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EP 0 750 226 A1 (11)

(12)

### **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

27.12.1996 Bulletin 1996/52

(21) Application number: 96109200.4

(22) Date of filing: 07.06.1996

(84) Designated Contracting States: BE DE FR GB NL

(30) Priority: 09.06.1995 JP 167100/95

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#### (54)A method for processing a silver halide color photographic light-sensitive material

(57)There is disclosed a method for processing a silver halide color photographic light-sensitive material, comprising steps of color developing a silver halide color photographic light-sensitive material, then desilvering it, and washing and/or stabilizing it, wherein a processing solution having a bleaching capacity in the desilvering step contains a ferric complex salt of a biodegradable monoamine-type bleaching agent, and wherein a processing solution used in the desilvering step or subsequent steps therefrom contains a specific nitrogen-containing or phenolic compound, or an aminoglycoside. According to the method, the adhesion of the processed light-sensitive material, the wet-heat fading of a yellow dye, and the magnetic output capacity of a light-sensitive material having a magnetic recording layer, can be improved.

#### Description

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#### FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic light-sensitive material (hereinafter referred to "a light-sensitive material" according to the occasion). In particular, the present invention relates to a processing method having improved adhesion of the processed light-sensitive material, improved wet-heat fading of a yellow dye, and improved magnetic output capacity of a light-sensitive material having a magnetic recording layer, even when a processing is conducted over a long period of time using a bleaching agent that is excellent in biodegradability (spontaneous decomposability).

#### **BACKGROUND OF THE INVENTION**

In general, fundamentals for the photographic process of a silver halide color photographic light-sensitive material consist of a color development step and a desilvering step, and the light-sensitive material is processed by these fundamental steps and other auxiliary steps using a processing apparatus, which is called an autoprocessor. In the desilvering step, the developed silver produced in the color development step is oxidized, to become a silver salt, by an action of an oxidant (a bleaching agent) contained in a processing solution having a bleaching capacity, and further, the silver salt is removed from the light-sensitive material, by an agent capable of dissolving a silver ion (a fixing agent), which is contained in a processing solution having a fixing capacity.

On the other hand, the use of materials having good biodegradability has lately been called for, from a global environmental protection point of view, in a movement against materials that are hardly biodegraded in the natural world, such as ethylenediamine-N,N,N',N'-tetraacetic acid and 1,3-propanediamine-N,N,N',N'-tetraacetic acid, which have been generally used as bleaching agents up to the present time. Such materials having good biodegradability include diamine-type compounds, as disclosed in JP-A-("JP-A" means an unexamined published Japanese patent application) No. 313752/1992, and monoamine-type compounds, as disclosed in JP-A-Nos. 265159/1993 and 161065/1994.

Further, since a nitrogen ingredient in a processing solution is an environment-corrupting element, the monoamine-type compounds, which contain less of a nitrogen ingredient, are preferred of these materials having good biodegradability, from the environmental protection point of view. However, the following facts have been confirmed: when a light-sensitive material is processed for a long period of time using a monoamine-type compound having good biodegradability, sometimes the processed light-sensitive material takes on adhesiveness, and consequently such problems arise that a color negative film is difficult to remove from an envelope, which is called a nega sheet; and further, such monoamine-type compounds tend to deteriorate wet-heat fading of a yellow dye, among image-forming dyes.

Additionally, with respect to a light-sensitive material having a magnetic recording layer, as disclosed in International Publication WO 90/04205, it has also been confirmed that such monoamine-type compounds considerably lower the reading capacity of the magnetic record. JP-A-95318/1994 describes processing the light-sensitive material having a magnetic recording layer with a bleaching solution containing a ferric complex salt of aminopolycarboxylic acid. Although, the said publication describes effects of a change in density of the processed light-sensitive material with a lapse of time under wet heat, and a solution's storage stability, it is silent on an influence on the reading capacity of the magnetic record.

The mechanism of these phenomena has not been made clear yet, but it is assumed that they might be caused by a difference in adhesion of a processing solution's ingredient to the processed light-sensitive material.

#### **SUMMARY OF THE INVENTION**

An object of the present invention is to provide a method for processing a silver halide color photographic light-sensitive material, whereby adhesion of the processed light-sensitive material and wet-heat fading of a yellow dye are not deteriorated, even though a processing is conducted over a long time using a material having excellent biodegradability.

Another object of the present invention is to provide a processing method that does not lower the reading capacity of the magnetic record, even when a light-sensitive material having a magnetic recording layer is processed thereby.

Other and further objects, features, and advantages of the invention will appear more evident from the following description.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The above objects of the present invention are accomplished by the following processing method, which is:

A method for processing a silver halide color photographic light-sensitive material, which method comprises steps of color developing a silver halide color photographic light-sensitive material, and then desilvering, and further washing and/or stabilizing it, wherein a processing solution having a bleaching capacity in the desilvering step contains a ferric

complex salt of at least one compound represented by general formula(X) as set forth below, and further, a processing solution used in the desilvering step or subsequent steps therefrom contains at least one compound represented by general formulae (A) to (I), or at least one aminoglycoside selected from the group consisting of gentamicins, amikacin, tobramicin, dibekacin, albekacin, micronomicin, isepamicin, sisomicin, netilmicin, and astromicin: general formula (X)

 $R-N < L_1 - CO_2M_1$   $L_2 - CO_2M_2$ 

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wherein R represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group;  $L_1$  and  $L_2$  each represent an alkylene group; and  $M_1$  and  $M_2$  each represent a hydrogen atom or a cation: general formulae (A) to (I)

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formula (A)

formula (B)

$$\left(\begin{array}{c}
R_2 \\
R_1 - N - R_3 \\
I \\
R_4
\end{array}\right) \stackrel{\textcircled{\scriptsize }}{=} Y$$

$$\begin{pmatrix}
R_2 \\
I \\
I \\
I \\
I \\
R_4
\end{pmatrix}$$
 $\bigcirc$ 

$$R_6$$

$$\begin{pmatrix}
N \\
N \\
N \\
I \\
R_5
\end{pmatrix}$$
 $(CH_2)_n - C$ 

$$\downarrow
Z_1$$

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formula (C)

formula (D)

$$R_7 - NH + \begin{pmatrix} NH \\ II \\ C - NH \end{pmatrix}_m R$$

$$\begin{array}{c|c} & & & & \\ NH & & & \\ R_7 - NH + C - NH + R_8 & & & \\ \end{array} \qquad \begin{array}{c} & & & \\ L_3 & - NH + (C - NH)_{\frac{11}{m}} \\ \end{array} \begin{array}{c} \\ k \end{array}$$

formula(E)

formula (F)

$$\begin{array}{c|c}
0 & R_9 \\
N-S-C-R_{10} & R_{2N}
\end{array}$$

$$\begin{array}{c|c}
R_{12} & R_{13}
\end{array}$$

$$H_2N \longrightarrow SO_2N < R_{12}$$

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formula(G)

formula(H)

$$R_{14} \xrightarrow{0} N - R_{16} \qquad HO \xrightarrow{CO_2 R_{17}}$$

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formula([)

$$\langle - \rangle - 0 - L_4 - 0H$$

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wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>7</sub>, and R<sub>8</sub> each represent a hydrogen atom, an alkyl group, or an aryl group; R<sub>6</sub> represents a hydrogen atom, an alkyl group, an aryl group, a nitro group, a carboxyl group, a sulfo group, a sulfamoyl group, a hydroxyl group, a halogen atom, an alkoxy group, or a thiazolyl group; L3 and L4 each represent an alkylene

group or an arylene group;  $R_9$ ,  $R_{10}$ , and  $R_{11}$  each represent a halogen atom or an alkyl group;  $R_{12}$  and  $R_{13}$  each represent a hydrogen atom, an alkyl group, an aryl group, or a nitrogen-containing heterocyclic residue group;  $R_{14}$  and  $R_{15}$  each represent a hydrogen atom, a halogen atom, an alkyl group, or an aryl group, with the proviso that  $R_{14}$  and  $R_{15}$  may bond together to form a benzene ring;  $R_{16}$  represents a hydrogen atom or an alkyl group;  $R_{17}$  represents an alkyl group or an aryl group; Y represents a halogen atom;  $Z_1$  represents a group of non-metallic atoms necessary to complete a thiazolyl ring;  $Z_2$  represents a group of non-metallic atoms necessary to complete a 6-membered hydrocarbon ring; n is 0 or 1; m is 1 or 2; and k is an integer of 3 to 20.

In the present invention, the light-sensitive material is processed with a color-developing solution and then desilvered; then it is further processed with a washing solution and/or a stabilizing solution.

In the desilvering step, basically bleaching is performed with a processing solution having a bleaching capacity, and then fixing is conducted with a processing solution having a fixing capacity. The bleaching and the fixing may be conducted separately, as described above, or alternatively they may be conducted simultaneously with a bleach-fixing solution having both a bleaching capacity and a fixing capacity, which is called blix processing. These bleaching, fixing, and blix processing may be carried out in a bath, or two or more baths, respectively.

The processing solution having a bleaching capacity referred to in the present invention means a processing solution containing a bleaching agent among processing solutions used in the desilvering step, and more specifically both a bleaching solution and a blix solution. Specific embodiments of the desilvering processing for use in the present invention are illustrated below, but the invention is not limited to them.

- bleach-fix
  - 2. blix
  - 3. bleach-blix
  - 4. blix-blix
  - 5. bleach-blix-fix
  - 6. bleach-blix-blix
  - 7. bleach-fix-fix
  - 8. bleach-fix-blix
  - 9. blix-fix
  - 10. blix-bleach

A washing step may be discretionally added between the above-described processings.

A compound represented by general formula (X) for use in the present invention is described in detail below. The number of carbon atoms hereinafter referred to means carbon atoms, excluding a substituent.

Examples of the aliphatic hydrocarbon group represented by R include a straight, branched, or cyclic alkyl group having preferably 1 to 12, more preferably 1 to 10, and still more preferably 1 to 8 carbon atoms; an alkenyl group having preferably 2 to 12, more preferably 2 to 10, and still more preferably 2 to 7 carbon atoms; and an alkynyl group having preferably 2 to 12, more preferably 2 to 10, and still more preferably 2 to 7 carbon atoms, each of which may be substituted with a substituent.

