Comparative)		4.0	
1-8 (Comparative)		3.0	
1-9 (Comparative)		2.0	
2-1 (Comparative)	Exemplary compound No. I - 1	8.0	Exemplary compound No. II - 1 (0.20)
2-2 (Comparative)		7.0	
2-3 (Comparative)		6.8	
2-4 (Present invention)		6.7	
2-5 (Present invention)		6.5	
2-6 (Present invention)		5.0	
2-7 (Present invention)		4.0	
2-8 (Present invention)		3.0	
2-9 (Present invention)		2.0	
3-1 (Comparative)	Exemplary compound No. I - 2	8.0	Exemplary compound No. II - 1 (0.20)
3-2 (Comparative)		7.0	
3-3 (Present invention)		6.8	
3-4 (Present invention)		6.7	
3-5 (Present invention)		6.5	
3-6 (Present invention)		5.0	
3-7 (Present invention)		4.0	
3-8 (Present invention)		3.0	
3-9 (Comparative)		2.0	

Table 1 (cont'd)

Bleach-fixing solution No.	Organic acid which forms ferric complex	pH	Preservative (amount, mol/lit.)
4-1 (Comparative)	Exemplary compound No. I - 3	8.0	Exemplary compound No. II - 1 (0.20)
4-2 (Comparative)		7.0	
4-3 (Present invention)		6.8	
4-4 (Present invention)		6.7	
4-5 (Present invention)		6.5	
4-6 (Present invention)		5.0	
4-7 (Present invention)		4.0	
4-8 (Present invention)		3.0	
4-9 (Comparative)		2.0	
5-1 (Comparative)	Ethylenediaminetetraacetic acid (EDTA)	8.0	Exemplary compound No. III - 1 (0.10)
5-2 (Comparative)		7.0	
5-3 (Comparative)		6.8	
5-4 (Comparative)		6.7	
5-5 (Comparative)		6.5	
5-6 (Comparative)		5.0	
5-7 (Comparative)		4.0	
5-8 (Comparative)		3.0	
5-9 (Comparative)		2.0	
6-1 (Comparative)	Exemplary compound No. I - 1	8.0	Exemplary compound No. III - 1 (0.10)
6-2 (Comparative)		7.0	
6-3 (Present invention)		6.8	
6-4 (Present invention)		6.7	
6-5 (Present invention)		6.5	
6-6 (Present invention)		5.0	
6-7 (Present invention)		4.0	
6-8 (Present invention)		3.0	
6-9 (Comparative)		2.0	

Table 1 (cont'd)

Bleach-fixing solution No.	Organic acid which forms ferric complex	pH	Preservative (amount, mol/lit.)
7-1 (Comparative)	Exemplary compound No. I - 2	8.0	Exemplary compound No. III - 1 (0.10)
7-2 (Comparative)		7.0	
7-3 (Present invention)		6.8	
7-4 (Present invention)		6.7	
7-5 (Present invention)		6.5	
7-6 (Present invention)		5.0	
7-7 (Present invention)		4.0	
7-8 (Present invention)		3.0	
7-9 (Comparative)		2.0	
8-1 (Comparative)	Exemplary compound No. I - 3	8.0	Exemplary compound No. III - 1 (0.10)
8-2 (Comparative)		7.0	
8-3 (Present invention)		6.8	
8-4 (Present invention)		6.7	
8-5 (Present invention)		6.5	
8-6 (Present invention)		5.0	
8-7 (Present invention)		4.0	
8-8 (Present invention)		3.0	
8-9 (Comparative)		2.0	

The bleach-fixing solutions available after the above processing were stored with time for 1 week at 38°C under the open ratio of 10 cm^2/lit. (which is the open condition corresponding to that of usual automatic processing machine, and meant that the solution has an air contact area of 10 cm^2 based on 1 liter of the bleach-fixing solution), and the above processing was again repeated with use of the bleach-fixing solutions available after storage. After the processing, the residual silver amount (mg/dm^2) at the maximum density portion of the film samples (the respective samples available before and after the storage with time, of the bleach-fixing solutions) was measured according to a fluorescent X-ray method, and the cyan dye density was further measured with use of Sakura Photoelectric Densitometer PDA-65 (produced by Konishiroku Photo Industry Co., Ltd.) to determine the color reproduction percentage.

Results obtained are shown in Table 2 together.

Table 2

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
1- 1 (Comparative)	1 - 1	1.4	93	3.5	93
1- 2 (Comparative)	1 - 2	1.2	94	3.1	92
1- 3 (Comparative)	1 - 3	1.1	93	2.2	93
1- 4 (Comparative)	1 - 4	0.8	91	2.1	91
1- 5 (Comparative)	1 - 5	0.7	92	2.1	92
1- 6 (Comparative)	1 - 6	0.6	89	1.9	89
1- 7 (Comparative)	1 - 7	0.4	87	1.8	87
1- 8 (Comparative)	1 - 8	0.2	85	1.4	85
1- 9 (Comparative)	1 - 9	0.1	84	1.1	84
1-10 (Comparative)	2 - 1	1.0	100	1.3	100
1-11 (Comparative)	2 - 2	0.9	100	1.0	100
1-12 (Present invention)	2 - 3	0.2	100	0.5	100
1-13 (Present invention)	2 - 4	0.1	100	0.3	100
1-14 (Present invention)	2 - 5	0.1	100	0.2	100
1-15 (Present invention)	2 - 6	0.1	100	0.1	100
1-16 (Present invention)	2 - 7	0.1	99	0.1	98
1-17 (Present invention)	2 - 8	0.1	98	0.1	96
1-18 (Comparative)	2 - 9	0.1	94	0.1	91

Table 2 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
1-19 (Comparative)	3 - 1	1.1	100	1.2	100
1-20 (Comparative)	3 - 2	1.0	100	1.1	100
1-21 (Present invention)	3 - 3	0.5	100	0.6	100
1-22 (Present invention)	3 - 4	0.3	100	0.3	100
1-23 (Present invention)	3 - 5	0.2	100	0.2	100
1-24 (Present invention)	3 - 6	0.2	100	0.2	100
1-25 (Present invention)	3 - 7	0.2	98	0.2	97
1-26 (Present invention)	3 - 8	0.2	97	0.2	95
1-27 (Comparative)	3 - 9	0.1	92	0.1	90
1-28 (Comparative)	4 - 1	1.1	100	1.4	100
1-29 (Comparative)	4 - 2	0.9	100	1.3	100
1-30 (Present invention)	4 - 3	0.7	99	0.8	99
1-31 (Present invention)	4 - 4	0.5	99	0.5	99
1-32 (Present invention)	4 - 5	0.3	99	0.3	99
1-33 (Present invention)	4 - 6	0.2	99	0.2	99
1-34 (Present invention)	4 - 7	0.2	99	0.2	97
1-35 (Present invention)	4 - 8	0.2	98	0.2	95
1-36 (Comparative)	4 - 9	0.1	89	0.2	86

Table 2 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
1-37 (Comparative)	5 - 1	1.4	95	3.9	92
1-38 (Comparative)	5 - 2	1.2	94	3.5	91
1-39 (Comparative)	5 - 3	1.0	93	2.4	90
1-40 (Comparative)	5 - 4	0.8	93	2.0	86
1-41 (Comparative)	5 - 5	0.7	91	2.4	84
1-42 (Comparative)	5 - 6	0.6	88	1.3	82
1-43 (Comparative)	5 - 7	0.4	86	2.1	80
1-44 (Comparative)	5 - 8	0.2	87	1.5	74
1-45 (Comparative)	5 - 9	0.1	85	1.3	72
1-46 (Comparative)	6 - 1	1.0	100	1.4	100
1-47 (Comparative)	6 - 2	1.0	100	1.0	100
1-48 (Present invention)	6 - 3	0.3	100	0.4	100
1-49 (Present invention)	6 - 4	0.1	100	0.3	100
1-50 (Present invention)	6 - 5	0.1	100	0.1	100
1-51 (Present invention)	6 - 6	0.1	100	0.1	100
1-52 (Present invention)	6 - 7	0.1	99	0.1	99
1-53 (Present invention)	6 - 8	0.1	99	0.1	97
1-54 (Comparative)	6 - 9	0.2	95	0.2	90

Table 2 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
1-55 (Comparative)	7 - 1	1.1	100	1.5	100
1-56 (Comparative)	7 - 2	1.0	100	1.1	100
1-57 (Present invention)	7 - 3	0.5	100	0.4	100
1-58 (Present invention)	7 - 4	0.3	100	0.3	100
1-59 (Present invention)	7 - 5	0.2	100	0.2	100
1-60 (Present invention)	7 - 6	0.2	100	0.2	100
1-61 (Present invention)	7 - 7	0.2	99	0.2	98
1-62 (Present invention)	7 - 8	0.2	98	0.2	96
1-63 (Comparative)	7 - 9	0.2	93	0.2	91
1-64 (Comparative)	8 - 1	3.6	100	3.6	100
1-65 (Comparative)	8 - 2	1.6	100	1.6	100
1-66 (Present invention)	8 - 3	0.7	99	0.7	99
1-67 (Present invention)	8 - 4	0.6	99	0.6	99
1-68 (Present invention)	8 - 5	0.4	99	0.4	99
1-69 (Present invention)	8 - 6	0.3	99	0.3	99
1-70 (Present invention)	8 - 7	0.4	99	0.4	96
1-71 (Present invention)	8 - 8	0.2	98	0.2	93
1-72 (Comparative)	8 - 9	0.3	88	0.3	86

* Residual silver amount is expressed in terms of the residual silver mg number per 1 dm^2 (100 cm^2).

** Color reproduction percentage is shown by a percentage corresponding to the proportion of a perfectly color developed dye when the state where no leuco dye is present at all is assumed as 100 %.

It is understood from the above Table 2 that in the case the bleach-fixing solutions with pH range of 3.0 to 6.8 are used with use of the organic acid ferric complex salt according to this invention, there is seen only small residual silver and good color reproduction percentage regardless of whether the solutions were stored with time. In particular, good results are obtained when the pH is 4.0 to 6.7, and particularly good results are obtained when the pH is 5.0 to 6.5.

However, according to the comparative bleach-fixing solutions employing a comparative EDTA as the organic acid result in insufficient desilvering performance and color reproduction performance regardless of whether the solutions were stored with time.

Similar effect was confirmed also when exemplary compounds Nos. II-1 and III-1 used as preservatives in the above bleach-fixing solutions Nos. 1-1 to 8-9 are replaced by II-2 to II-6 and III-2 to III-5, respectively.

(Experiment 2)

In bleach-fixing solutions Nos. 1-1 and 2-1 used in the above Experiment 1, the types of the preservatives in the bleach-fixing solutions and the concentration for the addition were changed as shown in Table 3 below and the pH was adjusted to 6.0, to prepare bleach-fixing solutions Nos. 9-1 to 9-3 and Nos. 10-1 to 10-3. Using the above bleach-fixing solutions, the light-sensitive materials corresponding to those in Experiment 1 were processed, and the resulting bleach-fixing solutions having been used for the processing were stored with time in the same manner as in Experiment 1. Using the bleach-fixing solutions stored with time, the desilvering performance and color reproduction performance were measured in the same manner as in Experiment 1 to obtain the results shown together in Table 3.

Also, after storage for 1 week, the storage was further continued under the open ratio of 10 times to visually observe the days elapsing before the precipitation occurred.

Results obtained above are shown together in Table 3.

Table 3

Test No.	Bleach-fixing solution			Bleach fixing after storage with time		
	No.	Organic acid which forms ferric complex salt	Preservative (amount, mol/lit.)	Residual silver amount	Color reproduction percentage	Precipitation (days)*
1-73 (Comparative)	9-1	EDTA	$(NH_4)_2SO_3$ (0.16)	0.1	95	10
1-74 (Comparative)	9-2		Exemplary compound No. II-2 (0.16)	0.2	94	17
1-75 (Comparative)	9-3		Exemplary compound No. III-2 (0.08)	0.2	93	16
1-76 (Comparative)	10-1	Exemplary compound No. I-1	$(NH_4)_2SO_3$ (0.16)	0.1	99	9
1-77 (Present invention)	10-2		Exemplary compound No. II-2 (0.16)	0.1	100	21
1-78 (Present invention)	10-3		Exemplary compound No. III-2 (0.08)	0.1	100	23

* Indicated in terms of the days elapsing before the precipitation occurred.

As will be clear from Table 3, it is understood that, in contrast to the comparative bleach-fixing solutions in which the organic acid which forms the comparative ferric complex salt and the preservative are used, the bleach-fixing solutions in which the organic acid which forms the ferric complex salt of this invention and the bisulfite addition compound are used can delay the occurrence of precipitation to have good shelf stability even when stored with time, and also can achieve good desilvering performance and color reproduction performance of a dye image to be obtained by use of said solution.

It is seen from the results in the above Experiment 1 and Experiment 2 that the bleach-fixing solutions according to this invention, in other words, the bleach-fixing solutions having the pH ranging between 3.0 and 6.8, containing a ferric complex salt having a ligand comprising a compound represented by General Formula (I), and further containing the bisulfite addition compound of this invention can have a good desilvering performance particularly even after storage with time, can favorably prevent color reproduction inferiority from being occurred, and can have good shelf stability. In addition, the bleach-fixing solutions of this invention had no ammoniacal odor at all.

Example 2

Bleach-fixing solutions were stored with time in the same manner as in Experiment 1 of Example 1. Here, however, the bisulfite addition compound and exemplary compound No. II-4 in the bleach-fixing solutions were used in concentration of 0.25 mol/lit., the types of the bleaching agents were selected as shown in Table 4, and the concentration of the bleaching agents was varied as shown in Table 4. The pH of the bleach-fixing solutions was adjusted to 6.0.

After storage with time, the same evaluation as in Experiment 1 of Example 1 was carried out. Results are shown in Table 4.

Next, all of the bleach-fixing solutions were continuously stored in the same manner as in Experiment 2 of Example 1 to measure the days elapsing before the solutions were sulfidized. Results are shown together in Table 4.

Table 4

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/100cm^2)	Color repro-duction per-centage (%)	Days before sulfidi-zing (days)
		No.	Amount (mol/lit.)			
2- 1 (Present invention)	2-11	Exemplary compound No. I - 1	0.02	1.1	88	24
2- 2 (Present invention)	2-12		0.10	0.9	94	25
2- 3 (Present invention)	2-13		0.18	0.6	95	25
2- 4 (Present invention)	2-14		0.20	0.3	98	24
2- 5 (Present invention)	2-15		0.40	0.2	100	22
2- 6 (Present invention)	2-16		0.60	0.2	100	20
2- 7 (Present invention)	2-17		0.80	0.2	100	19
2- 8 (Present invention)	2-18		0.85	0.2	100	15
2- 9 (Present invention)	2-19		1.20	0.2	100	15
2-10 (Present invention)	2-20		1.30	0.2	100	10

Table 4 (Cont.)

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/ 100cm^2)	Color reproduction percentage (%)	Days before sulfidizing (days)
		No.	Amount (mol/lit.)			
2-11 (Present invention)	3-11	Exemplary compound No. I - 2	0.02	1.2	84	28
2-12 (Present invention)	3-12		0.10	1.0	92	26
2-13 (Present invention)	3-13		0.18	0.9	93	25
2-14 (Present invention)	3-14		0.20	0.5	97	25
2-15 (Present invention)	3-15		0.40	0.3	98	23
2-16 (Present invention)	3-16		0.60	0.3	99	23
2-17 (Present invention)	3-17		0.80	0.3	99	22
2-18 (Present invention)	3-18		0.85	0.3	99	15
2-19 (Present invention)	3-19		1.20	0.3	99	11
2-20 (Present invention)	3-20		1.30	0.3	99	12

Table 4 (Cont.)

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/100cm^2)	Color reproduction percentage	Days before sulfidizing (days)
		No.	Amount (mol/lit.)			
2-21 (Present invention)	4-11	Exemplary compound No. I - 3	0.02	1.4	84	27
2-22 (Present invention)	4-12		0.10	1.3	92	26
2-23 (Present invention)	4-13		0.18	0.9	94	26
2-24 (Present invention)	4-14		0.20	0.8	96	26
2-25 (Present invention)	4-15		0.40	0.8	96	24
2-26 (Present invention)	4-16		0.60	0.8	96	24
2-27 (Present invention)	4-17		0.80	0.8	96	24
2-28 (Present invention)	4-18		0.85	0.7	97	20
2-29 (Present invention)	4-19		1.20	0.7	97	19
2-30 (Present invention)	4-20		1.30	0.7	97	15

As will be clear from Table 4, among the bleach-fixing solutions of this invention, particularly those having the content of bleaching agent in the range of 0.02 mol/lit. to 1.30 mol/lit., preferably 0.10 to 1.20 mol/lit., and more preferably 0.20 to 0.8 mol/lit., are seen to be good bleach-fixing solutions that can have high desilvering and color reproduction performances and may not be sulfidized for a long period even if they are stored with time.

Example 3

Bleach-fixing solutions were stored with time in the same manner as in Experiment 1 of Example 1. Here, however, as the preservative in the bleach-fixing solutions, the preservative in bleach-fixing solution No. 1-1 used in Experiment 1 of Example 1 was replaced by exemplary compound No. II-6 (concentration: 0.2 mol/lit), the bleaching agent and the amount thereof were changed as shown in Table 5, and the concentration of KI in the bleach-fixing solutions was varied as shown in Table 5 The pH of the bleach-fixing solutions was adjusted to 6.0.

After storage with time, evaluation on the desilvering performance was carried out in the same manner as in Experiment 1 of Example 1. Results obtained are shown in Table 5.

The samples having been processed were also subjected to bleaching and fixing according to the CNK-4 standard processing (color negative processing by Konishiroku Photo Industry Co., Ltd.), and, after the residual silver was perfectly removed by carrying out bleaching and fixing, transmission density of magenta dyes was measured. The value obtained was designated as D_{R1}. Next, after color developing was carried out in the same manner as in Experiment 1 of Example 1, the transmission density of magenta dyes of the samples subjected to bleaching and fixing according to the CNK-4 standard processing was measured, and the resulting value was designated as D_{R2}. The difference between D_{R1} and D_{R2} was determined (ΔD_R) to evaluate the magenta stain.

Table 5

Test No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount (x 10^{-3} mol/lit.)	Residual silver amount (mg/ $100cm^2$)	Magenta stain (ΔD_R)
3- 1 (Comparative)	Ethylene-diamine-tetraacetic acid (0.3 mol/lit.)	0	5.8	0.07
3- 2 (Comparative)		0.5	7.4	0.05
3- 3 (Comparative)		0.9	8.6	0.04
3- 4 (Comparative)		1.0	9.8	0.01
3- 5 (Comparative)		2.0	11.0	0.01
3- 6 (Present invention)	Exemplary compound (I - 1) (0.30 mol/ lit.)	0	0.2	0.06
3- 7 (Present invention)		0.5	0.2	0.04
3- 8 (Present invention)		0.9	0.3	0.04
3- 9 (Present invention)		1.0	0.3	0.02
3-10 (Present invention)		2.0	0.4	0.00
3-11 (Present invention)	Exemplary compound (I - 2) (0.30 mol/ lit.)	0	0.3	0.07
3-12 (Present invention)		0.5	0.3	0.06
3-13 (Present invention)		0.9	0.4	0.05
3-14 (Present invention)		1.0	0.6	0.02
3-15 (Present invention)		2.0	0.7	0.00

Table 5 (Cont.)

Test No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount (x 10^{-3} mol/lit.)	Residual silver amount (mg/100cm^2)	Magenta stain (ΔD_R)
3-16 (Present invention)	Exemplary compound (I - 3) (0.30 mol/lit.)	0	0.6	0.07
3-17 (Present invention)		0.5	0.6	0.06
3-18 (Present invention)		0.9	0.7	0.04
3-19 (Present invention)		1.0	0.8	0.01
3-20 (Present invention)		2.0	1.0	0.00

As will be clear from Table 5, in the comparative bleach-fixing solutions, the addition of KI can make small the magenta stain, but the desilvering performance is greatly lowered. However, in the bleach-fixing solutions of this invention, not only the addition of KI can suppress the magenta stain to a lower level, but also the desilvering performance is only slightly lowered to obtain good results.

Example 4

Bleach-fixing solutions Nos. 1-11 to 1-16 and Nos. 2-21 to 2-26 were prepared in the same manner as in Experiment 1 of Example 1 except that, in the bleach-fixing solutions No. 1-1 and No. 2-1 prepared in Experiment 1 of Example 1, the pH was adjusted to 6.0, exemplary compound No. II-4 (concentration: 0.1 mol/lit.) was used as the preservative, and the bleaching accelerator was added as shown in Table 6 below.

Using the bleach-fixing solutions thus obtained, evaluation was carried out in the same manner as in Experiment 1 and Experiment 2 of Example 1 except that the bleach-fixing time 4 minutes 20 seconds in Experiment 1 was set to 3 minutes 15 seconds.

Results obtained are shown in Table 6.

Table 6

Test No.	Bleach-fixing solution No.	Bleaching accelerator (1g/lit.)	Bleach-fixing solution before storage		Bleach-fixing solution after storage		Days before occurence of precipitation
			Residual silver amount	Color reproduction per-centage	Residual silver amount	Color reproduction per centage	
4- 1 (Comparative)	1 - 11	-	7.2	84	9.8	77	30
4- 2 (Comparative)	1 - 12	A - 1	5.4	85	4.0	86	21
4- 3 (Comparative)	1 - 13	A - 2	6.8	87	4.1	85	22
4- 4 (Comparative)	1 - 14	A - 4	6.6	87	4.2	85	20
4- 5 (Comparative)	1 - 15	A - 6	6.4	85	4.3	86	23
4- 6 (Comparative)	1 - 16	A - 9	3.2	87	3.4	88	22
4- 7 (Present invention)	2 - 21	-	1.6	91	1.9	89	32
4- 8 (Present invention)	2 - 22	A - 1	0.2	98	0.1	99	34
4- 9 (Present invention)	2 - 23	A - 2	0.2	99	0.1	99	32
4-10 (Present invention)	2 - 24	A - 4	0.2	99	0.1	98	33
4-11 (Present invention)	2 - 25	A - 6	0.2	99	0.1	99	35
4-12 (Present invention)	2 - 26	A - 9	0.2	99	0.2	98	32

As will be clear from Table 6 , in the case the bleach accelerator is added, the bleach-fixing solutions of this invention can maintain good effect in any of the desilvering performance, color reproduction performance and shelf stability even when stored. In contrast thereto, the bleach-fixing solutions outside this invention, which can be effective for any of the performances observed immediately after the solutions were prepared, result in further deterioration of the desilvering performance, color reproduction performance and shelf stability when they are stored.

Example 5

(Experiment 1)

On a triacetate film support, a halation-preventive layer and a gelatin layer were provided, and coated thereon were a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a filter layer containing yellow colloidal silver, and a blue-sensitive silver halide emulsion layer so as to give a total silver amount of 90 mg per 100 cm^2. The above emulsion layers comprised silver iodobromide having silver iodide mol % of about 4.1 %, and there were used the above (Y-1) as a yellow coupler in the blue-sensitive silver halide emulsion layer, the above (M-1) as a magenta coupler in the green-sensitive silver halide emulsion layer, and the above (C-1) as a cyan coupler in the red-sensitive silver halide emulsion layer. To the respective emulsion layers, conventional additives such as a sensitizing dye, a hardening agent and a spreading agent were added. A light-sensitive silver halide color negative materials thus prepared was used as a sample.

Using samples obtained by cutting the above sample into pieces and subjected to wedge exposure according a conventional method, processing was carried out according to the following steps with use of a processing apparatus for pieces (hereinafter called "hand developing").

Processing step	Processing temp. (°C)	Number of tanks	Processing time
1. Color developing	37.8	1 tank	3 min 15 sec
2. Bleach-fixing	37.8	1 tank	4 min 20 sec
3. Washing	30 to 34	2 tanks	4 min 20 sec
4. Stabilizing	30 to 34	1 tank	2 min 10 sec
5. Drying			

As for the color developing solution, bleach-fixing solution and stabilizing solution, the solutions as shown below were used.

[Color developing solution]

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	5.0 g
Sodium bromide	1.2 g
Potassium iodide	2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
Sodium diethylenetriaminepentaacetate	2.0 g
N-ethyl-N-β-hydroxyethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Potassium hydroxide	1.2 g

Made up to 1 liter by adding water, and adjusted to pH 10.06 with use of sodium hydroxide or 20 % sulfuric acid.

[Bleach-fixing solution]

Ferric ammonium complex salt of organic acid as shown in Table 7	0.25 mol
Ammonium thiosulfate (a 70 % solution)	300 ml
Ammonium sulfite	10 g
Exemplary vinyl pyrrolidone polymer (2)	1.0 g
Silver powder	2.0 g

Made up to 1 liter in total amount by adding water, and adjusted the pH as shown in Table 7 with use of acetic acid and ammonia water.