Examples of such a substituent include an aryl group having preferably 6 to 12, more preferably 6 to 10, and particularly preferably 6 to 8 carbon atoms (e.g. phenyl, methylphenyl); an alkoxy group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methoxy, ethoxy); an aryloxy group having preferably 6 to 12, more preferably 6 to 10, and particularly preferably 6 to 8 carbon atoms (e.g. phenyloxy); an acyl group having preferably 1 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. acetyl); an alkoxycarbonyl group having preferably 2 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. methoxycarbonyl); an acyloxy group having preferably 1 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. acetoxy); an acylamino group having preferably 1 to 10, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. acetylamino); a sulfonylamino group having preferably 1 to 10, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfonylamino); a sulfamoyl group having preferably 0 to 10, more preferably 0 to 6, and particularly preferably 0 to 4 carbon atoms (e.g. sulfamoyl and methylsulfamoyl); a carbamoyl group having preferably 1 to 10, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. carbamoyl and methylcarbamoyl); an alkylthio group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methylthio and ethylthio); a sulfonyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfonyl); a sulfinyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfinyl); a hydroxyl group, a halogen atom (e.g. fluorine, chlorine, bromine, and iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group; and a heterocyclic group (e.g. imidazolyl, pyridyl). These groups may be further substituted. When there are two or more subsituents, they are the same or different.

Preferred among the above-listed substituents for the aliphatic hydrocarbon groups represented by R, are an alkoxy group, a carboxyl group, a hydroxyl group, and a sulfo group, and more preferred are a carboxyl group and a

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hydroxyl group.

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Preferred among the aliphatic hydrocarbon groups represented by R, is an alkyl group, more preferably a chain alkyl group. Still more preferable examples thereof include methyl, ethyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxyethyl, 2-bydroxyethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-sulfoethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-(4-imidazolyl)ethyl, 1-carboxy-2-phenylethyl, 1-carboxy-3-methylthiopropyl, 2-carboxyethyl, and 4-imidazolylmethyl; and the particularly preferred are methyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 1-carboxy-2-phenylethyl, and 1-carboxy-3-methylthiopropyl.

Preferred among the aryl groups represented by R, is an aryl group composed of a single ring or twin rings, each having 6 to 20 carbon atoms (e.g. phenyl and naphthyl); more preferred is a phenyl group having 6 to 15 carbon atoms; and still more preferred is a phenyl group having 6 to 10 carbon atoms.

The aryl group represented by R may have a substituent, examples of which include an alkyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methyl and ethyl); an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituents for the aliphatic hydrocarbon group represented by R.

Preferred among the substituents for the aryl group represented by R, are an alkyl group, an alkoxy group, a hydroxyl group, and a sulfo group; and more preferred are an alkyl group, a carboxyl group, and a hydroxyl group.

Specific examples of the aryl group represented by R include 2-carboxyphenyl and 2-carboxymethoxyphenyl.

The heterocyclic group represented by R is a residue of a 3- to 10-membered saturated or unsaturated heterocyclic compound containing at least one of N, O, and S atoms, which may be a single ring or a condensed ring.

Preferred among the heterocyclic groups, is a 5-or 6-membered aromatic heterocyclic group, with a more preferred example being a 5- or 6-membered nitrogen atom-containing aromatic heterocyclic group. Still more preferred is a 5- or 6-membered aromatic heterocyclic group containing one or two nitrogen atoms.

Specific examples of the heterocyclic group include pyrrolidinyl, piperidyl, piperazinyl, imidazolyl, pyrazolyl, pyridyl, and quinolyl. Preferred among these groups are an imidazolyl group and a pyridyl group.

The heterocyclic group represented by R may have a substituent, examples of which include an alkyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methyl and ethyl); an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituents for the aliphatic hydrocarbon group represented by R.

Preferred among the substituents for the heterocyclic group represented by R, are an alkyl group, an alkoxy group, a hydroxyl group, and a sulfo group; and more preferred are an alkyl group, a carboxyl group, and a hydroxyl group.

R is preferably a hydrogen atom, or an alkyl group having 1 to 8 carbon atoms, and more preferred are a hydrogen atom, a methyl group, an ethyl group, a 1-carboxyethyl group, a 2-carboxyethyl group, a hydroxyethyl group, or a 2-carboxy-2-hydroxyethyl group. A hydrogen atom is especially preferred.

The alkylene groups represented by  $L_1$  and  $L_2$  are the same or different, and they may be straight chain, branched chain, or cyclic groups. Further, they may have a substituent, examples of which include an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituent for the aliphatic hydrocarbon group represented by R.

Preferred among the substituents for the alkylene groups represented by  $L_1$  and  $L_2$ , are an aryl group, an alkoxy group, a hydroxy group, a carboxyl group, and a sulfo group; and more preferred are an aryl group, a carboxyl group, and a hydroxyl group. Preferred alkylene groups represented by  $L_1$  and  $L_2$  are groups whose alkylene moieties have 1 to 6 carbon atoms, and more preferably 1 to 4 carbon atoms. Still more preferred alkylene groups are substituted or unsubstituted methylene and ethylene groups.

Preferred specific examples of the alkylene group include methylene, ethylene, trimethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1,2-cyclohexylene, 1-carboxymethylene, carboxymethylmethylene, carboxymethylmethylene, benzylmethylene, hydroxymethylmethylene, 2-hydroxyethylmethylene, carbamoylmethylmethylene, phenylmethylene, benzylmethylene, 4-imidazolylmethylene, and 2-methylthioethylmethylene; and more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 4-imidazolylmethylene, carboxymethylmethylene, and 2-methylthioethylmethylene; and still more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, hydroxymethylmethylene, hydroxymethylene, and benzylmethylene.

The cation represented by M<sub>1</sub> or M<sub>2</sub> is an organic or inorganic cation, examples of which include an alkali metal ion

(e.g. Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>), an alkali earth metal ion (e.g.  $Mg^{2+}$ ,  $Ca^{2+}$ ), an ammonium ion (e.g. ammonium, trimethylammonium, triethylammonium, tetraethylammonium, tetraethylammonium, tetrabutylammonium, 1,2-ethanediammonium), a pyridinium ion, an imidazolium ion, and a phosphonium ion (e.g. tetrabutylphosphonium). Preferred examples of  $M_1$  and  $M_2$  are an alkali metal ion and an ammonium ion, and more preferred are  $Na^+$ ,  $K^+$ , and  $NH_4^+$ .

When the compound represented by general formula (X) has an asymmetric carbon atom in its molecule, it is preferred, from the spontaneous decomposability point of view, that at least one asymmetric carbon atom is a L type (L form). Further, when the compound has at least two asymmetric carbon atoms, the more L-type asymmetric carbon atoms there are in the molecule, the more the compound is preferred.

Preferred among the compounds represented by general formula (X), are those represented by the following general formula (1-a):

general formula (1-a)

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$$H-N = \begin{array}{c} L_1 - CO_2M_1 \\ CH - CO_2Ma_1 \\ CH_2 - CO_2Ma_2 \end{array}$$

wherein  $L_1$  and  $M_1$  each have the same meanings as those in general formula (X), and therefore their preferred ones are also same;  $M_{a_1}$  and  $M_{a_2}$  each have the same meanings as  $M_2$  in general formula (X).

Preferred among the compounds represented by general formula (1-a), are those in which  $L_1$  is a substituted or unsubstituted methylene or ethylene group, and  $M_1$ ,  $Ma_1$ , and  $Ma_2$  are any one of a hydrogen atom, an alkali metal ion, and an ammonium ion, respectively. More preferred compounds are ones in which  $L_1$  is a substituted or unsubstituted methylene group having 1 to 10 total carbon atoms, including a substituent thereof, and  $M_1$ ,  $Ma_1$ , and  $Ma_2$  are any one of a hydrogen atom,  $Na^+$ ,  $K^+$ , and  $NH_4^+$ , respectively.

Specific examples of the compound represented by general formula (X) are illustrated below, but examples are not limited to those shown.

The compounds marked with L therein indicate that the asymmetric carbon atom, marked with L therein, is an L type. On the other hand, the compounds without L indicate a mixture of D and L types.

9. 10. 11. 5 CH2CO2H 10 CH2CO2H ĊH₂CO₂H ÇH2CH2SCH3 12. 13. 14. CH2CONH2 15 CHCO2H ĊHCO₂H ÇHCO₂H CH2CH2CO2H ÇHCO₂H ĊH₂CO₂H 20 ĊH₂CO₂H 15. 16. CH2CH2CO2H HO-ÇHCO₂H 25 ÇHCO₂H ĊH2CO2H HO-CHCO₂H 30

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CH2CO2H HN CHCO2H 17. CH<sub>2</sub> CHCO<sub>2</sub>H

HN

CH<sub>2</sub> CO<sub>2</sub>H 5 10 20. 21. CH<sub>2</sub>CO<sub>2</sub>H
CH<sub>2</sub>CO<sub>2</sub>H 15 20 23.  $C_2H_5-N < CH_2CO_2H$   $CH_2CO_2H$  $CH_3 - N < CH_2CO_2H$   $CH_2CO_2H$ 25 30 25. 26.  $HO_2CCH_2CH_2N < CH_2CO_2H \\ CH_2CO_2H$ HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H
CH<sub>2</sub>CO<sub>2</sub>H 35 27. 28.  $HOCH_2CH_2N < CH_2CO_2H < CH_2CO_2H$  $\begin{array}{c} CH_3 \\ \downarrow \\ HO_2 CCH - N \\ CH_2 CO_2 H \end{array}$ 40 29. 30. 45

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31. 32. 33. ÇH₃ ÇH₃ ĊHCO2H CHCO2H ĊHCO₂H 5 CH2CO2H ĊH<sub>2</sub>CO<sub>2</sub>H ĊH₂CO₂H 10 34 35. 36. Ç₂H₅ C<sub>2</sub>H<sub>5</sub> Ç<sub>2</sub>H<sub>5</sub> CHCO2H ,chco₂h L 15 с́нсо₂н ζ́НСО₂Н CH2CO2H CH2CO2H ĊH<sub>2</sub>CO<sub>2</sub>H 20 37. 38. ÇH2CO2H CH2CO2H HN \ CHCO⁵H ĊHCO2H 25 ÇHCO₂H ĊH<sub>2</sub>CO<sub>2</sub>H CH2CO2H 30 35 39. ÇH2CO2H 40. 41. 40 CH2CO2H CH2CO2H ĊH2CO2H 45 42. 43.

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The above-listed compounds may be ones in which a hydrogen atom of the carboxyl group is substituted with a cation, respectively. In this case, the cation has the same meanings as those represented by  $M_1$  and  $M_2$  in general formula (X)

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The compound represented by general formula (X) for use in the present invention can be prepared according to the methods described in, for example, <u>Journal of Inorganic and Nuclear Chemistry</u>. Vol. 35, p. 523 (1973), Swiss patent No. 561504, German patent No. 391255A1, ibid. 3939755A1, ibid. 3939756A1, JP-A-No. 265159/1993, ibid. 59422/1994 (methods for preparing L types of exemplified compounds 1-42, 1-43, 1-46, 1-52, and 1-53 are described in the synthesis examples 1, 2, 3, 4 and 6), ibid. 95319/1994 (methods for preparing L types of exemplified compounds 1-8, 1-11, 1-37, 1-38, and 1-40 are described in the synthesis examples 2 to 6), ibid. 161054/1994, and ibid. 161065/1994.

In the present invention, a ferric (iron (III)) complex salt of a compound represented by general formula (X) may be added in the form of an isolated compound. Alternatively, the compound of general formula (X) and a ferric salt (e.g. ferric nitrate and ferric chloride) may be added in a solution to coexist therein, and subjected to a complex formation in

a processing solution.

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Further, the compound of general formula (X) for use in the present invention may be used singly or in a combination of two or more kinds thereof.

In the present invention, the compound of general formula (X) may be used somewhat in excess of the amount necessary to form a complex salt of ferric ion (e.g. 0.5, 1, or 2 times the molar amount per the ferric ion). When the compound is used in such an excess amount, preferably the excess amount is generally regulated to the range of 0.01 to 15 mol%.

In the present invention, a ferric complex salt of a compound represented by general formula (X) can be contained in a processing solution such as a blix solution and a bleaching solution, with preference given to a bleaching solution.

A ferric complex salt of an organic acid contained in a processing solution having a bleaching capacity for use in the present invention may be used in the form of an alkali metal salt or an ammonium salt. Example alkali metal salts are a lithium salt, a sodium salt, and a potassium salt. On the other hand, example ammonium salts are an ammonium salt and a tetraethylammonium salt. In the present invention, the concentration of an ammonium ion in a processing solution having a bleaching capacity is preferably 0 to 0.4 mol/l, and especially preferably 0 to 0.2 mol/l.

In the present invention, as a bleaching agent, the ferric complex salt of a compound represented by general formula (X) can be used in combination with a ferric complex salt of known compounds, such as ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediaminetetraacetic acid, gly-coletherdiaminetetraacetic acid, and 1,3-propanediamine-N,N,N',N'-tetraacetic acid, and/or in combination with an inorganic oxidizing agent, such as potassium ferricyanide, a salt of persulfuric acid, hydrogen peroxide, and a salt of bromic acid. However, in the present invention it is preferred, from such points of view as environmental protection and safety for handling, that the compound represented by general formula (X) occupies an amount of 70 to 100 mol%, more preferably 80 to 100 mol%, and especially preferably 100 mol%, of the total bleaching agent.

An amount of the compound represented by general formula (X) to be used in the present invention is generally 0.003 to 3.0 mol/l, preferably 0.02 to 2.00 mol/l, more preferably 0.05 to 1.00 mol/l, and especially preferably 0.08 to 0.5 mol/l. However, the total concentration of the ferric complex salt in combination with the above-mentioned inorganic oxidizing agent, is preferably 0.005 to 0.030 mol/l.

A processing solution for use in the desilvering step or subsequent steps in the present invention contains at least one of the compounds represented by the above-described general formulae (A) to (I), or at least one of aminoglycosides selected from gentamicins, amikacin, tobramicin, dibekacin, albekacin, micronomicin, isepamicin, sisomicin, netilmicin, and astromicin.

Gentamicins are preferred of the aminoglycosides.

The compounds represented by general formulae (A) to (I) are explained below.

Preferred among the compounds represented by general formulae (A) to (I), are those represented by general formulae (B), (G), and (H); and more preferred are those represented by general formulae (G) and (H).

The alkyl groups of  $R_1$  to  $R_{17}$  may be substituted with a substituent, and they are preferably straight chain, branched chain, or cyclic alkyl groups having 1 to 30 carbon atoms, specific examples of which include methyl, ethyl, octyl, dodecyl, tetradecyl, and octadecyl.

The aryl groups of  $R_1$  to  $R_8$  may be substituted with a substituent, and they may have a single ring or a condensed ring; and preferably they are groups having 6 to 20 carbon atoms, such as a phenyl group and a naphthyl group.

The sulfamoyl group of  $R_6$  may be substituted with a substituent, and preferably it has 0 to 30 carbon atoms. Specific examples of the sulfamoyl group are sulfamoyl and N,N'-dimethylsulfamoyl. The alkoxy group of  $R_6$  may be substituted with a substituent, and preferably it has 1 to 30 carbon atoms. Specific examples of the alkoxy group are methoxy, ethoxy, and octyloxy. The thiazolyl group of  $R_6$  may be substituted with a substituent at the 2-, 4-, or 5-position thereof.

The alkylene groups of  $L_1$  and  $L_2$  may be substituted with a substituent, and they are preferably straight chain, branched chain, or cyclic ones having 1 to 10 carbon atoms, specific examples of which include methylene, ethylene, and propylene. The arylene group of  $L_1$  and  $L_2$  may be substituted with a substituent, and they are preferably ones having 6 to 10 carbon atoms, such as phenylene and naphthylene.

Halogen atoms of R<sub>6</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>14</sub>, R<sub>15</sub>, and Y are a chlorine atom, a fluorine atom, and a bromine atom.

The nitrogen-containing heterocyclic residue groups of  $R_{12}$  and  $R_{13}$  are preferably 5- to 8-membered saturated or unsaturated groups, and preferable hetero atoms, in addition to a nitrogen atom, are an oxygen atom and a sulfur atom. Specific examples of the nitrogen-containing heterocyclic residue group include 2-oxazolyl, 3-isoxazolyl, 3-pyrrolyl, 2-imidazolyl, 5-pyrazolyl, 5-isothiazolyl, 2-1,3,4-thiadiazolyl, 4-thiadiazolyl, 2-pyridyl, and 2-pyrimidyl.

 $Z_1$  represents a group of non-metallic atoms necessary to complete a thiazolyl ring, which may be substituted with a substituent at the 2-, 4-, or 5-position.  $Z_2$  represents a group of non-metallic atoms necessary to complete a 6-membered hydrocarbon ring that may be saturated or unsaturated, such as a cyclohexane ring and a cyclohexene ring.

Examples of the above-mentioned substituent include an alkyl group (e.g. methyl, ethyl), an aralkyl group (e.g. phenylmethyl), an alkenyl group (e.g. allyl), an alkynyl group, an alkoxy group (e.g. methoxy, ethoxy), an aryl group (e.g. phenyl, p-methylphenyl), an amino group (e.g. dimethylamino), an acylamino group (e.g. acetylamino), a sulfonylamino group (e.g. methanesulfonylamino), a ureido group, a urethane group, an aryloxy group (e.g. phenyloxy), a sulfamoyl

group (e.g. methylsulfamoyl), a carbamoyl group (e.g. carbamoyl, methylcarbamoyl), an alkylthio group (e.g. methylthio), an arylthio group (e.g. phenylthio), a sulfonyl group (e.g. methanesulfonyl), a sulfinyl group (e.g. methanesulfinyl), a hydroxyl group, a halogen atom (e.g. chlorine, bromine, fluorine), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (e.g. phenyloxycarbonyl), an acyl group (e.g. acetyl, benzoyl), an alkoxycarbonyl group (e.g. methoxycarbonyl), an acyloxy group (e.g. acetoxy), a carbonamido group, a sulfonamido group, and a nitro group.

In general formula (A), preferably  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  each represent an alkyl group, and more preferably at least one of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  is an alkyl group having 5 to 20 carbon atoms. Especially preferably, Y is a chlorine atom.

In general formula (B), each of  $R_5$  and  $R_6$  is preferably a hydrogen atom. n is preferably 0.  $Z_1$  preferably represents a group of non-metallic atoms necessary to complete an unsubstituted 4-thiazolyl ring.

In general formula (C),  $R_7$  is preferably a hydrogen atom.  $R_8$  is preferably an alkyl group, and more preferably an alkyl group having 5 to 20 carbon atoms.

In general formula (D),  $L_3$  is preferably an alkylene group having 5 to 10 carbon atoms. k is preferably 3 to 10.

In general formula (E), each of  $R_9$ ,  $R_{10}$ , and  $R_{11}$  is preferably an alkyl group substituted with at least one halogen atom, or a halogen atom. Especially preferably,  $R_9$ ,  $R_{10}$ , and  $R_{11}$  each represent a halogen atom.  $Z_2$  preferably represents a group of non-metallic atoms necessary to complete a cyclohexene ring.

In general formula (F), preferably each of  $R_{12}$  and  $R_{13}$  represents a hydrogen atom, an alkyl group, or a nitrogen-containing heterocyclic residue group.  $R_{12}$  is more preferably a hydrogen atom, and  $R_{13}$  is more preferably a hydrogen atom or a 5- or 6-membered nitrogen-containing unsaturated heterocyclic residue group.

In general formula (G), preferably each of  $R_{14}$  and  $R_{15}$  represents a hydrogen atom, or they combine with each other to form a benzene ring. The latter benzene ring combination is more preferable.  $R_{16}$  is preferably a hydrogen atom.

In general formula (H), R<sub>17</sub> is preferably an unsubstituted alkyl group having 1 to 4 carbon atoms.

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In general formula (I), L<sub>4</sub> is preferably an unsubstituted alkylene group having 2 to 4 carbon atoms.

Specific examples of the compounds represented by general formulae (A) to (I) for use in the present invention are illustrated below, but the present invention is not limited to those shown.