[Stabilizing solution]

Formalin (a 37 % aqueous solution)	2 ml
Conidax (produced by Konishiroku Photo Industry Co., Ltd.)	5 ml

Made up to 1 liter by adding water.

Table 7

Bleach-fixing solution No.	Organic acid which forms ferric ammonium salt	pH
11- 1 (Comparative)	Ethylenediamine-tetraacetic acid (EDTA)	8.0
11- 2 (Comparative)		7.5
11- 3 (Comparative)		7.0
11- 4 (Comparative)		6.8
11- 5 (Comparative)		6.7
11- 6 (Comparative)		6.5
11- 7 (Comparative)		5.0
11- 8 (Comparative)		4.0
11- 9 (Comparative)		3.0
11-10 (Comparative)		2.0
12- 1 (Comparative)	Diethylenetriamine-pentaacetic acid (DTPA)	8.0
12- 2 (Comparative)		7.5
12- 3 (Comparative)		7.0
12- 4 (Comparative)		6.8
12- 5 (Comparative)		6.7
12- 6 (Comparative)		6.5
12- 7 (Comparative)		5.0
12- 8 (Comparative)		4.0
12- 9 (Comparative)		3.0
12-10 (Comparative)		2.0
13- 1 (Comparative)	Exemplary compound No. I - 1	8.0
13- 2 (Comparative)		7.5
13- 3 (Comparative)		7.0
13- 4 (Present invention)		6.8
13- 5 (Present invention)		6.7
13- 6 (Present invention)		6.5
13- 7 (Present invention)		5.0
13- 8 (Present invention)		4.0
13- 9 (Present invention)		3.0
13-10 (Comparative)		2.0

Table 7 (cont'd)

Bleach-fixing solution No.	Organic acid which forms ferric ammonium salt	pH
14- 1 (Comparative)	Exemplary compound No. I - 2	8.0
14- 2 (Comparative)		7.5
14- 3 (Comparative)		7.0
14- 4 (Present invention)		6.8
14- 5 (Present invention)		6.7
14- 6 (Present invention)		6.5
14- 7 (Present invention)		5.0
14- 8 (Present invention)		4.0
14- 9 (Present invention)		3.0
14-10 (Comparative)		2.0
15- 1 (Comparative)	Exemplary compound No. I - 3	8.0
15- 2 (Comparative)		7.5
15- 3 (Comparative)		7.0
15- 4 (Present invention)		6.8
15- 5 (Present invention)		6.7
15- 6 (Present invention)		6.5
15- 7 (Present invention)		5.0
15- 8 (Present invention)		4.0
15- 9 (Present invention)		3.0
15-10 (Comparative)		2.0

The bleach-fixing solutions available after the above processing were stored with time for 1 week at 38°C under the open ratio of 10 cm^2/lit. (which is the open condition corresponding to that of usual automatic processing machine, and meant that the solution have an air contact area of 10 cm^2 based on 1 liter of the bleach-fixing solution), and the above processing was again repeated with use of the bleach-fixing solutions available after storage. After the processing, the residual silver amount (mg/dm^2) at the maximum density portion of the film samples (the respective samples available before and after the storage with time, of the bleach-fixing solutions) was measured according to a fluorescent X-ray method, and the cyan dye density was further measured with use of Sakura Photoelectric Densitometer PDA-65 (produced by Konishiroku Photo Industry Co., Ltd.) to determine the color reproduction percentage.

Results obtained are shown in Table 8 together.

Table 8

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
5- 1 (Comparative)	11 - 1	10.4	100	11.3	89
5- 2 (Comparative)	11 - 2	9.0	99	10.9	91
5- 3 (Comparative)	11 - 3	7.0	96	9.8	88
5- 4 (Comparative)	11 - 4	6.3	95	8.2	85
5- 5 (Comparative)	11 - 5	5.8	93	7.3	80
5- 6 (Comparative)	11 - 6	5.1	90	6.1	75
5- 7 (Comparative)	11 - 7	3.8	78	4.8	72
5- 8 (Comparative)	11 - 8	2.5	72	2.7	68
5- 9 (Comparative)	11 - 9	1.2	68	1.8	61
5-10 (Comparative)	11 - 10	0.8	65	1.0	52
5-11 (Comparative)	12 - 1	1.3	100	4.8	95
5-12 (Comparative)	12 - 2	0.4	100	4.3	94
5-13 (Comparative)	12 - 3	0.3	100	4.0	94
5-14 (Comparative)	12 - 4	0.3	98	3.8	90
5-15 (Comparative)	12 - 5	0.3	96	3.7	87
5-16 (Comparative)	12 - 6	0.3	92	3.4	80
5-17 (Comparative)	12 - 7	0.3	82	3.0	75
5-18 (Comparative)	12 - 8	0.3	75	2.1	61
5-19 (Comparative)	12 - 9	0.2	69	1.6	55
5-20 (Comparative)	12 - 10	0.3	65	1.1	48

Table 8 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
5-21 (Comparative)	13 - 1	3.0	100	2.7	100
5-22 (Comparative)	13 - 2	1.3	100	1.6	100
5-23 (Comparative)	13 - 3	1.0	100	1.3	100
5-24 (Present invention)	13 - 4	0.5	100	0.5	100
5-25 (Present invention)	13 - 5	0.4	100	0.4	100
5-26 (Present invention)	13 - 6	0.2	100	0.3	100
5-27 (Present invention)	13 - 7	0.1	100	0.2	99
5-28 (Present invention)	13 - 8	0.1	100	0.2	95
5-29 (Present invention)	13 - 9	0.2	98	0.2	93
5-30 (Comparative)	13 - 10	0.2	92	0.2	88
5-31 (Comparative)	14 - 1	4.2	100	4.9	98
5-32 (Comparative)	14 - 2	2.6	100	2.9	98
5-33 (Comparative)	14 - 3	1.5	100	1.8	100
5-34 (Present invention)	14 - 4	0.7	100	0.8	100
5-35 (Present invention)	14 - 5	0.5	100	0.6	98
5-36 (Present invention)	14 - 6	0.3	100	0.4	97
5-37 (Present invention)	14 - 7	0.2	98	0.4	95
5-38 (Present invention)	14 - 8	0.2	96	0.4	93
5-39 (Present invention)	14 - 9	0.2	92	0.3	92
5-40 (Comparative)	14 - 10	0.2	85	0.3	85

Table 8 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
5-41 (Comparative)	15 - 1	5.6	100	7.2	95
5-42 (Comparative)	15 - 2	3.8	100	4.2	95
5-43 (Comparative)	15 - 3	2.1	100	2.8	97
5-44 (Present invention)	15 - 4	1.0	100	1.2	99
5-45 (Present invention)	15 - 5	0.8	100	1.1	97
5-46 (Present invention)	15 - 6	0.7	99	0.8	95
5-47 (Present invention)	15 - 7	0.6	97	0.7	94
5-48 (Present invention)	15 - 8	0.5	95	0.7	90
5-49 (Present invention)	15 - 9	0.5	92	0.6	88
5-50 (Comparative)	15 - 10	0.4	82	0.6	79

* Residual silver amount is expressed in terms of the residual silver mg number per 1 dm^2 (100 cm^2).

** Color reproduction percentage is shown by a percentage corresponding to the proportion of a perfectly color developed dye when the state where no leuco dye is present at all is assumed as 100 %.

It is understood from the above Table 8 that in the case the bleach-fixing solutions with pH range of 3.0 to 6.8 are used with use of the organic acid ferric complex salt according to this invention, there is seen only small residual silver and good color reproduction percentage regardless of whether the solutions were stored with time. In particular, good results are obtained when the pH is 4.0 to 6.7, and particularly good results are obtained when the pH is 5.0 to 6.5.

However, according to the comparative bleach-fixing solutions employing a comparative DTPA as the organic acid, the desilvering performance and color reproduction performance, though very good before storage with time at pH 7 or 8, become insufficient after storage for 1 week. It is further understood that the employment of EDTA results in insufficient desilvering performance and color reproduction performance regardless of whether the solutions were stored with time.

(Experiment 2)

Exemplary vinyl pyrrolidone polymer (2) in bleach-fixing solution No. 13 used in the above Experiment 1 was changed for a control, exemplary vinyl pyrrolidone polymers Nos. (1), (3) and (5), respectively, and the pH was adjusted to 6.0, to prepare bleach-fixing solutions Nos. 16-1 to 16-5. Light-sensitive materials corresponding to those in Experiment 1 and employing the above bleach-fixing solutions were processed, and the resulting bleach-fixing solutions having been used for the processing were stored with time in the same manner as in Experiment 1. Using the bleach-fixing solutions stored with time, the desilvering performance and color reproduction performance were measured in the same manner as in Experiment 1 to obtain the results shown together in Table 9.

Also, after storage for 1 week, the storage was further continued under the open ratio of 10 times to visually observe the days elapsing before the precipitation occurred.

Results obtained above are shown together in Table 9.

Table 9

Test No.	Bleach-fixing solution		Bleach fixing after storage with time		
	No.	Polyvinyl-pyrrolidone	Residual silver amount	Color reprodution percentage	Precipi-tation
5-51 (Present invention)	16-1	Exemplary No. (2)	0.3	100	30
5-52 (Compara-tive)	16-2	-	0.6	97	13
5-53 (Present invention)	16-3	Exemplary No. (1)	0.3	100	28
5-54 (Present invention)	16-4	Exemplary No. (3)	0.4	100	28
5-55 (Present invention)	16-5	Exemplary No. (5)	0.4	97	24

* Indicated in terms of the days elapsing before the precipitation occurred.

As will be clear from the above Table 8, it is understood that the employment of the vinyl pyrrolidone polymer according to this invention can not only greatly prolong the days elapsing before the precipitation occurs but also achieve good results for the residual silver amount and color reproduction performance.

In addition, the tests same as in Experiment 2 were repeated except that exemplary vinyl pyrrolidone polymer (5) used in Experiment No. 5-55 of Experiment 2 was replaced by (7), (8), (9) and (4), respectively, to obtain substantially the same results as those for No. 5-55 of Experiment 2

It is seen from the results in the above Experiment 1 and Experiment 2 that the bleach-fixing solutions according to this invention, in other words, the bleach-fixing solutions having the pH ranging between 3.0 and 6.8, containing a ferric complex salt having a ligand comprising a compound represented by General Formula (I), and further containing polyvinyl pyrrolidone of this invention can have a good desilvering performance particularly even after storage with time, can favorably prevent color reproduction inferiority from being occurred, and can have good shelf stability. In addition, the bleach-fixing solutions of this invention had no ammoniacal odor at all.

Example 6

Bleach-fixing solutions were stored with time in the same manner as in Experiment 1 of Example 5. Here, however, the ammonium sulfite concentration in the bleach-fixing solutions was controlled to 12 g/lit., the types of the bleaching agents were selected as shown in Table 10, and the concentration of the bleaching agents was varied as shown in Table 10. The pH of the bleach-fixing solutions was adjusted to 6.0.

After storage with time, the same evaluation as in Experiment 1 of Example 5 was carried out. Results are shown in Table 10.

Next, all of the bleach-fixing solutions were continuously stored in the same manner as in Experiment 2 of Example 5 to measure the days elapsing before the solutions were sulfidized. Results are shown together in Table 10.

Table 10

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/100cm^2)	Color repro-duction per-centage (%)	Days before sulfidi-zing (days)
		No.	Amount (mol/lit.)			
6- 1 (Present invention)	13-22	Exemplary compound No. I - 1	0.02	1.0	89	33
6- 2 (Present invention)	13-23		0.10	0.8	94	32
6- 3 (Present invention)	13-24		0.18	0.6	95	32
6- 4 (Present invention)	13-25		0.20	0.3	100	30
6- 5 (Present invention)	13-26		0.40	0.2	100	28
6- 6 (Present invention)	13-27		0.60	0.2	100	27
6- 7 (Present invention)	13-28		0.80	0.2	100	26
6- 8 (Present invention)	13-29		0.85	0.2	100	22
6- 9 (Present invention)	13-30		1.20	0.2	100	20
6-10 (Present invention)	13-31		1.30	0.2	100	16

Table 10 (Cont.)

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/100cm^2)	Color reproduction percentage (%)	Days before sulfidizing (days)
		No.	Amount (mol/lit.)			
6-11 (Present invention)	14-11	Exemplary compound No. I - 2	0.02	1.1	85	34
6-12 (Present invention)	14-12		0.10	0.9	91	33
6-13 (Present invention)	14-13		0.18	0.8	92	33
6-14 (Present invention)	14-14		0.20	0.5	97	31
6-15 (Present invention)	14-15		0.40	0.4	97	30
6-16 (Present invention)	14-16		0.60	0.4	98	28
6-17 (Present invention)	14-17		0.80	0.4	98	27
6-18 (Present invention)	14-18		0.85	0.3	98	22
6-19 (Present invention)	14-19		1.20	0.3	98	20
6-20 (Present invention)	14-20		1.30	0.3	98	14

Table 10 (Cont.)

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt		Residual silver amount (mg/100cm^2)	Color reproduction percentage (%)	Days before sulfidizing (days)
		No.	Amount (mol/lit.)			
6-21 (Present invention)	15-11	Exemplary compound No. I - 3	0.02	1.2	83	33
6-22 (Present invention)	15-12		0.10	1.0	89	32
6-23 (Present invention)	15-13		0.18	0.8	90	32
6-24 (Present invention)	15-14		0.20	0.8	94	31
6-25 (Present invention)	15-15		0.40	0.8	94	31
6-26 (Present invention)	15-16		0.60	0.8	95	31
6-27 (Present invention)	15-17		0.80	0.8	95	30
6-28 (Present invention)	15-18		0.85	0.7	96	23
6-29 (Present invention)	15-19		1.20	0.7	96	20
6-30 (Present invention)	15-20		1.30	0.7	96	15

As will be clear from Table 10, among the bleach-fixing solutions of this invention, particularly those having the content of bleaching agent in the range of 0.02 mol/lit. to 1.30 mol/lit., preferably 0.10 to 1.20 mol/lit., and more preferably 0.20 to 0.8 mol/lit., are seen to be good bleach-fixing solutions that can have high desilvering and color reproduction performances and may not be sulfidized for a long period even if they are stored with time.

Example 7

Bleach-fixing solutions were stored with time in the same manner as in Experiment 1 of Example 5. Here, however, the bleaching agent in bleach-fixing solution No. 11-1 used in Experiment 1 of Example 5 as the bleach-fixing solution and the amount thereof were changed as shown in Table 11, and the concentration of KI in the bleach-fixing solutions was varied as shown in Table 11. The pH of the bleach-fixing solutions was adjusted to 6.0.

After storage with time, evaluation on the desilvering performance was carried out in the same manner as in Experiment 1 of Example 5. Results obtained are shown in Table 11.

The samples having been processed were also subjected to bleaching and fixing according to the CNK-4 standard processing (color negative processing by Konishiroku Photo Industry Co., Ltd.), and, after the residual silver was perfectly removed by carrying out bleaching and fixing, transmission density of magenta dyes was measured. The value obtained was designated as D_{R1}. Next, after color developing was carried out in the same manner as in Experiment 1 of Example 5, the transmission density of magenta dyes of the samples subjected to bleaching and fixing according to the CNK-4 standard processing was measured, and the resulting value was designated as D_{R2}. The difference between D_{R1} and D_{R2} was determined (ΔD_R) to evaluate the magenta stain.

Table 11

Test No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount (x 10^{-3} mol/lit.)	Residual silver amount (mg/ $100cm^2$)	Magenta stain (ΔD_R)
7- 1(Comparative)	Ethylene-diamine-tetraacetic acid (0.3 mol/lit.)	0	6.0	0.07
7- 2(Comparative)		0.5	6.3	0.07
7- 3(Comparative)		0.9	7.1	0.06
7- 4(Comparative)		1.0	9.1	0.03
7- 5(Comparative)		2.0	10.3	0.02
7- 6(Present invention)	Exemplary compound (I - 1) (0.30 mol/lit.)	0	0.2	0.04
7- 7(Present invention)		0.5	0.2	0.03
7- 8(Present invention)		0.9	0.3	0.03
7- 9(Present invention)		1.0	0.3	0.01
7-10(Present invention)		2.0	0.4	0.00
7-11(Present invention)	Exemplary compound (I - 2) (0.30 mol/lit.)	0	0.3	0.04
7-12(Present invention)		0.5	0.3	0.04
7-13(Present invention)		0.9	0.4	0.03
7-14(Present invention)		1.0	0.5	0.02
7-15(Present invention)		2.0	0.6	0.01

Table 11 (Cont.)

Test No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount ($\times 10^{-3}$ mol/lit.)	Residual silver amount (mg/100cm^2)	Magenta stain (ΔD_R)
7-16(Present invention)	Exemplary compound (I - 3) (0.30 mol/lit.)	0	0.7	0.04
7-17(Present invention)		0.5	0.7	0.04
7-18(Present invention)		0.9	0.8	0.03
7-19(Present invention)		1.0	0.9	0.02
7-20(Present invention)		2.0	1.0	0.01

As will be clear from Table 11, in the comparative bleach-fixing solutions, the addition of KI can make small the magenta stain, but the desilvering performance is greatly lowered. However, in the bleach-fixing solutions of this invention, not only the addition of KI can suppress the magenta stain to a lower level, but also the desilvering performance is only slightly lowered to obtain good results.

Example 8

Bleach-fixing solutions Nos. 11-11 to 11-16 and Nos. 13-32 to 13-37 were prepared in the same manner as in Experiment 1 of Example 5 except that, in the bleach-fixing solutions No. 11-1 and No. 13-1 prepared in Experiment 1 of Example 5, the pH was adjusted to 6.0 and the bleaching accelerator was added as shown in Table 12 below.

Using the bleach-fixing solutions thus obtained, evaluation was carried out in the same manner as in Experiment 1 and Experiment 2 of Example 5 except that the bleach-fixing time 4 minutes 20 seconds in Experiment 1 was set to 3 minutes 15 seconds.

Results obtained are shown in Table 12.

Table 12

Test No.	Bleach-fixing solution No.	Bleaching accelerator (1g/lit.)	Bleach-fixing solution before storage		Bleach-fixing solution after storage		Days before occurence of precipitation
			Residual silver amount	Color reproduction percentage	Residual silver amount	Color reproduction per centage	
8- 1 (Comparative)	11- 11	-	7.6	86	9.7	75	28
8- 2 (Comparative)	11- 12	A - 1	5.2	84	5.5	79	20
8- 3 (Comparative)	11- 13	A - 2	6.3	86	6.7	81	18
8- 4 (Comparative)	11- 14	A - 4	5.1	85	8.9	78	18
8- 5 (Comparative)	11- 15	A - 6	5.4	83	9.1	76	20
8- 6 (Comparative)	11- 16	A - 9	3.8	89	4.2	74	19
8- 7 (Present invention)	13- 32	-	1.4	91	2.1	89	32
8- 8 (Present invention)	13- 33	A - 1	0.2	100	0.1	99	33
8- 9 (Present invention)	13- 34	A - 2	0.6	96	0.7	94	36
8-10 (Present invention)	13- 35	A - 4	0.7	96	0.9	91	34
8-11 (Present invention)	13- 36	A - 6	0.4	92	0.6	94	33
8-12 (Present invention)	13- 37	A - 9	0.3	97	0.2	95	35

As will be clear from Table 12, in the case the bleaching accelerator is added, the bleach-fixing solutions of this invention can maintain good effect in any of the desilvering performance, color reproduction performance and shelf stability even when stored. In contrast thereto, the bleach-fixing solutions outside this invention, which can be effective for any of the performances observed immediately after the solutions were prepared, result in further deterioration of the desilvering performance, color reproduction performance and shelf stability when they are stored.

Example 9

(Experiment 1)

On a triacetate film support, a halation-preventive layer and a gelatin layer were provided, and coated thereon were a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a filter layer containing yellow colloidal silver, and a blue-sensitive silver halide emulsion layer so as to give a total silver amount of 93 mg per 100 cm^2. The above emulsion layers comprised silver iodobromide having silver iodide mol % of about 5.0 %, and there were used the above (Y-1) as a yellow coupler in the blue-sensitive silver halide emulsion layer, the above (M-1) as a magenta coupler in the green-sensitive silver halide emulsion layer, and the above (C-1) as a cyan coupler in the red-sensitive silver halide emulsion layer. To the respective emulsion layers, a sensitizing dye, a hardening agent and a spreading agent were added. A light-sensitive silver halide color negative materials thus prepared was used as a sample.

Using samples obtained by cutting the above sample into pieces and subjected to wedge exposure according to a conventional method, processing was carried out according to the following steps with use of a processing apparatus for pieces (hereinafter called "hand developing").

Processing step	Processing temp. (°C)	Number of tanks	Processing time
1. Color developing	37.8	1 tank	3 min 15 sec
2. Bleach-fixing	37.8	1 tank	4 min 20 sec
3. Washing	30 to 34	2 tanks	4 min 20 sec
4. Stabilizing	30 to 34	1 tank	2 min 10 sec
5. Drying			

As for the color developing solution, bleach-fixing solution and stabilizing solution, the solutions as shown below were used.

[Color developing solution]

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	5.0 g
Sodium bromide	1.2 g
Potassium iodide	2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
Sodium diethylenetriaminepentaacetate	2.0 g
N-ethyl-N-β-hydroxyethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Potassium hydroxide	1.2 g

Made up to 1 liter by adding water, and adjusted to pH 10.06 with use of sodium hydroxide or 20 % sulfuric acid.

[Bleach-fixing solution]

Ferric ammonium complex salt of organic acid as shown in Table 13	Amount as shown in Table 13

Ammonium thiosulfate (a 70 % solution)	300 ml
Ammonium sulfite	5 g
Silver powder	2.0 g

Made up to 1 liter in total amount by adding water, and adjusted the pH as shown in Table 13 with use of acetic acid and ammonia water.

[Stabilizing solution]

Formalin (a 37 % aqueous solution)	2 ml
Conidax (produced by Konishiroku Photo Industry Co., Ltd.)	5 ml

Made up to 1 liter by adding water.

Table 13

Bleach-fixing solution No.	Organic acid which forms ferric ammonium salt	pH
17- 1 (Comparative)	Exemplary compound No. VI - 3) (0.25 mol/lit.)	8.0
17- 2 (Comparative)		7.5
17- 3 (Comparative)		7.0
17- 4 (Comparative)		6.8
17- 5 (Comparative)		6.7
17- 6 (Comparative)		6.5
17- 7 (Comparative)		5.0
17- 8 (Comparative)		4.0
17- 9 (Comparative)		3.0
17-10 (Comparative)		2.0
18- 1 (Comparative)	Exemplary compound No. (VI - 7) (0.25 mol/lit.)	8.0
18- 2 (Comparative)		7.5
18- 3 (Comparative)		7.0
18- 4 (Comparative)		6.8
18- 5 (Comparative)		6.7
18- 6 (Comparative)		6.5
18- 7 (Comparative)		5.0
18- 8 (Comparative)		4.0
18- 9 (Comparative)		3.0
18-10 (Comparative)		2.0
19- 1 (Comparative)	Exemplary compound No. (I - 1) (0.2 mol/lit.) Exemplary compound No. (VI - 7) (0.05 mol/lit.)	8.0
19- 2 (Comparative)		7.5
19- 3 (Comparative)		7.0
19- 4 (Present invention)		6.8
19- 5 (Present invention)		6.7
19- 6 (Present invention)		6.5
19- 7 (Present invention)		5.0
19- 8 (Present invention)		4.0
19- 9 (Present invention)		3.0
19-10 (Comparative)		2.0

Table 13 (cont'd)

Bleach-fixing solution No.	Organic acid which forms ferric ammonium salt	pH
20- 1 (Comparative)	Exemplary compound No. (I - 2) (0.2 mol/lit.)	8.0
20- 2 (Comparative)		7.5
20- 3 (Comparative)		7.0
20- 4 (Present invention)		6.8
20- 5 (Present invention)		6.7
20- 6 (Present invention)	Exemplary compound No. (VI - 7) (0.05 mol/lit.)	6.5
20- 7 (Present invention)		5.0
20- 8 (Present invention)		4.0
20- 9 (Present invention)		3.0
20-10 (Comparative)		2.0
21- 1 (Comparative)	Exemplary compound No. (I - 3) (0.2 mol/lit.)	8.0
21- 2 (Comparative)		7.5
21- 3 (Comparative)		7.0
21- 4 (Present invention)		6.8
21- 5 (Present invention)		6.7
21- 6 (Present invention)	Exemplary compound No. (VI - 7) (0.05 mol/lit.)	6.5
21- 7 (Present invention)		5.0
21- 8 (Present invention)		4.0
21- 9 (Present invention)		3.0
21-10 (Comparative)		2.0

The bleach-fixing solutions available after the above processing were stored with time for 1 week at 38°C under the open ratio of 10 cm^2/lit. (which is the open condition corresponding to that of usual automatic processing machine, and meant that the solution have an air contact area of 10 cm^2 based on 1 liter of the bleach-fixing solution, and the above processing was again repeated with use of the bleach-fixing solutions available after storage. After the processing, the residual silver amount (mg/dm^2) at the maximum density portion of the film samples (the respective samples available before and after the storage with time, of the bleach-fixing solutions) was measured according to a fluorescent X-ray method, and the cyan dye density was further measured with use of Sakura Photoelectric Densitometer PDA-65 (produced by Konishiroku Photo Industry Co., Ltd.) to determine the color reproduction percentage.