(A-1)5  $\left(\begin{array}{c} CH_3 \\ \vdots \\ H_{17}C_8 - N - CH_2 \end{array}\right) \stackrel{\bigoplus}{\bullet} \cdot C1 \stackrel{\bigcirc}{\bullet}$ 10

(A-2)

 $\left( \begin{array}{c} CH_3 \\ H_{25}C_{12} - N - CH_2 \\ OH \end{array} \right) \oplus C1$ 15

(A - 3)20  $\left(\begin{array}{c}
CH_3 \\
H_2 \circ C_{14} - N - CH_2 \\
CU
\end{array}\right)^{\oplus} \cdot C1^{\ominus}$ 

25 (A-4)

 $\left(\begin{array}{c} CH_3 \\ H_{25}C_{12} - N - CH_3 \\ \vdots \\ OV \end{array}\right)$   $\bullet$  C1 30

(A - 5)35 

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(A-6) $\left(\begin{array}{c} CH_3 & CH_3 \\ H_3C - C - CH_2 - C \\ - CH_2 & CH_2 \end{array}\right) OCH_2CH_2OCH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c} CH_3 \\ - N - CH_2 \\ - N - CH_2 \end{array}\right) OCH_2CH_2CH_2 - N - CH_2 \longrightarrow \left(\begin{array}{c}$ 45

$$(A-7)$$

$$N$$

$$N$$

$$N$$

$$(A-8)$$

$$H_2N$$

$$N$$

$$N$$

$$N$$

(A-9)

$$\begin{array}{c|c} H & N \\ \hline N & N \\ \end{array}$$

$$(A-1 0)$$

$$H \longrightarrow CH_2 \longrightarrow N$$

(A-11)

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$$NaO_3S$$
 $H$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 

(A-13)

$$(A-14)$$

$$0_2N$$

$$N$$

$$N$$

$$N$$

$$N$$

(A-15)

$$\begin{array}{c|c} H & S \\ \hline & N \\ \hline & N \\ \end{array}$$

$$(A-16)$$

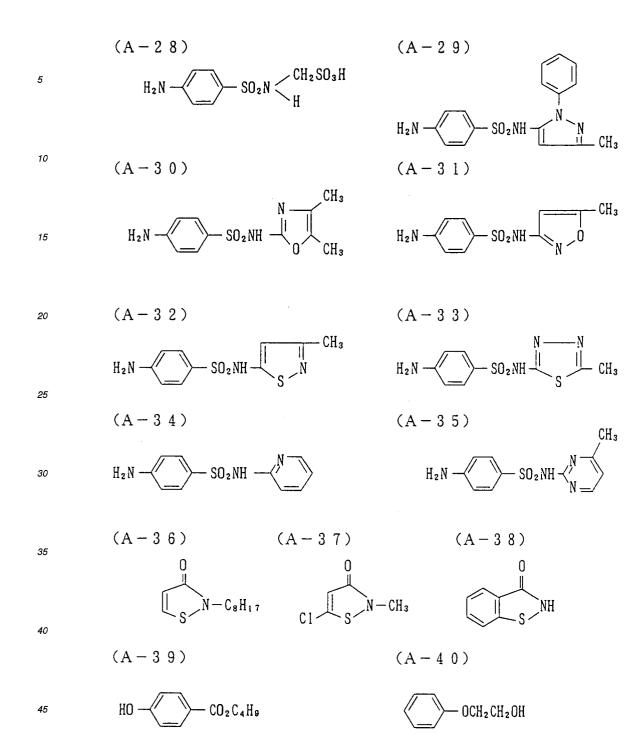
(A - 1 2)

$$(A-17)$$

$$H0 \qquad H \qquad S$$

$$C1 \xrightarrow{H} N$$

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A - 41

$$A - 42$$

$$\sqrt{\frac{1}{S}N-H}$$

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$$A - 44$$

$$A - 45$$

$$C1 \longrightarrow 0$$
  $C1 \longrightarrow 0$   $0 \longrightarrow 0$   $0$ 

$$\frac{1}{100}$$
  $\frac{1}{100}$   $\frac{1}$ 

$$A - 46$$

$$A - 47$$

$$A - 48$$

$$0$$
 $N-CH_3$ 
 $H_3C$ 
 $S$ 
 $NH$ 
 $H_2N$ 
 $S$ 
 $NH$ 

A - 49

$$A - 50$$

$$N-CH_3$$

A - 52

$$A - 53$$

$$0_2N$$
 $N-CH_3$ 

2 
$$A-53$$

$$C1 O C_2H_4OH$$

$$C1 S N-C_2H_4OH$$

$$A - 54$$

$$A - 55$$

$$0 \\ \text{N-CH}_3$$

$$\begin{array}{c|c}
0 \\
\hline
N - C_2 H_5
\end{array}$$

$$A - 56$$

$$A - 57$$

$$A - 58$$

$$c_1$$

$$\begin{array}{c|c}
C1 & O \\
C1 & S \\
\end{array}$$

Br 
$$N-CH_3$$

$$A - 60$$

$$A - 61$$

$$A - 62$$

HO S NI

$$H_2N$$
  $NH$ 

$$0$$
 $N-CH_3$ 

A - 63

$$A - 64$$

$$A - 65$$

HO3S NE

$$\begin{array}{c|c} C & C \\ C & C$$

$$0_2N$$
 $0_2N$ 
 $0_2N$ 
 $0_2N$ 
 $0_2N$ 
 $0_2N$ 

A -67

$$0$$

$$N - C_2 H_5$$

$$A-68$$
HOOC
 $N-CH_3$ 

The compounds represented by general formulae (A) to (I) include compounds described in, for example, JP-A-263938/1985, ibid. 228247/1984, ibid. 27424/1979, and ibid. 211751/1989, in addition to the above-exemplified compounds.

The above-described aminoglycosides for use in the present invention are explained below.

The aminoglycosides for use in the present invention are compounds known as antibiotics. For example, gentamicins can be referred to U.S. patent Nos. 3,091,572 and 3,136,704, and likewise amikacin to U.S. patent No. 3,781,268, albekacin to U.S. patent No. 4,107,424 and German patent No. 2,350,169, dibekacin to German patent No. 2,135,191, isepamicin to U.S. patent No. 4,002,742, micronomicin to U.S. patent No. 4,045,298 and German patent No. 2,326,781, netilmicin to U.S. patent Nos. 4,002,742 and 4,029,882 and German patent No. 2,437,160, and sisomicin to U.S. patent No. 3,832,286.

In the present invention, the use of gentamicins are particularly preferred among these aminoglycosides. Typical specific examples of the gentamicins are illustrated below.

10 Compound No. B-1 (gentamicin A<sub>2</sub>) B-2 (gentamicin A) B-3 (gentamicin A<sub>1</sub>) B-4 (gentamicin B) B-5 (gentamicin X<sub>2</sub>) 15 B-6 (antibiotic JI-20A) B-7 (gentamicin B<sub>1</sub>) B-8 (antibiotic G418) B-9 (antibiotic JI-20B) B-10 (gentamicin C<sub>1</sub>) 20 B-11 (gentamicin C<sub>1a</sub>) B-12 (gentamicin C<sub>2</sub>) B-13 (gentamicin C<sub>2a</sub>) B-14 (gentamicin C<sub>2b</sub>) 25

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Preparation of the aminoglycosides for use in the present invention is described in the above-listed patents, and these materials on the market are also available. Further, properties of these materials are described in THE MERCK INDEX AN ENCYCLOPEDIA OF CHEMICALS, DRUGS, AND BIOLOGICALS, Eleventh edition (1989), MERCK & CO., INC.

The compounds represented by general formulae (G) and (H) and gentamicins are preferred in the present invention. The compounds represented by general formulae (G) and (H) are particularly preferred.

The compounds represented by general formulae (A) to (I) and the aminoglycosides according to the present invention are used in a processing solution that is used in the desilvering step or subsequent steps, as described above. Such a processing solution is preferably a processing solution having a bleaching capacity (e.g. a bleaching solution, a blix solution), a washing water, or a stabilizing solution, and a washing water or a bleaching solution is more preferred.

The amount of these compounds to be added is preferably 1 mg to 1 g, and more preferably 5 mg to 500 mg, per liter of the processing solution used in the desilvering step or subsequent steps. Addition of these compounds to the above-described processing solution may be performed by directly adding the compounds to the processing solution, or by adding the compounds to a replenishing agent and/or a replenisher, or by carrying the compounds from a preceding bath to incorporate the same in the above-described processing solution. Further, these compounds may be added into a light-sensitive material. Further, these compounds may be used singly or in combination of two or more kinds.

When these compounds are sparingly soluble in the processing solution, various auxiliary solvents can be added thereto. Specific examples of the auxiliary solvents include methanol, ethanol, propanol, ethylene glycol, diethylene glycol, monoethanolamine, diethanolamine, triethanolamine, and ethylenediamine.

It is preferred to incorporate a pH buffer in a processing solution having a bleaching capacity for use in the present invention. Preferred pH buffers are an odorless organic acid, such as glycolic acid, succinic acid, maleic acid, maleic acid, maleic acid, maleic acid, and glutaric acid, and particularly preferred are glycolic acid, maleic acid, and succinic acid. The concentration of these buffer is preferably 0 to 3 mol/l, and particularly preferably 0.2 to 1.5 mol/l.

A replenishing agent for a processing solution having a bleaching capacity in the present invention may be a liquid or a solid (a powder, a granule, a tablet). For a granular or tablet form of a replenishing agent, the use of a polyethylene glycol-type surfactant is preferred, because such the compound also works as a binder.

In order to solidify a photographic processing agent, use can be made of various methods described in, for example, JP-A-29136/1992, ibid. 85535/1992, ibid. 85536/1992, ibid. 85534/1992, and ibid. 172341/1992. For example, the solidification can be accomplished by kneading a dense-liquid, or a fine-powdered or granular photographic processing agent with a water-soluble binder and then molding the same, or by atomizing a water-soluble binder on the surface of a provisionally molded photographic processing agent, and then forming a coating layer thereon.

A tablet processing agent can be obtained by a general preparation method described in, for example, JP-A-61837/1976, ibid. 155038/1979, ibid. 88025/1977, and British patent No. 1213808, and, further, a granular processing

agent can be obtained by a general preparation method described in, for example, JP-A-109042/1990, ibid. 109043/1990, ibid. 39735/1991, and ibid. 39739/1991. Further, a powdered processing agent can be obtained by a general preparation method described in, for example, JP-A-133332/1979, British patent No. 725892, ibid. 729862, and German patent No. 3733861.