Results obtained are shown together in Table 14.

Table 14

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
9- 1 (Comparative)	17 - 1	11.0	100	12.0	87
9- 2 (Comparative)	17 - 2	9.7	99	11.3	89
9- 3 (Comparative)	17 - 3	7.3	97	10.0	89
9- 4 (Comparative)	17 - 4	6.7	96	8.6	84
9- 5 (Comparative)	17 - 5	6.2	95	7.4	81
9- 6 (Comparative)	17 - 6	5.3	92	6.2	77
9- 7 (Comparative)	17 - 7	4.2	76	4.9	73
9- 8 (Comparative)	17 - 8	2.8	74	3.1	69
9- 9 (Comparative)	17 - 9	1.6	71	1.8	60
9-10 (Comparative)	17 - 10	1.0	67	1.2	51
9-11 (Comparative)	18 - 1	1.2	100	4.7	94
9-12 (Comparative)	18 - 2	0.5	100	4.4	93
9-13 (Comparative)	18 - 3	0.4	100	4.1	92
9-14 (Comparative)	18 - 4	0.4	99	3.9	90
9-15 (Comparative)	18 - 5	0.4	96	3.8	86
9-16 (Comparative)	18 - 6	0.4	91	3.5	81
9-17 (Comparative)	18 - 7	0.4	79	3.1	74
9-18 (Comparative)	18 - 8	0.3	75	2.2	60
9-19 (Comparative)	18 - 9	0.4	70	1.7	54
9-20 (Comparative)	18 - 10	0.4	67	1.2	49

Table 14 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
9-21 (Comparative)	19 - 1	3.2	100	3.5	100
9-22 (Comparative)	19 - 2	1.6	100	1.8	100
9-23 (Comparative)	19 - 3	1.2	100	1.4	100
9-24 (Present invention)	19 - 4	0.7	100	0.8	100
9-25 (Present invention)	19 - 5	0.5	100	0.6	100
9-26 (Present invention)	19 - 6	0.3	100	0.4	100
9-27 (Present invention)	19 - 7	0.3	100	0.4	99
9-28 (Present invention)	19 - 8	0.3	100	0.4	95
9-29 (Present invention)	19 - 9	0.3	99	0.3	92
9-30 (Present invention)	19 - 10	0.2	92	0.3	89
9-31 (Comparative)	20 - 1	4.5	100	5.1	100
9-32 (Comparative)	20 - 2	2.9	100	3.0	99
9-33 (Comparative)	20 - 3	1.7	100	1.9	100
9-34 (Present invention)	20 - 4	0.8	100	1.0	100
9-35 (Present invention)	20 - 5	0.6	100	0.8	97
9-36 (Present invention)	20 - 6	0.4	99	0.6	96
9-37 (Present invention)	20 - 7	0.4	98	0.4	96
9-38 (Present invention)	20 - 8	0.4	97	0.4	93
9-39 (Present invention)	20 - 9	0.4	93	0.4	91
9-40 (Comparative)	20 - 10	0.3	84	0.4	87

Table 14 (cont'd)

Test No.	Used bleach-fixing solution No.	Bleach-fixing solution before storage		Bleach-fixing solution after storage	
		Residual silver amount*	Color reproduction percentage**	Residual silver amount*	Color reproduction percentage**
9-41 (Comparative)	21 - 1	5.7	100	7.3	96
9-42 (Comparative)	21 - 2	4.2	100	4.2	97
9-43 (Comparative)	21 - 3	2.3	100	2.9	96
9-44 (Present invention)	21 - 4	1.0	100	1.3	98
9-45 (Present invention)	21 - 5	0.8	99	1.1	97
9-46 (Present invention)	21 - 6	0.6	99	0.9	96
9-47 (Present invention)	21 - 7	0.5	97	0.8	95
9-48 (Present invention)	21 - 8	0.5	94	0.8	93
9-49 (Present invention)	21 - 9	0.5	91	0.7	91
9-50 (Comparative)	21 - 10	0.5	83	0.7	82

* Residual silver amount is expressed in terms of the residual silver mg number per 1 dm^2 (100 cm^2).

** Color reproduction percentage is shown by a percentage corresponding to the proportion of a perfectly color developed dye when the state where no leuco dye is present at all is assumed as 100 %.

It is understood from the above Table 14 that in the case the bleach-fixing solutions with pH range of 3.0 to 6.8 are used with combined use of the organic acid ferric complex salt according to this invention, there is seen only small residual silver and good color reproduction percentage regardless of whether the solutions were stored with time.

(Experiment 2)

The concentration and combination of the ferric complex salt comprising the organic acid in bleach-fixing solution No. 19 used in the above Experiment 1 was varied as shown in Table 15 below to prepare bleach-fixing solutions Nos. 22-1 to 24-10. Using the above bleach-fixing solutions, the light-sensitive materials corresponding to those in Experiment 1 were processed, and the resulting bleach-fixing solutions having been used for the processing were stored with time in the same manner as in Experiment 1. Using the bleach-fixing solutions stored with time, the desilvering performance and color reproduction performance were measured in the same manner as in Experiment 1 to obtain the results shown together in Table 15.

Also, after storage for 1 week, the storage was further continued under the open ratio of 10 times to visually observe the days elapsing before the precipitation occurred.

Results obtained above are shown together in Table 15.

Table 15

Test No.	Bleach fixing solution			Bleach-fixing after storage with time		
	No.	Organic acid which forms ferric complex salt	pH	Residual silver amount	Color reproduction percentage	Precipitation * (days)
9-51 (Comparative)	22- 1	Exemplary compound No. I - 1 (0.25 mol/lit.)	8.0	3.4	100	30
9-52 (Comparative)	22- 2		7.5	1.7	100	28
9-53 (Comparative)	22- 3		7.0	1.5	100	27
9-54 (Comparative)	22- 4		6.8	0.9	100	19
9-55 (Comparative	22- 5		6.7	0.7	99	16
9-56 (Comparative)	22- 6		6.5	0.3	99	15
9-57 (Comparative)	22- 7		5.0	0.3	99	10
9-58 (Comparative)	22- 8		4.0	0.3	95	8
9-59 (Comparative)	22- 9		3.0	0.3	91	6
9-60 (Comparative)	22-10		2.0	0.2	87	5
9-61 (Comparative)	23- 1		8.0	3.5	100	29
9-62 (Comparative)	23- 2		7.5	1.9	100	28
9-63 (Comparative)	23- 3		7.0	1.4	100	27

Table 15 (Cont.)

Test No.	Bleach fixing solution			Bleach-fixing after storage with time		
	No.	Organic acid which forms ferric complex salt	pH	Residual silver amount	Color reproduction percentage	Precipitation * (days)
9-64 (Present invention)	23- 4	Exemplary compound No. I - 1 (0.15 mol/lit.) Exemplary compound No. VI - 3 (0.10 mol/lit.)	6.8	0.8	100	23
9-65 (Present invention)	23- 5		6.7	0.8	100	23
9-66 (Present invention)	23- 6		6.5	0.4	99	21
9-67 (Present invention)	23- 7		5.0	0.4	99	21
9-68 (Present invention)	23- 8		4.0	0.3	94	20
9-69 (Present invention)	23- 9		3.0	0.3	90	14
9-70 (Comparative)	23-10		2.0	0.3	86	7
9-71 (Comparative)	24- 1	Exemplary compound No. I - 1 (0.15 mol/lit.) Exemplary compound No. VI - 7 (0.10 mol/lit.)	8.0	3.5	100	29
9-72 (Comparative)	24- 2		7.5	1.8	100	28
9-73 (Comparative)	24- 3		7.0	1.6	100	28
9-74 (Present invention)	24- 4		6.8	0.9	100	27
9-75 (Present invention)	24- 5		6.7	0.8	100	26
9-76 (Present invention)	24- 6		6.5	0.4	99	26

Table 15 (Cont.)

Test No.	Bleach fixing solution			Bleach-fixing after storage with time		
	No.	Organic acid which forms ferric complex salt	pH	Residual silver amount	Color reproduction percentage	Precipitation * (days)
9-77 (Present invention)	24- 7	Exemplary compound No. I - 1 (0.15 mol/ lit.)	5.0	0.4	99	26
9-78 (Present invention)	24- 8		4.0	0.4	95	25
9-79 (Present invention)	24- 9	Exemplary compound No. VI - 7 (0.10 mol/ lit.)	3.0	0.3	91	18
9-80 (Comparative)	24-10		2.0	0.3	87	9

* Indicated in terms of the days elapsing before the precipitation occurred.

As will be clear from Table 15, it is understood that the combined use of the bleaching agents of General Formula (I) and of at least one selected from General Formulas (IV) to (VII) can achieve the effect of improving the shelf stability in the pH range of 3.0 to 6.8, and good results can be obtained particularly at pH 4.0 to pH 6.7, more particularly at pH 5.0 to 6.5.

(Experiment 3)

Using bleach-fixing solutions Nos. 19-4 and 20-4 used in Experiment 1, the experiments same as in Experiment 2 were repeated. Here, however, the concentration of the organic acid ferric complex salt and the organic acid ferric complex salt to be used in combination were varied as shown in Table 16, and the pH was adjusted to 6.0.

Results obtained are shown together in Table 16.

Table 16

Test No.	Bleach-fixing solution No.	Iron (III) ammonium salt of organic acid		Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9- 81(Comparative)	25	I-1 0.25 mol	-	0.3	100	14
9- 82(Present invention)	26	I-1 0.10 mol	VI-3 0.15 mol	0.4	99	21
9- 83(Present invention)	27	I-1 0.10 mol	VI-7 0.15 mol	0.3	99	26
9- 84(Present invention)	28	I-1 0.10 mol	IV-6 0.15 mol	0.5	99	18
9- 85(Present invention)	29	I-1 0.10 mol	IV-2 0.15 mol	0.4	99	17
9- 86(Present invention)	30	I-1 0.10 mol	IV-5 0.15 mol	0.4	99	18

Table 16 (Cont.)

Test No.	Bleach-fixing solution No.	Iron (III) ammonium salt of organic acid		Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9- 87(Comparative)	31	I-2 0.25 mol	-	0.4	99	15
9- 88(Present invention)	32	I-2 0.10 mol	VI-3 0.15 mol	0.4	99	22
9- 89(Present invention)	33	I-2 0.10 mol	VI-7 0.15 mol	0.3	99	27
9- 90(Present invention)	34	I-2 0.10 mol	IV-6 0.15 mol	0.4	99	19
9- 91(Present invention)	35	I-2 0.10 mol	IV-2 0.15 mol	0.5	98	18
9- 92(Present invention)	36	I-2 0.10 mol	IV-5 0.15 mol	0.4	99	18

Table 16 (Cont.)

Test No.	Bleach-fixing solution No.	Iron (III) ammonium salt of organic acid		Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9- 93(Comparative)	37	I-3 0.25 mol	-	0.5	99	14
9- 94(Present invention)	38	I-3 0.10 mol	VI-3 0.15 mol	0.7	98	21
9- 95(Present invention)	39	I-3 0.10 mol	VI-7 0.15 mol	0.5	99	26
9- 96(Present invention)	40	I-3 0.10 mol	IV-6 0.15 mol	0.8	99	17
9- 97(Present invention)	41	I-3 0.10 mol	IV-2 0.15 mol	0.7	98	17
9- 98(Present invention)	42	I-3 0.10 mol	IV-5 0.15 mol	0.6	99	18

Table 16 (Cont.)

Test No.	Bleach-fixing solution No.	Iron (III) ammonium salt of organic acid		Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9- 99(Comparative)	43	VI-3 0.25 mol	-	4.9	73	14
9-100(Comparative)	44	VI-3 0.10 mol	VI-7 0.15 mol	3.1	72	15
9-101(Comparative)	45	VI-3 0.10 mol	IV-6 0.15 mol	4.8	73	14
9-102(Comparative)	46	VI-3 0.10 mol	IV-2 0.15 mol	4.7	73	13
9-103(Comparative)	47	VI-3 0.10 mol	IV-5 0.15 mol	4.7	73	14
9-104(Comparative)	48	VI-3 0.10 mol	VI-4 0.15 mol	4.8	74	14

As will be clear from Table 16, it is understood that only the combination of the organic acid ferric complex salts of this invention can show good desilvering performance, color reproduction performance and shelf stability. It is also understood that there can be exhibited higher effect of improving the shelf stability particularly in the combination of I-1 with VI-3 or VI-7, the combination of I-2 with VI-3 or VI-7, and the combination of I-3 with VI-3 or VI-7, and preferred are the combination of I-1 with VI-7 and the combination of I-2 with VI-7.