When a replenishing agent for the processing solution having a bleaching capacity is composed of a liquid, the liquid may be a single liquid, or a combination of liquids having different components. From such points of view as storage space for the replenishing agent and operability at the time of chemical mixing, preferred are one liquid or two sets of liquids, and particularly preferred is one liquid. In such cases, preferably the specific gravity of the replenishing agent to that of a replenisher is in range of from 1.0 to 5 times, and particularly preferably from 1.5 to 3 times.

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The pH of the processing solution having a bleaching capacity according to the present invention is generally in the range of from 3.0 to 7.0. In the case of the bleaching solution, the pH is preferably from 3.5 to 5.0, in particular. On the other hand, in the case of the blix solution, the pH is preferably from 4.0 to 6.5, in particular. In order to adjust the pH to these ranges, it is preferred to add the above-mentioned organic acid as a buffer in the present invention. As an alkali for adjusting the pH, preferred are an aqueous ammonia, potassium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate, and the like.

The pH of a processing solution having a bleaching capacity for use in the present invention can be adjusted to the above-mentioned ranges by means of the above-listed alkali and a known acid (inorganic acids and organic acids).

Preferably these processings with a solution having a bleaching capability for use in the present invention are conducted directly after the color development. However, in the case of a reversal processing, usually they are conducted via a compensating bath (or alternatively a bleach-accelerating bath) or the like. This compensating bath may contain an image stabilizer, as described below.

Further, the solution having a bleaching capacity for use in the present invention may contain, in addition to a bleaching agent, a rehalogenizing agent, a pH buffer, and known additives, as described on page 12 of JP-A-144446/1991, and further the solution may contain aminopolycarboxylic acids and organic phosphonic acids. Preferred rehalogenizing agents are sodium bromide, potassium bromide, ammonium bromide, potassium chloride, etc. The addition amount thereof is preferably from 0.1 to 1.5 mol, more preferably from 0.1 to 1.0 mol, and particularly preferably from 0.1 to 0.8 mol, per liter of the solution having a bleaching capacity.

Further, preferably the solution having a bleaching capacity for use in the present invention contains a nitric acid compound, such as ammonium nitrate and sodium nitrate. In the present invention, the concentration of the nitric acid compound per liter of the solution having a bleaching capacity is preferably from 0 to 0.3 mol, and more preferably from 0 to 0.2 mol.

Usually, such nitric acid compounds as ammonium nitrate and sodium nitrate are used to prevent corroding of stainless steel. In the present invention, even a small amount of nitric acid compound prevents the corrosion, and desilvering is well done.

The replenishing amount of the solution having a bleaching capacity is preferably from 30 to 600 ml, and more preferably from 50 to 400 ml, per m<sup>2</sup> of the light-sensitive material.

The processing time, when processed with a bleaching solution, is preferably 7 minutes or less, especially preferably from 10 sec to 5 min, and particularly preferably from 15 sec to 3 min.

Preferably the total processing time in the desilvering step is shorter in a range in which no desilvering defect arises. That is, the preferred processing time is from 1 min to 12 min, and more preferably from 1 min to 8 min. Further, the processing temperature is generally from 25 °C to 50 °C, and preferably from 35 °C to 45 °C. In such a preferred temperature range, the desilvering speed is improved, and the appearance of stain generated after the processing can be prevented effectively.

Especially preferably, the processing solution having a bleaching capacity for use in the present invention is subjected to aeration at the time of the processing, because such aeration keeps photographic properties extremely stable. Various means known in this technical field can be used for the aeration. For example, there are several methods, such as blowing of air into the processing solution having a bleaching capacity, and absorption of air by means of an ejector.

At the time of the blowing of air, it is preferred to deliver air into a solution through a gas-scattering tube having fine pores. The air-scattering tube is generally used for an airing tub in the activated sludge method. For further particulars about the aeration, the articles described in Z-121, Using Process C-41, Third edition (1982), published by Eastman Kodak Co. Ltd., pp. BL-1 to BL-2, can be referred to. It is preferred to vigorously stir the processing solution having a bleaching capacity for use in the present invention. A method described in JP-A-33847/1991, page 8, right upper column, line 6, to the left lower column, line 2, can be used to accomplish the above-mentioned purpose.

Further, in the present invention, a bath that precedes the processing solution having a bleaching capacity may contain various bleach-accelerating agents. Examples of these bleach-accelerating agents to be used include compounds having a mercapto group or a disulfide group, as described in U.S. patent No. 3,893,858, German patent No. 1,290,821, British patent No. 1,138,842, JP-A-95630/1978, and Research Disclosure No. 17129 (July, 1978); thiazolidine derivatives, as described in JP-A-140129/1975; thiourea derivatives, as described in U.S. patent No. 3,706,561; iodides, as described in JP-A-16235/1983; polyethylene oxides, as described in German patent No. 2,748,430; and

polyamine compounds, as described in JP-B-("JP-B" means an examined and published Japanese patent application) 8836/1970. Further, compounds described in U.S. patent No. 4,552,834 are also preferably used. These bleach-accelerating agents may be added into a light-sensitive material.

The light-sensitive material for use in the present invention is processed with a washing water and/or a stabilizing solution after the desilvering step.

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The stabilizing solution herein referred to in the present invention is a stabilizing solution that has been used in the last processing step for a color negative film and a color reversal film hitherto, and it includes a stabilizing solution that has been used in the stabilizing step for a bath that precedes to the last processing step or a rinse step (preceding bath). However, preferably the stabilizing solution is employed as the last bath.

The stabilizing solution for use in the present invention is able to prevent a dye-image formed by a color development from fading and discoloration caused with a lapse of time by the action of a compound capable of stabilizing a dye-image (e.g. aldehyde compounds, such as formalin, as described below), which is contained therein.

A compound capable of stabilizing a dye-image (hereinafter referred to an image stabilizer) can be added to the stabilizing solution. Examples of the image stabilizer include formalin; benzaldehydes, such as m-hydroxybenzaldehyde; an adduct of formaldehyde and hydrogensulfite; hexamethylenetetramine and its derivatives; hexahydrotriazine and its derivatives; N-methylol compounds, such as dimethylol urea and N-methylolpyrazole; and azolylmethylamines, such as N, N'-bis(1,2,4-triazole-1-ylmethyl)piperazine. These image stabilizers are described in, for example, JP-A-153348/1990, ibid. 270344/1992; ibid. 313753/1992, corresponding to EP 504609A2; ibid. 359249/1992, corresponding to EP 0519190A2; ibid. 34889/1993, and EP 0521477A1.

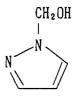
In the present invention, preferably the density of a free formaldehyde in a solution is in a range of from 0 to 0.01%, especially from 0 to 0.005%, which provides a large effect.

Of these image stabilizers that provide such a density of the free formaldehyde, preferred are m-hydroxybenzaldehyde, hexamethylenetetramine; N-methylolazoles, as described in JP-A-270344/1992 (e.g. N-methylolpyrazole); and azolylmethylamines, as described in JP-A-313753/1992 (corresponding to EP 0504609A2) (e.g. N, N'-bis(1,2,4-triazole-1-ylmethyl)piperazine). It is especially preferred to use azoles, as described in JP-A-359249/1992 (corresponding to EP 0519190A2) (e.g. 1,2,4-triazole), and azolylmethylamine or its derivatives (e.g. 1,4-bis(1,2,4-triazole-1-ylmethyl)piperazine), in combination.

Preferred examples of the image stabilizer are illustrated below, but the present invention is not limited to those shown.

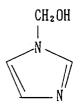
K-1

K-2



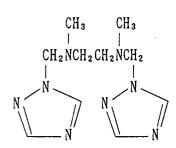
K - 3

K - 4



K - 5

K-6



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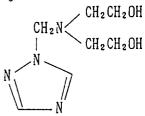
$$K-8$$

$$CH_{2}N$$

$$CH_{2}CH_{2}OH$$

$$N$$

K - 9



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K - 1 0K - 1 15 N-CH2-N 10 K - 1 3K - 1 215 0 CH₃ CCHO 20 K - 14K - 1525 0 CH<sub>3</sub>OCCHO 30 K - 16K - 17K - 18K - 19CHO CHO CHO 35 OH 40 K - 21K - 20K - 2 2

CHO

0

K-23 Hexamethylenetetramine

CHO

OH

HO

K-24 N-methylolurea

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In the present invention, the addition amount of the image stabilizer is preferably from 0.001 to 0.1 mol, and more

CHO

CHO

CHO

OH

preferably from 0.001 to 0.05 mol, per liter of the stabilizing solution.

The stabilizing solution for use in the present invention may contain an organic acid, such as acetic acid, citric acid, and sulfuric acid. In order to further increase an effect of the stabilizing solution in the present invention, it is preferred to add, to the stabilizing solution, a mono base organic acid having a hydroxyl group. The mono base organic acid having a hydroxyl group comprises a straight chain or branched alkyl group having both a hydroxyl group portion and an organic acid portion. The mono base organic acid has preferably from 2 to 6, and more preferably from 2 to 4 carbon atoms. Preferred organic acid portions are a carboxylic acid, a sulfonic acid, and a phosphoric acid. A carboxylic acid is especially preferred.

Examples of the above-mentioned monobase organic acid having a hydroxyl group are a glycolic acid and a butyric acid. A glycolic acid is especially preferred.

The content of the organic acid in the stabilizing solution for use in the present invention is preferably from 0.0001 to 0.5 mol, and more preferably from 0.0001 to 0.1 mol, per liter of the stabilizing solution.

Various surfactants are preferably contained in a washing water and/or a stabilizing solution for use in the present invention. In particular, the employment of the surfactant in a processing solution used just before the drying step (i.e. the final bath) is effective for preventing the processed light-sensitive material from unevenness caused by a water mark in a drying step. The final bath may be a washing water or a stabilizing solution, with the latter preferred.