(Experiment 4)

Using bleach-fixing solution No. 19-4 used in Experiment 1, the tests same as in Experiment 2 were repeated. Here, however, the composition of the organic acid ferric complex salt was varied as shown in Table 17, and the pH was adjusted to 5.5

Results obtained are shown together in Table 17.

Table 17

Test No.	Bleach-fixing solution No.	Concentration of ferric complex of I-1 (mol/lit.)	Concentration of ferric complex salt of VI-7 (ratio of VI-7 to ferric complex salt, mol %)	Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9-105(Comparative)	49	0.2500	-	0.3	99	14
9-106(Present invention)	50	0.2480	0.0020 (0.8%)	0.3	99	14
9-107(Present invention)	51	0.2475	0.0025 (1.0%)	0.4	100	18
9-108(Present invention)	52	0.2390	0.0110 (4.4%)	0.4	100	18
9-109(Present invention)	53	0.2375	0.0125 (5.0%)	0.3	99	22
9-110(Present invention)	54	0.2300	0.0200 (8.0%)	0.3	99	22

Table 17 (Cont.)

Test No.	Bleach-fixing solution No.	Concentration of ferric complex of I-1 (mol/lit.)	Concentration of ferric complex salt of VI-7 (ratio of VI-7 to ferric complex salt, mol %)	Residual silver	Color reproduction percentage	Days before generation of silver sulfide
9-111(Present invention)	55	0.2250	0.0250 (10.0%)	0.4	99	26
9-112(Present invention)	56	0.1500	0.1000 (40%)	0.4	100	26
9-113(Present invention)	57	0.0500	0.2000 (80%)	0.4	100	27
9-114(Present invention)	58	0.0400	0.2100 (84%)	0.4	92	24
9-115(Present invention)	59	0.0250	0.2250 (90%)	0.3	85	22
9-116(Present invention)	60	0.0125	0.2375 (95%)	0.4	77	20
9-117(Present invention)	61	0.0075	0.2425 (97%)	0.4	76	20

As will be clear from Table 17, it is understood that substantially good results can be obtained when the ferric complex salt of organic acid VI-7 is used in the range of 1 mol % to 95 mol %, and goods results for all the desilvering, color reproduction and storage performances can be obtained particularly when it is used in the range of 5 mol % to 90 mol %, more particularly 10 mol % to 80 mol %.

It is seen from the results in the above Experiment 1 to Experiment 4 that the bleach-fixing solutions according to this invention, in other words, the bleach-fixing solutions having the pH ranging between 3.0 and 6.8, containing a ferric complex salt having a ligand comprising a compound represented by General Formula (I), and further containing a ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas of General Formulas (IV) to (VII) can have a good desilvering performance particularly even after storage with time, can favorably prevent color reproduction inferiority from being occurred, and can have good shelf stability. In addition, the bleach-fixing solutions of this invention had no ammoniacal odor at all.

Example 10

Using bleach-fixing solutions Nos. 19-1 to 19-10, Nos. 20-1 to 20-10 and Nos. 21-1 to 21-10 employed in Experiment 1 of Example 9, the experiments same as in Experiment 2 of Example 9 were repeated. Here, however, the proportion of the two types of ferric complex salts used in combination was not changed, but the concentration of the ferric complex salt was varied as shown in Table 18, and the pH was adjusted to 5.0. Results obtained are shown together in Table 18.

Table 18

Test No.	Bleach-fixing solution	Ferric complex salt of the compound represented by General Formula (I) (mol/lit.)	Ferric complex salt of VI-7 (mol/lit.)	Total amount of ferric complex salt (mol/lit.)	Residual silver amount	Color reproduction percentage	Days before sulfidizing
10- 1 (Present invention)	19 - 11	0.016	0.004	0.02	1.2	87	27
10- 2 (Present invention)	19 - 12	0.08	0.02	0.10	0.8	95	27
10- 3 (Present invention)	19 - 13	0.144	0.036	0.18	0.6	95	27
10- 4 (Present invention)	19 - 14	0.16	0.04	0.20	0.4	100	26
10- 5 (Present invention)	19 - 15	0.32	0.08	0.40	0.4	100	26
10- 6 (Present invention)	19 - 16	0.48	0.12	0.60	0.4	99	25
10- 7 (Present invention)	19 - 17	0.64	0.16	0.80	0.4	100	25
10- 8 (Present invention)	19 - 18	0.68	0.17	0.85	0.3	100	19
10- 9 (Present invention)	19 - 19	0.96	0.24	1.20	0.3	100	17
10-10 (Present invention)	19 - 20	1.04	0.26	1.30	0.3	100	13

Table 18 (cont'd)

Test No.	Bleach-fixing solution	Ferric complex salt of the compound represented by General Formula (I) (mol/lit.)	Ferric complex salt of VI-7 (mol/lit.)	Total amount of ferric complex salt (mol/lit.)	Residual silver amount	Color reproduction percentage	Days before sulfidizing
10-11 (Present invention)	20 - 11	0.016	0.004	0.02	1.4	85	27
10-12 (Present invention)	20 - 12	0.08	0.02	0.10	0.9	90	27
10-13 (Present invention)	20 - 13	0.144	0.036	0.18	0.7	91	27
10-14 (Present invention)	20 - 14	0.16	0.04	0.20	0.4	96	26
10-15 (Present invention)	20 - 15	0.32	0.08	0.40	0.4	95	26
10-16 (Present invention)	20 - 16	0.48	0.12	0.60	0.4	96	26
10-17 (Present invention)	20 - 17	0.64	0.16	0.80	0.4	96	25
10-18 (Present invention)	20 - 18	0.68	0.17	0.85	0.3	97	20
10-19 (Present invention)	20 - 19	0.96	0.24	1.20	0.3	98	18
10-20 (Present invention)	20 - 20	1.04	0.26	1.30	0.3	98	12

Table 18 (cont'd)

Test No.	Bleach-fixing solution	Ferric complex salt of the compound represented by General Formula (I) (mol/lit.)	Ferric complex salt of VI-7 (mol/lit.)	Total amount of ferric complex salt (mol/lit.)	Residual silver amount	Color reproduction percentage	Days before sulfidizing
10-21 (Present invention)	21 - 11	0.016	0.004	0.02	1.5	84	27
10-22 (Present invention)	21 - 12	0.08	0.02	0.10	1.2	89	27
10-23 (Present invention)	21 - 13	0.144	0.036	0.18	1.0	89	27
10-24 (Present invention)	21 - 14	0.16	0.04	0.20	0.8	94	26
10-25 (Present invention)	21 - 15	0.32	0.08	0.40	0.7	94	26
10-26 (Present invention)	21 - 16	0.48	0.12	0.60	0.8	95	25
10-27 (Present invention)	21 - 17	0.64	0.16	0.80	0.7	95	25
10-28 (Present invention)	21 - 18	0.68	0.17	0.85	0.6	97	19
10-29 (Present invention)	21 - 19	0.96	0.24	1.20	0.6	98	18
10-30	21 - 20	1.04	0.26	1.30	0.6	99	13

As will be clear from Table 18, among the bleach-fixing solutions of this invention, particularly those having the content of bleaching agent in the range of 0.02 mol/lit. to 1.30 mol/lit., preferably 0.10 to 1.20 mol/lit., and more preferably 0.20 to 0.8 mol/lit., are seen to be good bleach-fixing solutions that can have high desilvering and color reproduction performances and may not be sulfidized for a long period even if they are stored with time.

Example 11

Using bleach-fixing solutions Nos. 17-1, 19-4, 20-4 and 21-4 used in Experiment 1 of Example 9, the experiments same as in Experiment 1 of Example 9 were repeated. Here, however, the concentration of the ferric complex salt was controlled as shown in Table 19 below, and the pH of the bleach-fixing solutions was adjusted to 6.0.

After storage with time, evaluation on the desilvering performance was carried out in the same manner as in Experiment 1 of Example 9. Results obtained are shown in Table 19.

The samples having been processed were also subjected to bleaching and fixing according to the CNK-4 standard processing (color negative processing by Konishiroku Photo Industry Co., Ltd.), and, after the residual silver was perfectly removed by carrying out bleaching and fixing, transmission density of magenta dyes was measured. The value obtained was designated as D_{R1}. Next, after color developing was carried out in the same manner as in Experiment 1 of Example 9, the transmission density of magenta dyes of the samples subjected to bleaching and fixing according to the CNK-4 standard processing was measured, and the resulting value was designated as D_{R2}. The difference between D_{R1} and D_{R2} was determined (ΔD_R) to evaluate the magenta stain. Results obtained are shown together in Table 19.

Table 19

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount ($\times 10^{-3}$ mol/lit.)	Residual silver amount	Magenta stain (ΔD_R)
11- 1 (Comparative)	17-11	VI - 3 (0.45 mol/lit.)	0	5.5	0.06
11- 2 (Comparative)	17-12		0.5	6.1	0.05
11- 3 (Comparative)	17-13		0.9	6.9	0.04
11- 4 (Comparative)	17-14		1.0	8.9	0.01
11- 5 (Comparative)	17-15		2.0	10.1	0.00
11- 6 (Present invention)	19-21	I - 1 (0.30 mol/lit.)	0	0.4	0.06
11- 7 (Present invention)	19-22		0.5	0.3	0.05
11- 8 (Present invention)	19-23		0.9	0.3	0.04
11- 9 (Present invention)	19-24	VI - 7 (0.15 mol/lit.)	1.0	0.4	0.02
11-10 (Present invention)	19-25		2.0	0.4	0.01

Table 19 (Cont.)

Test No.	Bleach-fixing solution No.	Organic acid which forms ferric complex salt (mol/lit.)	KI amount ($\times 10^{-3}$ mol/lit.)	Residual silver amount	Magenta stain (ΔD_R)
11-11 (Present invention)	20-21	I - 2 (0.30 mol/lit.)	0	0.4	0.07
11-12 (Present invention)	20-22		0.5	0.3	0.04
11-13 (Present invention)	20-23		0.9	0.4	0.04
11-14 (Present invention)	20-24	VI - 7 (0.15 mol/lit.)	1.0	0.4	0.02
11-15 (Present invention)	20-25		2.0	0.4	0.00
11-16 (Present invention)	21-21	I - 3 (0.30 mol/lit.)	0	0.7	0.06
11-17 (Present invention)	21-22		0.5	0.7	0.04
11-18 (Present invention)	21-23		0.9	0.8	0.04
11-19 (Present invention)	21-24	VI - 7 (0.15 mol/lit.)	1.0	0.9	0.02
11-20 (Present invention)	21-25		2.0	0.9	0.01

As will be clear from Table 19, in the comparative bleach-fixing solutions, the addition of KI can make small the magenta stain, but the desilvering performance is greatly lowered. However, in the bleach-fixing solutions of this invention, not only the addition of KI can suppress the magenta stain to a lower level, but also the desilvering performance is only slightly lowered to obtain good results.

Example 12

Bleach-fixing solutions Nos. 17-21 to 17-26 and Nos. 19-31 to 19-36 were prepared in the same manner as in Experiment 1 of Example 9 except that, in bleach-fixing solutions No. 17-1 and No. 19-1 prepared in Experiment 1 of Example 9, the pH was adjusted to 6.0 and the bleaching accelerator was added as shown in Table 20 below.

Using the bleach-fixing solutions thus obtained, evaluation was carried out in the same manner as in Experiment 2 of Example 9 except that the bleach-fixing time 4 minutes 20 seconds in Experiment 1 was set to 3 minutes 15 seconds.

Results obtained are shown in Table 20.

Table 20

Test No.	Bleach-fixing solution No.	Bleaching accelerator (1g/lit.)	Bleach-fixing solution before storage		Bleach-fixing solution after storage		Days before accurence of precipitation
			Residual silver amount	Color reproduction percentage	Residual silver amount	Color reproduction per centage	
12- 1 (Comparative)	17 - 21	-	7.0	84	8.6	77	14
12- 2 (Comparative)	17 - 22	A - 1	4.9	83	5.5	76	10
12- 3 (Comparative)	17 - 23	A - 2	5.3	83	5.9	78	9
12- 4 (Comparative)	17 - 24	A - 4	5.2	82	6.2	79	9
12- 5 (Comparative)	17 - 25	A - 6	5.1	83	6.1	78	8
12- 6 (Comparative)	17 - 26	A - 9	3.9	83	4.9	78	7
12- 7 (Present invention)	19 - 31	-	2.1	92	2.2	91	28
12- 8 (Present invention)	19 - 32	A - 1	0.2	99	0.1	98	26
12- 9 (Present invention)	19 - 33	A - 2	0.5	95	0.4	94	25
12-10 (Present invention)	19 - 34	A - 4	0.6	95	0.6	94	25
12-11 (Present invention)	19 - 35	A - 6	0.5	91	0.5	91	24
12-12 (Present invention)	19 - 36	A - 9	0.4	96	0.5	95	24

As will be clear from Table 20, in the case the bleach accelerator is added, the bleach-fixing solutions of this invention can maintain good effect in any of the desilvering performance, color reproduction performance and shelf stability even when stored, even if the bleach-fixing time is shortened. In contrast thereto, the bleach-fixing solutions outside this invention, which can be effective for any of the performances observed immediately after the solutions were prepared, result in further deterioration of the desilvering performance, color reproduction performance and shelf stability when they are stored.

Claims:

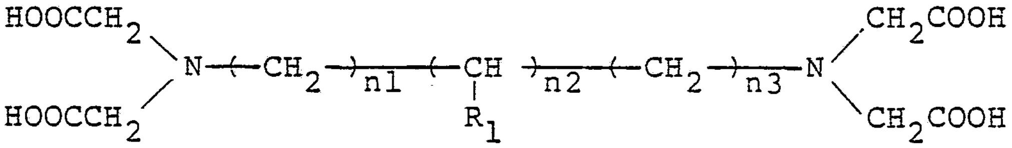
1. A bleach-fixing solution for processing a light-sensitive silver halide photographic material for photographing, wherein said solution has the pH ranging between 3.0 and 6.8, contains a ferric complex salt having a ligand comprising a compound represented by General Formula (I) shown below, and further contain at least one of;

i) at least one compound selected from the compounds represented respectively by General Formula (II) and General Formula (III) shown below;

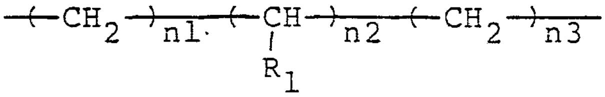
ii) a polymer having a unit of a pyrrolidone nucleus in the molecular structure; and

iii) a ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII),

General Formula (I):



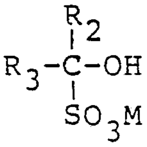
wherein R_1 represents a hydrogen atom or an alkyl group having 1 to 3 carbon atoms; and n_1, n_2 and n_3 each represent an integer of 0 to 3, provided that the sum of n_1, n_2 and n_3 is an integer of 2 to 4 and the total sum of the carbon atoms in



$$-(CH_2)_{n1}-(\underset{R_1}{CH})_{n2}-(CH_2)_{n3}-$$

is 3 or more,

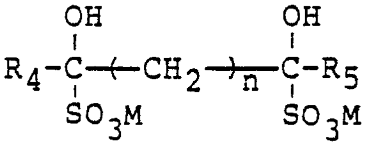
General Formula (II):



$$R_3-\overset{R_2}{\underset{SO_3M}{C}}-OH$$

wherein R_2 and R_3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; and M represents an alkali metal atom or an ammonium group,

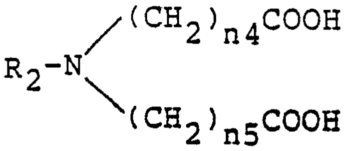
General Formula (III):



$$R_4-\underset{SO_3M}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-(CH_2)_n-\underset{SO_3M}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R_5$$

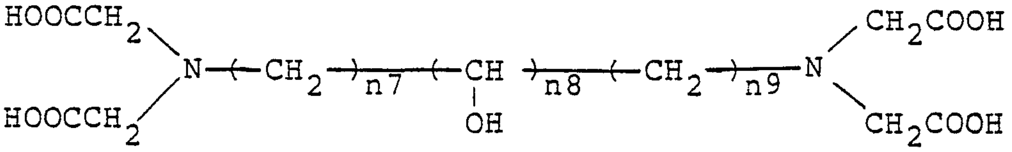
wherein R_4 and R_5 each represent a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; M represents an alkali metal atom or an ammonium group; and n represents an integer of 0 to 6,

General Formula (IV):



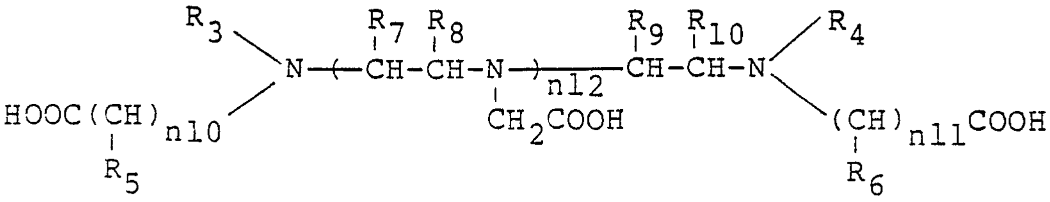
wherein R_2 represents an alkyl group having 1 to 5 carbon atoms, a hydroxyl-substituted alkyl group having 1 to 5 carbon atoms, or $-(CH_2)_{n6}COOH$; and n_4, n_5 and n_6 each represents an integer of 1 or 2,

General Formula (V):



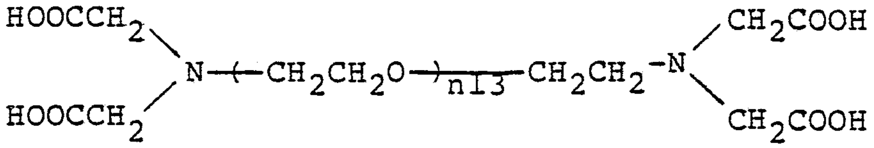
wherein n_7 and n_9 each represent an integer of 0 to 3, and n_8 represents an integer of 1 to 3, provided that the sum of n_7, n_8 and n_9 is 2 or more,

General Formula (VI):



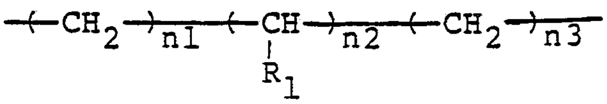
wherein R_3 and R_4 each represent a hydrogen atom, a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, or a carboxyl-substituted alkyl group having 1 or 2 carbon atoms; R_5 and R_6 each represent a hydrogen atom or a hydroxyl-substituted phenyl group; R_7, R_8, R_9 and R_{10} each represent a hydrogen atom or a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, provided that R_7, R_8, R_9 and R_{10} each may combine to form a ring having 5 to 8 carbon atoms; n_{10} and n_{11} each represent an integer of 1 to 3; and n_{12} represents an integer of 0 to 4,

General Formula (VII):



wherein n_{13} represents an integer of 1 to 8.

2. The bleach-fixing solution according to Claim 1, wherein R_1 of General Formula (I) is a hydrogen atom and the total sum of the carbon atoms in



$-(CH_2)_{n1}-(\underset{R_1}{CH})_{n2}-(CH_2)_{n3}-$ is 3.

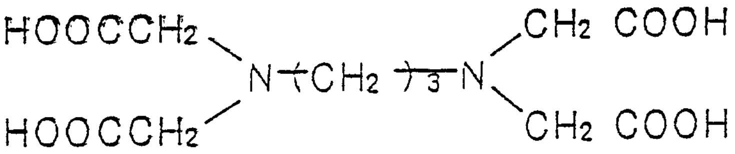
3. The bleach-fixing solution according to Claim 1, wherein the solution has the pH value ranging between 4.0 and 6.7.

4. The bleach-fixing solution according to Claim 3, wherein the solution has the pH value ranging between 5.0 and 6.5.

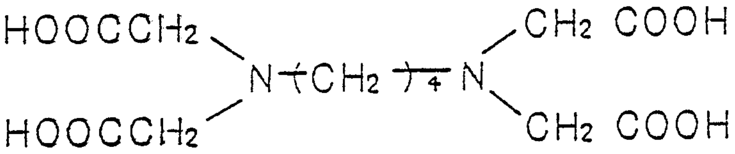
5. The bleach-fixing solution according to Claim 1, wherein the ferric complex salt is contained in the range of 0.02 to 1.30 mol/lit.

6. The bleach-fixing solution according to Claim 1, wherein the compound represented by General Formula (I) is at least one compound represented by the following formulae:

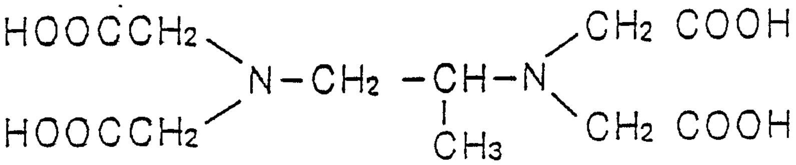
I-1



I-2



I-3



7. The bleach-fixing solution according to Claim 1, wherein the sulfite is ammonium sulfite, sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite or sodium metabisulfite.

8. The bleach-fixing solution according to Claim 1, wherein the alkyl group represented by R_2 and R_3 of General Formula (II) is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

9. The bleach-fixing solution according to Claim 1, wherein the alkyl group represented by R_4 and R_5 of General Formula (III) is an alkyl group having 1 to 2 carbon atoms and n represents an integer of 1 to 4.

10. The bleach-fixing solution according to Claim 1, wherein the compound selected from the compounds of General Formula (II) and (III) is contained in an amount of 0.01 to 2 mol/lit.

11. The bleach-fixing solution according to Claim 1, wherein the polymer having a unit of a pyrrolidone nucleus has an average molecular weight of 500 to 800,000.

12. The bleach-fixing solution according to Claim 1, wherein the polymer having a unit of a pyrrolidone nucleus is contained in an amount of 0.1 to 100 g per one liter of the bleach-fixing solution.

13. The bleach-fixing solution according to Claim 1, wherein, when the bleach-fixing solution contains the polymer having a unit of a pyrrolidone nucleus, the bleach-fixing solution further contains a sulfite or sulfite releasable compound in an amount of 1 x 10^{-1} mol/lit.

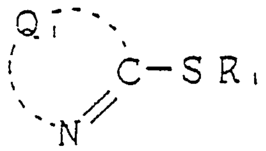
14. The bleach-fixing solution according to Claim 1, wherein the ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII) is contained in an amount of 1 to 95 mol % based on the total amount of said ferric complex salt and the ferric complex salt having a ligand comprising a compound represented by General Formula (I).

15. The bleach-fixing solution according to Claim 1, the ferric complex salt having a ligand comprising the compound represented by General Formula (I) and that having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII) is contained in the range of 0.02 to 1.30 mol/lit. in the total amount of them.