Example surfactants include a polyalkylene glycol-type nonionic surfactant, a polyhydric alcohol-type nonionic surfactant, an alkylbenzenesulfonic acid salt-type anionic surfactant, a higher alcohol/sulfuric acid ester salt-type anionic surfactant, an alkylnaphthalenesulfonic acid salt-type anionic surfactant, a quaternary ammonium salt-type cationic surfactant, an amine salt-type cationic surfactant, an amine salt-type cationic surfactant, an amine salt-type amphoteric surfactant, and a betain-type amphoteric surfactant. Preferred among these surfactants are polyalkylene glycol-type nonionic surfactants, and especially preferred are those represented by general formula (W), as illustrated below, such as alkylphenoxypolyethylene oxides and alkylphenoxypolyhydroxypropylene oxides. general formula (W)

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$$R_{18} \longrightarrow O (W)_{m} H$$

wherein W represents  $-CH_2CH_2O$ - or  $-CH_2CH(OH)CH_2O$ -,  $R_{18}$  and  $R_{19}$  each represent an alkyl group, n represents 0 or 1, and m represents the number of added moles of the  $-CH_2CH_2O$ - group or the  $-CH_2CH(OH)CH_2O$ -group.

The alkyl groups represented by  $R_{18}$  and  $R_{19}$  each have from 3 to 20, preferably from 6 to 12 carbon atoms. Among these alkyl group, especially preferred are an octyl group, a nonyl group, and a dodecyl group. Further, m (the addition mole number) is preferably 6 to 14.

In the present invention, a polyhydroxypropylene oxide-type nonionic surfactant in which W represents a - CH<sub>2</sub>CH(OH)CH<sub>2</sub>O- group is preferred, because the same considerably increases the effect obtained by the present invention

Further, the use of a silicon-type surfactant that has an excellent foamless effect is preferred.

Examples of these preferred surfactants are illustrated below, but the present invention is not limited to those shown.

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$$W-1 \qquad C_{8}H_{17} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{70}H$$

$$W-2 \qquad C_{9}H_{19} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{70}H$$

$$W-3 \qquad C_{12}H_{25}O \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{70}H$$

$$C_{6}H_{13} \qquad \qquad 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{70}H$$

$$W-5 \qquad C_{8}H_{17} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{75}H$$

$$W-6 \qquad C_{8}H_{17} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{75}H$$

$$W-7 \qquad C_{9}H_{19} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{75}H$$

$$W-8 \qquad C_{9}H_{19} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{70}H$$

$$W-9 \qquad C_{12}H_{25}NH \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{75}H$$

$$W-10 \qquad C_{12}H_{25}N \longleftarrow CH_{2}CH_{2}O \xrightarrow{}_{75}H$$

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The addition amount of the surfactant is generally from 0.005 g to 3 g, and preferably from 0.02 to 0.3 g, per liter of the washing water and/or the stabilizing solution.

The washing water and/or the stabilizing solution preferably contains other additives, such as ammonium compounds (e.g. ammonium chloride, ammonium sulfite), metal compounds (e.g. a bismuth compound, an aluminum compound), a fluorescent brightening agent, a hardener; alkanolamines, as described in U.S. patent No. 4,786,583; and sulfinic acid compounds, as described in JP-A-231051/1989, according to the occasion.

Further, the stabilizing solution for use in the present invention may contain water-soluble cellulose derivatives. Preferred water-soluble cellulose derivatives are hydroxycellulose and carboxymethylcellulose. The content thereof is preferably from 0.01 to 5.0 g, and more preferably from 0.05 to 1.0 g, per liter of the stabilizing solution.

The stabilizing solution for use in the present invention preferably contains various chelating agents, whereby the storage stability of the stabilizing solution is improved, and the generation of stain is lowered. Examples of preferred chelating agents are organic carboxylic acid-based chelating agents, organic phosphoric acid-based chelating agents, inorganic phosphoric acid-based chelating agents, and polyhydroxy compounds. Among these chelating agents, especially preferred are aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine-N,N'-disuccinic acid, and iminodiacetic acid monopropionic acid; organic phosphonic acids, such as 1-hydroxyethylidene-1,1-diphosphonic acid, N,N,N'-trimethylenephosphonic acid, and diethylenetriamine-N,N,N',N'-

tetramethylenephosphonic acid; and a hydrolyzed product of anhydrous maleic acid polymer, as described in EP 0345172A1. The addition amount of the chelating agent is preferably from 0.00001 to 0.01 mol per liter of the stabilizing agent.

The light-sensitive material for use in the present invention after desilvering may be subjected to stabilization via washing, or alternatively the light-sensitive material may be directly subjected to stabilization, omitting the washing step.

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The amount of washing water to be used in the washing step is selected from a broad range depending on characteristics of the light-sensitive material (e.g. the kind of photographic additives, such as couplers), the end use of the light-sensitive material, the temperature of washing water, the number of washing tanks (the number of stages), the replenishing system (e.g. counter-flow system or direct-flow system), and other various conditions. For example, the relation between the number of washing tanks and the quantity of water in a multi-stage counter-flow system can be obtained by the method described in <u>Journal of the Society of Motion Picture and Television Engineers</u>, Vol. 64, pp. 248-253 (May 1955). According to the disclosed multi-stage counter-flow system, the requisite amount of water can be greatly reduced.

The washing water and the stabilizing solution for use in the present invention each have a pH of usually 4 to 9, preferably 5 to 8. Processing conditions, though varying depending on the characteristics or the end use of the light-sensitive material and the like, are usually from 15 to 45 °C in temperature, and from 20 seconds to 10 minutes in time, and preferably from 25 to 40 °C in temperature, and from 30 seconds to 2 minutes in time. Further, the processing with the stabilizing solution according to the present invention markedly increases the effect of preventing stain, when stabilization is conducted with a stabilizing solution directly subsequent to desilvering, without washing.

Further, when stabilization is conducted with the stabilizing solution for use in the present invention, any of known stabilizing techniques described, for example, in JP-A-8543/1982, ibid. 14834/1983, and ibid. 220345/1985 can be utilized.

Each of the replenishing amounts of the washing water and the stabilizing solution for use in the present invention is preferably from 50 to 3000 ml, more preferably from 100 to 1200 ml, still more preferably from 100 to 900 ml, and particularly preferably 200 to 600 ml, per m<sup>2</sup> of the light-sensitive material. Further, the total replenishing amount of the washing water and stabilizing solution is preferably from 50 to 3000 ml, more preferably from 100 to 1500 ml, still more preferably from 100 to 900 ml, and particularly preferably from 200 to 700 ml, per m<sup>2</sup> of the light-sensitive material.

An overflow solution accompanied by a replenishment of the above-mentioned washing water and/or stabilizing solution can be used again in other steps, such as a desilvering.

In order to reduce an amount of the washing water, an ion exchange or a ultrafiltration is used, with the latter especially preferred.

The washing water and the stabilizing solution for use in the present invention may each contain various ionic ingredients, such as a calcium ion, a magnesium ion, a sodium ion, and a potassium ion, as a material eluded from a chemical mixing solution for use in preparation of the replenishing agent, or from a light-sensitive material. However, in the present invention, the concentration of sodium ions in the final processing bath at the washing and stabilizing steps is preferably from 0 to 50 mg/l, and particularly preferably from 0 to 20 mg/l.

In the present invention, wet-heat fading of a yellow dye is further improved by incorporating a compound represented by general formula (J) in a processing solution having a bleaching capacity (e.g. a bleaching solution, a blix solution). Moreover, reading abilities of the magnetic record are particularly increased thereby, when a light-sensitive material has a magnetic recording layer.

The compounds represented by general formula (J) for use in the present invention are explained in detail below: formula (J)

wherein Q represents a group of non-metallic atoms necessary to complete a heterocyclic ring, p represents 0 or 1, and Ma represents a hydrogen atom or a cation.

The heterocyclic residue completed by Q is a 3-to 10-membered saturated or unsaturated heterocyclic residue having at least one of N, O, or S atom. The heterocyclic ring may be a single ring or a condensed ring.

The heterocyclic residue is preferably a 5- or 6-membered aromatic heterocyclic residue, more preferably a 5- or 6-membered aromatic heterocyclic residue containing a nitrogen atom, and still more preferably a 5-or 6-membered aromatic heterocyclic residue containing 1 or 2 nitrogen atoms.

Specific examples of the heterocyclic residues include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 2-piperadinyl, 2-morpholinyl, 3-morpholinyl, 2-thienyl, 2-furyl, 3-furyl, 2-pyrrolyl, 3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyridyl, 4-pyridyl, 4-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 4-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl), 3-(1,2,4-triazinyl), 5-(1,2,4-triazinyl), 6-(1,2,4-triazinyl), 2-indolyl, 3-indolyl,

4-indolyl, 5-indolyl, 6-indolyl, 7-indolyl, 3-indazolyl, 4-indazolyl, 5-indazolyl, 6-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-phthalazinyl, 5-phthalazinyl, 6-phthalazinyl, 2-naphthylizinyl, 3-naphthylizinyl, 4-naphthylizinyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 6-quinoxalinyl, 5-quinoxalinyl, 5-quinazolinyl, 5-quinazolinyl, 6-quinazolinyl, 7-quinazolinyl, 8-quinazolinyl, 8-cinnolinyl, 4-cinnolinyl, 5-cinnolinyl, 6-cinnolinyl, 8-cinnolinyl, 2-puteridinyl, 4-puteridinyl, 6-puteridinyl, 7-puteridinyl, 1-acridinyl, 2-acridinyl, 3-acridinyl, 4-acridinyl, 9-acridinyl, 2-(1,10-phenanthrolinyl), 3-(1,10-phenanthrolinyl), 4-(1,10-phenanthrolinyl), 5-(1,10-phenanthrolinyl), 1-phenazinyl, 2-phenazinyl, 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolidinyl, 4-thiazolidinyl, and 5-thiazolidinyl.

Preferred heterocyclic residues are 2-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl), 3-(1,2,4-triazinyl), 5-(1,2,4-triazinyl), 6-(1,2,4-triazinyl), 2-indolyl, 3-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthalazinyl, 2-quinoxalinyl, 5-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 8-cinnolinyl, 2-(1,10-phenanthrolinyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl, and 4-oxazolyl; and more preferred are 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 2-indolyl, 3-indazolyl, 7-indazolyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl, and 4-oxazolyl; and still more preferred are 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl, and 8-quinolyl; and especially preferred are 2-imidazolyl, 4-imidazolyl, 4-pyridyl group is most preferred.