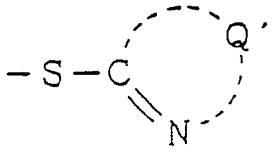
16. The bleach-fixing solution according to Claim 1, wherein the bleach-fixing solution further contains at

least one bleaching accelerator selected from the compounds represented by General Formulas (A-I) to (A-IV) shown below:

General Formula (A-I):

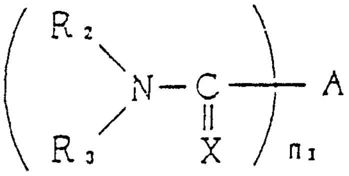


wherein, Q_1 represents a group of atoms necessary for the formation of a nitrogen-containing heterocyclic ring (including those condensed with a saturated or unsaturated ring of 5 or 6 members); R_1 represents a hydrogen atom, an alkali metal atom,

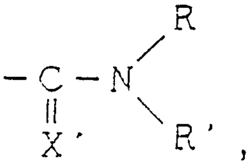


or an alkyl group, provided that Q' have the same meaning as defined for Q_1,

General Formula (A-II):



wherein, R_2 and R_3 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyl group, a carboxyl group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group or an alkenyl group; A represents a group of;



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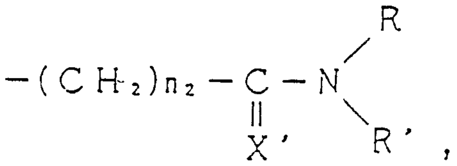

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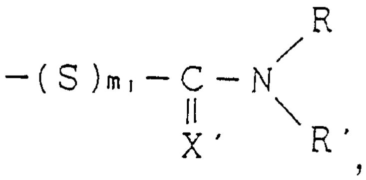

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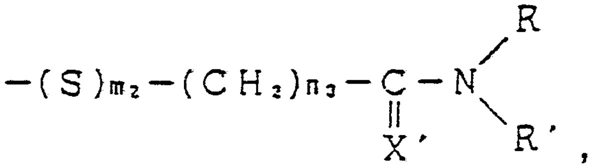
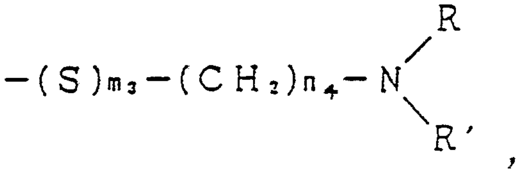
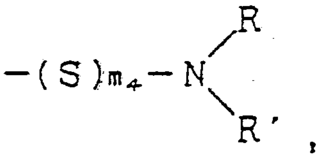


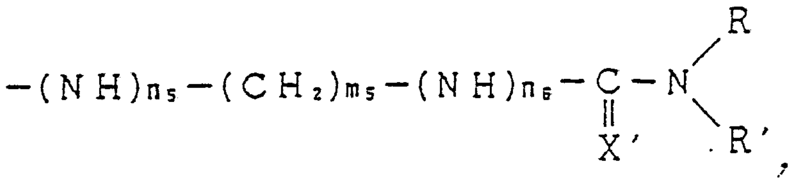
$-(S)_{m_2}-(CH_2)_{n_3}-\underset{\underset{X'}{\|}}{C}-N{<}^{R}_{R'}$,



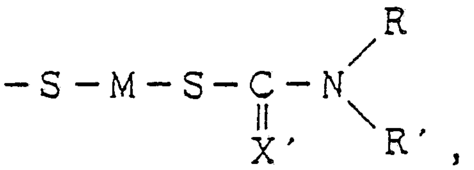
$-(S)_{m_3}-(CH_2)_{n_4}-N{<}^{R}_{R'}$,



$-(S)_{m_4}-N{<}^{R}_{R'}$,



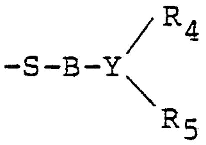
$-(NH)_{n_5}-(CH_2)_{m_5}-(NH)_{n_6}-\underset{\underset{X'}{\|}}{C}-N{<}^{R}_{R'}$,



$-S-M-S-\underset{\underset{X'}{\|}}{C}-N{<}^{R}_{R'}$,

$-SZ$

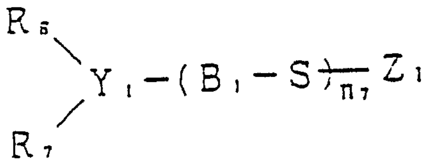
or a heterocyclic residual group with a valence of n_1 (including those condensed with an unsaturated ring of 5 or 6 members); and X represents =S, =O or =NR"; where, R and R' each have the same meaning as R_2 and R_3, X' have the same meaning as X; Z represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic group, an alkyl group or



$-S-B-Y{<}^{R_4}_{R_5}$; M represents a divalent metal atom;

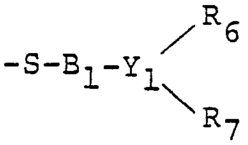
R" represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic residual group (including those condensed with an unsaturated ring of 5 or 6 members) or an amino group; and n_1 to n_6 and m_1 to m_5 each represent an integer of 1 to 6; B represents an alkylene group having 1 to 6 carbon atoms; Y represents $-N{<}$ or $-CH{<}$, R_4 and R_5 each have the same meaning as R_2 and R_3, provided that R_4 and R_5 each may represent -B-SZ, or R and R', R_2 and R_3, and R_4 and R_5 each may combine to form a ring; the compound represented by General Formula (A-II) may include compounds of enol form and salts thereof,

General Formula (A-III):



$$\begin{matrix} R_6 \\ & \searrow \\ & & Y_1-(B_1-S)_{n_7}-Z_1 \\ & \nearrow \\ R_7 \end{matrix}$$

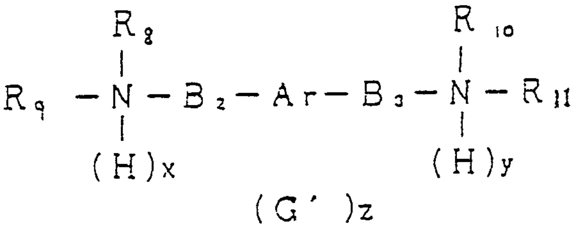
wherein, R_6 and R_7 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyl group, a carboxyl group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group, an alkenyl group or $-B_1-S-Z_1$, provided that R_6 and R_7 may combine to form a ring, Y_1 represents $>N-$ or $>CH-$; B_1 represents an alkylene group having 1 to 6 carbon atoms; Z_1 represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic residual group, or



$$-S-B_1-Y_1\begin{matrix} \nearrow R_6 \\ \searrow R_7 \end{matrix}$$

; and n_7 represents an integer of 1 to 6,

General Formula (IV):



$$R_9-\underset{\substack{| \\ (H)_x}}{\overset{\substack{R_8 \\ |}}{N}}-B_2-Ar-B_3-\underset{\substack{| \\ (H)_y}}{\overset{\substack{R_{10} \\ |}}{N}}-R_{11} \quad (G')_z$$

wherein, Ar represents a divalent arylene group or a divalent organic group comprising the combination of an aryl group with an oxygen atom and/or an alkylene group; B_2 and B_3 each represent a lower alkylene group; R_8, R_9, R_{10} and R_{11} each represent a hydroxyl-substituted lower alkyl group; and x and y each represent 0 or 1; G' represents an anion; and z represents 0, 1 or 2.

17. The bleach-fixing solution according to Claim 17, wherein the bleaching accelerator is contained in an

amount of 0.01 to 100 g per liter of the bleach-fixing solution.

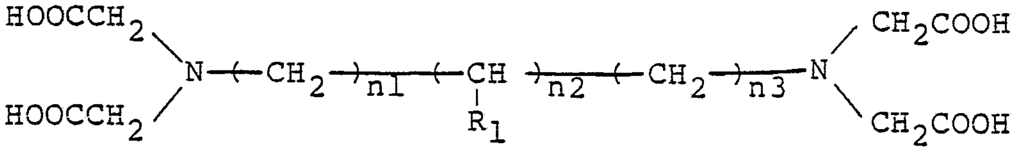
18. A method for processing a light sensitive silver halide photographic material for photographing, which comprises carrying out the processing by using a bleach-fixing solution having the pH ranging between 3.0 and 6.8, containing a ferric complex salt having a ligand comprising a compound represented by General Formula (I) shown below, and further containing at least one of;

i) at least one compound selected from the compounds represented respectively by General Formula (II) and General Formula (III) shown below;

ii) a polymer having a unit of a pyrrolidone nucleus in the molecular structure; and

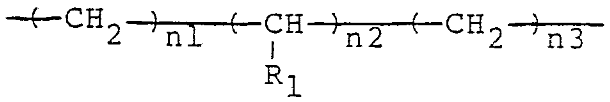
iii) a ferric complex salt having a ligand comprising at least one compound selected from the compounds represented respectively by General Formulas (IV) to (VII),

General Formula (I):



$$(HOOCCH_2)_2N{+}CH_2{+}_{n1}{+}\underset{R_1}{CH}{+}_{n2}{+}CH_2{+}_{n3}N(CH_2COOH)_2$$

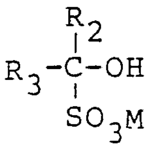
wherein R_1 represents a hydrogen atom or a lower alkyl group; and n_1, n_2 and n_3 each represent an integer of 0 to 3, provided that the sum of n_1, n_2 and n_3 is an integer of 2 to 4 and the total sum of the carbon atoms in



$$-{+}CH_2{+}_{n1}{+}\underset{R_1}{CH}{+}_{n2}{+}CH_2{+}_{n3}$$

is 3 or more,

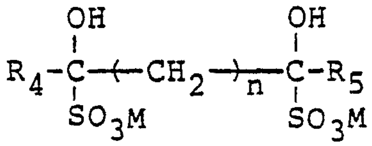
General Formula (II):



$$R_3-\overset{R_2}{\underset{SO_3M}{C}}-OH$$

wherein R_2 and R_3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; and M represents an alkali metal atom or an ammonium group,

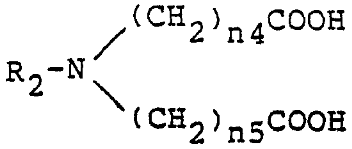
General Formula (III):



$$R_4-\underset{SO_3M}{\overset{OH}{C}}-(CH_2)_n-\underset{SO_3M}{\overset{OH}{C}}-R_5$$

wherein R_4 and R_5 each represent a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; M represents an alkali metal atom or an ammonium group; and n represents an integer of 0 to 6,

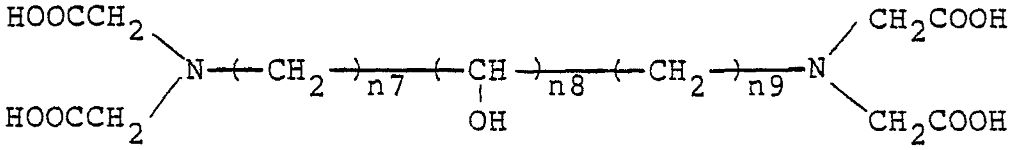
General Formula (IV):



$$R_2-N\begin{matrix}\diagup (CH_2)_{n4}COOH\\ \diagdown (CH_2)_{n5}COOH\end{matrix}$$

wherein R_2 represents an alkyl group having 1 to 5 carbon atoms, a hydroxyl-substituted alkyl group having 1 to 5 carbon atoms, or $(CH_2)_{n6}COOH$; and n_4, n_5 and n_6 each represents an integer of 1 or 2,

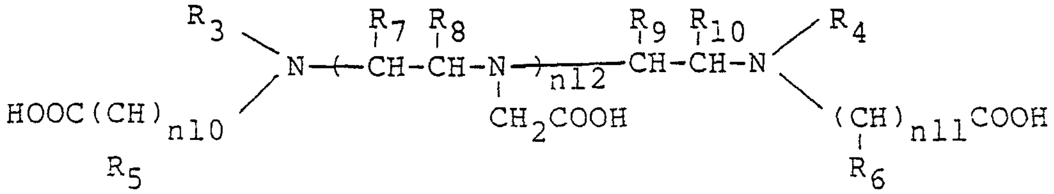
General Formula (V):



$$\begin{matrix}HOOCCH_2\diagdown\\ HOOCCH_2\diagup\end{matrix}N-(CH_2)_{n7}-(\underset{OH}{CH})_{n8}-(CH_2)_{n9}-N\begin{matrix}\diagup CH_2COOH\\ \diagdown CH_2COOH\end{matrix}$$

wherein n_7 and n_9 each represent an integer of 0 to 3, and n_8 represents an integer of 1 to 3, provided that the sum of n_7, n_8 and n_9 is 2 or more,

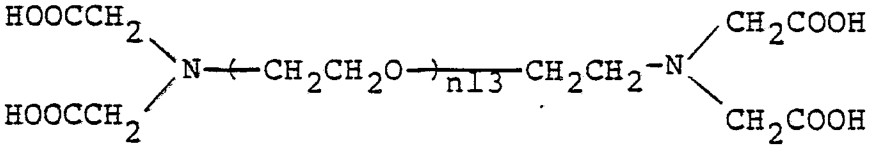
General Formula (VI):



$$\begin{matrix}R_3\diagdown\\ HOOC(\underset{R_5}{CH})_{n10}\diagup\end{matrix}N-(\overset{R_7}{CH}-\overset{R_8}{CH}-\underset{CH_2COOH}{N})_{n12}-\overset{R_9}{CH}-\overset{R_{10}}{CH}-N\begin{matrix}\diagup R_4\\ \diagdown(\underset{R_6}{CH})_{n11}COOH\end{matrix}$$

wherein R_3 and R_4 each represent a hydrogen atom, a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, or a carboxyl-substituted alkyl group having 1 or 2 carbon atoms; R_5 and R_6 each represent a hydrogen atom or a hydroxyl-substituted phenyl group; R_7, R_8, R_9 and R_{10} each represent a hydrogen atom or a hydroxyl-substituted alkyl group having 1 to 3 carbon atoms, provided that R_7, R_8, R_9 and R_{10} each may combine to form a ring having 5 to 8 carbon atoms; n_{10} and n_{11} each represent an integer of 1 to 3; and n_{12} represents an integer of 0 to 4,

General Formula (VII):



$$(HOOCCH_2)_2N{-}(CH_2CH_2O)_{n13}{-}CH_2CH_2{-}N(CH_2COOH)_2$$

wherein n_{13} represents an integer of 1 to 8.