The heterocyclic residue may have a substituent in addition to the (CH<sub>2</sub>)<sub>D</sub>CO<sub>2</sub>Ma group. Examples of the substituent include an alkyl group having preferably from 1 to 12, more preferably from 1 to 6, and particularly preferably from 1 to 3 carbon atoms (e.g. methyl and ethyl); an aralkyl group having preferably from 7 to 20, more preferably from 7 to 15, and particularly preferably from 7 to 11 carbon atoms (e.g. phenylmethyl and phenylethyl); an alkenyl group having preferably from 2 to 12, more preferably from 2 to 6, and particularly preferably from 2 to 4 carbon atoms (e.g. allyl); an alkynyl group having preferably from 2 to 12, more preferably from 2 to 6, and particularly preferably from 2 to 4 carbon atoms (e.g. propargyl); an aryl group having preferably from 6 to 20, more preferably from 6 to 15, and particularly preferably from 6 to 10 carbon atoms (e.g. phenyl and p-methylphenyl); an amino group having preferably 0 to 20, more preferably from 0 to 10, and particularly preferably from 0 to 6 carbon atoms (e.g. amino, methylamino, dimethylamino, and diethylamino); an alkoxy group having preferably from 1 to 8, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. methoxy and ethoxy); an aryloxy group having preferably from 6 to 12, more preferably from 6 to 10, and particularly preferably from 6 to 8 carbon atoms (e.g. phenyloxy); an acyl group having preferably from 1 to 12, more preferably from 2 to 10, and particularly preferably from 2 to 8 carbon atoms (e.g. acetyl); an alkoxycarbonyl group having preferably from 2 to 12, more preferably from 2 to 10, and particularly preferably from 2 to 8 carbon atoms (e.g. methoxycarbonyl); an acyloxy group having preferably from 1 to 12, more preferably from 2 to 10, and particularly preferably from 2 to 8 carbon atoms (e.g. acetoxy); an acylamino group having preferably from 1 to 10, more preferably from 2 to 6, and particularly preferably from 2 to 4 carbon atoms (e.g. acetylamino); a sulfonylamino group having preferably from 1 to 10, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. methanesulfonylamino); a sulfamoyl group having preferably from 0 to 10, more preferably from 0 to 6, and particularly preferably from 0 to 4 carbon atoms (e.g. sulfamoyl and methylsulfamoyl); a carbamoyl group having preferably from 1 to 10, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. carbamoyl and methylcarbamoyl); an alkylthio group having preferably from 1 to 8, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. methylthio and ethylthio); an arylthio group having preferably from 6 to 20, more preferably from 6 to 10, and particularly preferably from 6 to 8 carbon atoms (e.g. phenylthio); a sulfonyl group having preferably from 1 to 8, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. methanesulfonyl); a sulfinyl group having preferably from 1 to 8, more preferably from 1 to 6, and particularly preferably from 1 to 4 carbon atoms (e.g. methanesulfinyl), a ureido group, a hydroxyl group, a halogen atom (e.g. fluorine, chlorine, bromine, and iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group, a hydroxamic acid group, a mercapto group, and a heterocyclic group (e.g. imidazolyl and pyridyl).

These substituents may be further substituted with a substituent. When two or more substituents are present, they are the same or different from each other. Preferred substituents are an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, and a mercapto group; and more preferred are an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxyl group, and a halogen atom; and still more preferred are an amino group, a carboxyl group; and a hydroxyl group. A carboxyl group is especially preferred.

p represents 0 or 1, preferably 0.

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The cation represented by Ma is an organic or inorganic cation. Examples of the cation include an alkali metal ion (e.g. Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>), an alkali earth metal ion (e.g. Ca<sup>2+</sup>, Mg<sup>2+</sup>), an ammonium ion (e.g. ammonium, tetraethylammonium), a pyridium ion, and a phosphonium ion (e.g. tetrabutylphosphonium, tetraphenylphosphonium).

Of the compounds represented by general formula (J), preferred are those represented by the following general formula (J-a): general formula (J-a)

wherein p and Ma each have the same meanings as those in general formula (J), and Q<sup>1</sup> represents a group of non-metallic atoms necessary to complete a nitrogen-containing heterocyclic ring.

The nitrogen-containing heterocyclic residue completed by Q<sup>1</sup> is a 3- to 10-membered saturated or unsaturated heterocyclic residue containing at least a nitrogen atom. These rings may be a single ring or a condensed ring.

The nitrogen-containing heterocyclic residue is preferably a 5- or 6-membered nitrogen-containing aromatic heterocyclic residue, and more preferably a 5- or 6-membered nitrogen-containing aromatic heterocyclic residue containing one or two nitrogen atoms.

Specific examples and preferred examples of these nitrogen-containing heterocyclic residues, are those illustrated above with respect to general formula (J).

The nitrogen-containing heterocyclic residue may have a substituent in addition to the  $(CH_2)_pCO_2Ma$  group. Specific examples and preferred examples of the substituents are the same as exemplified above as a substituent for the heterocyclic residue completed by Q in general formula (J).

p and Ma each have the same meanings as those defined in general formula (J). Preferred ranges thereof are also the same as in general formula (J). Further, preferred of these compounds represented by general formula (J-a), are compounds represented by the following general formula (J-b): general formula (J-b)

$$0^2$$
  $CO_2Ma$ 

wherein Ma has the same meaning as in general formula (J), and  $Q^2$  represents a group of non-metallic atoms to complete a 5- or 6-membered nitrogen-containing heterocyclic group, which may be substituted with an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, or a mercapto group.

Of these compounds represented by general formula (J-b), more preferred are those represented by the following general formula (J-c): general formula (J-c)

wherein Ma has the same meaning as in general formula (J), and Q<sup>3</sup> represents a group of atoms necessary to complete a pyridine ring or an imidazole ring, which may be substituted with an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, or a mercapto group.

Specific examples of the compounds represented by general formula (J) are illustrated below, but the present invention is not limited to those shown.

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J - 1 5 10

J - 2

CO<sub>2</sub>H

J - 6

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25 J -10 CH2CO2H

J -12

J - 1335

J -14

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J -15

J -16

$$\left\langle N \right\rangle_{H} CO_2H$$

$$J-18$$
 $HO_2C$ 
 $N$ 

$$J-19$$
 $HO_2C$ 
 $N$ 
 $CO_2H$ 

$$\binom{N}{N}$$
  $CO_2H$ 

$$N-N$$
 $CO_2H$ 

J - 30

J -31 CH<sub>3</sub> CO<sub>2</sub>H

J -32

J -33

10

J-34  $N \longrightarrow CO_2H$ 

J - 35  $O_2H$ 

J −36

N
CO₂H

20 J −37

Z<sub>0</sub> CO₂H

J -39

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J-40  $\begin{array}{c}
0\\
N\\
CO_2H\\
CH_2CO_2H
\end{array}$ 

 $\begin{array}{c} J-41 \\ \\ N \\ CH_2CO_2H \\ CH_2CO_2H \end{array}$ 

J −42 N CO<sub>2</sub>H

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J -43

S

CO<sub>2</sub>H

CH<sub>2</sub>CO<sub>2</sub>H

J -44

CH<sub>3</sub>O H CO<sub>2</sub>H

J-45

N CO<sub>2</sub>H

CH<sub>2</sub>CO<sub>2</sub>H

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 $\begin{array}{c} J-46 \\ \underset{| CO_2H}{\overset{CH_2}{\swarrow}} \underset{H}{\overset{N}{\swarrow}} co_2H \end{array}$ 

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 $\begin{array}{c} \text{J} - 47 \\ \text{CH}_{3} \text{SCH}_{2} & \underset{\text{CH}_{2} \text{CO}_{2} \text{H}}{\text{H}} \end{array}$ 

J-48  $HO_2C$  N  $CO_2H$ 

J-49 CH<sub>3</sub> N CO<sub>2</sub>H

J −50 CO₂H

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J −51 CO₂H J - 52  $CO_2H \qquad CO_2H$ 

J −53 CH=CH−CO<sub>2</sub>H J −54

SCH₂CO₂H

J -55
CO₂H
CH₃

J -56

CH<sub>3</sub> CO<sub>2</sub>H

J-57
(n)C<sub>4</sub>H<sub>9</sub>
N CO<sub>2</sub>H

J −58

CO₂H

C1

J −59
Br CO₂H

J-60
C1 N CO<sub>2</sub>H

J-61
CH<sub>3</sub> N C1

J -62
HO N CO<sub>2</sub>H

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J -63

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J - 64

J -65

J −66

J - 67

J -68

<sub>20</sub> J -69

J -70

J -71

J - 72

j - 73

J -74

J -75

J -76

J -77

. .

$$J-79$$
  $J-80$   $J-81$   $CO_2H$   $HS$   $N$   $SH$   $HS$   $N$   $SH$ 

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The above-illustrated compounds can be used in the form of an ammonium salt or an alkali metal salt.

The compounds represented by the above-described general formula (J) can be synthesized according to the methods described in <u>Organic Syntheses Collective</u> Volume 3, page 740, and further, some of them are available as commercially marketed products.

Preferred among the above exemplified compounds are (J-6), (J-7), (J-8), (J-13), (J-14), (J-20), (J-29), and (J-49), with (J-7) especially preferred.

The addition amount of a compound represented by general formula (J) for use in the present invention is preferably from 0.001 to 0.3 mol, more preferably from 0.005 to 0.2 mol, and particularly preferably from 0.01 to 0.10 mol, per liter of the processing solution having a bleaching capacity. At this time, the compounds may be incorporated therein by carrying them into the processing solution from a preceding bath. These compounds may be used singly or in combination of two or more kinds thereof.

The processing solution having a fixing capacity may contain preservatives, including sulfite salts (e.g. sodium sulfite, potassium sulfite, ammonium sulfite), hydroxylamines, hydrazines, aldehyde compounds-bisulfite salt adducts (e.g. acetaldehyde-sodium bisulfite adduct; preferably compounds described in JP-A-158848/1991, in particular), and sulfinic acid compounds described in JP-A-231051/1989. Further, the processing solution may contain various fluorescent brightening agents and defoaming agents or a surface-active agent, and an organic solvent, such as polyvinyl pyrrolidone and methanol.

Further, the processing solution having a fixing capacity preferably contains a chelating agent, such as various aminopolycarboxylic acids and organic phosphonic, acids, for stabilization of the processing solution. Preferred examples of such a chelating agent include 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid), nitrilotrimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-teteraacetic acid, and 1,2-propylenediaminetetraacetic acid.

Further, a buffer is preferably added to keep the pH of the blix solution or the fixing solution constant; example buffers are phosphates; imidazoles, such as imidazole, 1-methylimidazole, 2-methylimidazole, and 1-ethylimidazole; triethanolamine, N-allylmorpholine, and N-benzoylpiperazine.

Stirring as vigorously possible is preferred in the desilvering step. Specific examples of methods of forced stirring include a method in which a jet of the processing solution is impinged on the surface of the emulsion of the light-sensitive material, as disclosed in JP-A-183460/1987 and ibid. 33847/1991, page 8, right upper column, line 6, to the left lower column, line 2; a method in which the stirring effect is increased using a rotating means, as disclosed in JP-A-183461/1987; a method in which the light-sensitive material is moved with a wiper blade installed in the solution, which blade is in contact with the surface of the emulsion, and the generated turbulent flow at the surface of the emulsion increases the stirring effect; and a method in which the circulating flow rate of the entire processing solution is increased. These stirring effect-improving methods are effective for any of the bleaching solution, the blix solution, and the fixing solution. It is supposed that improvement in the stirring accelerates the supply of the bleaching agent and the fixing agent into an emulsion layer, which results in enhancing the desilvering speed. Further, the above-described stirring effect-improving methods are more effective when a bleach-accelerating agent is used, whereby an accelerating effect is considerably increased, and a fixing-inhibiting action owing to the bleach-accelerating agent can be diminished.

An automatic processor that is used for processing a light-sensitive material according to the present invention, preferably has transportation means of the light-sensitive material as described in JP-A-191257/1985, ibid. 191258/1985, and ibid. 191259/1985. As described in the above-mentioned JP-A-191257/1985, these transportation means considerably decrease the amount of a solution carried from a preceding bath to a next bath, so that an effect for preventing deterioration of the processing solution can be enhanced. Consequently, this effect is particularly advantageous for shortening the processing time in each of steps and for reducing a replenishing amount of the processing solution.

The processing solution having a bleaching capacity for use in the present invention can be reused in the processing step by recovering the overflow liquid after use, and then compensating for the composition by the addition of components. Such a usage, which is generally called "regeneration," is preferably used in the present invention. With regard

to the details of the regeneration, the items disclosed in <u>Fuji Film Processing Manual</u>, <u>Fuji Color Negative Film</u>, <u>CN-16 Process</u> (revised in August 1990), pp 39-40 (published by Fuji Photo Film Co., Ltd.), can be referred to.

With regard to the regeneration of the processing solution having a bleaching capacity, in addition to the above described aeration methods, the methods disclosed in Shashin Kogaku no Kiso - Ginn-en Shashin Hen (The Fundamentals of Photographic Technology-Silver Salt Photography) (edited by Nippon Shashin Gakkai, published by Corona, Co., 1979), etc., can be utilized. Specific examples of the regeneration methods of the bleaching solution include a regeneration method by electrolysis and a regeneration method by a hydrogen peroxide, a bromous acid, ozone, etc., making use of a bromic acid, a chlorous acid, a bromine, a bromine precursor, a persulfate, a hydrogen peroxide, and a catalyst.

In the regeneration method by electrolysis, a regeneration processing is carried out by putting an anode and a cathode in the same bleaching bath, or by separating an anode bath from a cathode bath by a diaphragm, as well as that a bleaching solution and a developing solution and/or a fixing solution can be regeneration-processed at the same time, also using a diaphragm.

Regeneration of the fixing solution and the blix solution are carried out by an electrolytic reduction of the accumulated silver ion. In addition, the removal of the accumulated halogen ion by means of an anion exchange resin is also preferred, for maintaining the fixing ability.

The processing solution having a bleaching capacity for use in the present invention is preferably stored in sealed container having an oxygen-transmitting rate of 1 cc/m<sup>2</sup> • day • atm or more.

A replenishing solution for the processing solution having a bleach capacity basically contains each of ingredients in such a density as calculated according to the following equation:

$$C_R = C_T^*(V_1 + V_2)/V_1 + C_P$$

C<sub>R</sub>: Density of an ingredient in a replenishing solution,

C<sub>T</sub>: Density of an ingredient in a mother liquid (processing tank solution),

C<sub>P</sub>: Density of an ingredient consumed during a processing,

V<sub>1</sub>: Replenishing amount (ml) of the replenishing solution having a bleaching capacity per m<sup>2</sup> of the light-sen-

sitive material.

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V<sub>2</sub>: Amount (ml) of solution carried by m<sup>2</sup> of the light-sensitive material from a preceding bath to a subsequent

Each of the densities of ingredients in a mother liquid can be kept constant by the above-described replenishing solution.

A color-developing solution is explained below.

Compounds described in JP-A-121739/1992, page 9, right upper column, line 1, to page 11, left lower column, line 4, can be used in the color-developing solution. Preferred examples of the color-developing agent suitable for a rapid processing in particular include 2-methyl-4-[N-ethyl-N-(2-hydroxyethyl)amino]aniline, 2-methyl-4-[N-ethyl-N-(3-hydroxy-propyl)amino]aniline, and 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl)amino]aniline.

The addition amount of the color-developing agent is preferably from 0.01 to 0.08 mol, more preferably from 0.015 to 0.06 mol, and still more preferably from 0.02 to 0.05 mol, per liter of the color-developing solution. It is preferred to add the color-developing agent in a replenishing solution of the color-developing solution in an amount of from 1.1 to 3 times as much as the above-described amount.

The color-developing solution generally contains a pH buffer, such as a carbonate, borate, or phosphate of an alkali metal; and a development inhibitor or an antifoggant, such as a chloride, a bromide, an iodide, benzimidazoles, benzothiazoles, or a mercapto compound. The color-developing solution may also contain, if necessary, various preservatives, such as hydroxylamines, including hydroxylamine, diethylhydroxylamine, N,N-bis(2-sulfonatoethyl)hydroxylamine, and other hydroxylamines represented by general formula (I) in JP-A-144446/1991; sulfites, hydrazines (e.g. N,N-biscarboxymethylhydrazine), phenylsemicarbazides, triethanolamine, and catecholsufonic acids; an organic solvent, such as ethylene glycol and diethylene glycol; a development accelerator, such as benzyl alcohol, polyethylene glycol, a quaternary ammonium salt, and amines; a dye-forming coupler, a competitive coupler; an auxiliary developing agent, such as 1-phenyl-3-pyrazolidone; a tackifier, and various chelating agents, typified by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid, and phosphonocarboxylic acid (e.g. ethylenediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid)), and salts of these acids.

The processing temperature of the color-developing solution is generally from 20 °C to 55 °C, and preferably from 30 °C to 55 °C. The processing time is generally from 20 seconds to 10 minutes, preferably from 30 seconds to 8 minutes, more preferably from 1 minute to 6 minutes, and particularly preferably from 1 minute and 10 seconds to 3 minutes and 30 seconds, in the light-sensitive material for photographing; and it is generally from 10 seconds to 1 minute and

20 seconds, preferably from 10 seconds to 60 seconds, and more preferably from 10 seconds to 40 seconds, in the light-sensitive material for printing.

In case of carrying out a color reversal processing, a color development is generally preceded by black-and-white development. A black-and-white developing solution to be used for black-and-white development contains one or more of known black-and-white developing agents. Representative black-and-white developing agents include dihydroxybenzenes, such as hydroquinone and hydroquinone monosulfonate; 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone and 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone; and aminophenols, such as N-methyl-p-aminophenol. Further, the above-mentioned black-and-white developing solution can be also used in the process of a black-and-white light-sensitive material.

The color-developing solution or black-and-white developing solution generally has a pH in the range of from 9 to 12. Further, the rate of replenishment for these developing solutions, though varying depending on the kind of the color photographic light-sensitive material to be processed, is generally not more than 3 liters per m² of the light-sensitive material. The rate of replenishment can be reduced to 500 ml or less by the use of a replenishing solution having a low content of bromide ions. When processing is carried out at a reduced rate of replenishment, it is desirable to prevent evaporation and aerial oxidation of the processing solution by minimizing the contact area of the processing solution in processing tank with air. The contact area of the processing solution in processing tank with air is preferably 0.1 to 300 cm² and particularly preferably 0.2 to 150 cm².

The contact area between a photographic processing solution and air in the processing tank, that is the opening area in the processor, can be expressed in terms of the opening ratio, as defined below. That is,

Opening ratio=[contact area (cm<sup>2</sup>) of the processing

solution with air]÷[Volume (cm<sup>3</sup>) of the processing solution (tank volume of the processing solution)]

The above-defined opening ratio is preferably 0.1 or less, and more preferably from 0.001 to 0.05. The opening ratio can be reduced by, for example, putting a barrier, such as a floating lid, on the liquid surface of the processing tank, using a movable lid, as described in JP-A-82033/1989, or utilizing slit development processing, as described in JP-A-216050/1988. Further, the opening ratio can be reduced by contacting the liquid surface of the processing solution with a liquid capable of covering over the liquid surface, such as a liquid paraffin, or with a poorly oxidizable and/or non-oxidizable gas. Reduction of the opening ratio is desirable in not only color development and black-and-white development but also all the subsequent steps, such as blanching, blixing, fixing, washing, and stabilization. The rate of replenishment may also be reduced by using a means for suppressing accumulation of bromide ions in the developing solution.

Further, in case of reducing the rate of replenishment, or setting a concentration of bromide ions to a high level, it is also preferred to use a development-accelerating agent, including pyrazolidones, typified by 1-phenyl-3-pyrazolidone and 1-phenyl-2-methyl-2-hydroxymethyl-3-pyrazolidone; thioether compounds, typified by 3,6-dithia-1,8-octanediol; sodium thiosulfate, and potassium thiosulfate, for elevation of photographic speed.

These development-accelerating agents are also preferably used in a color-developing solution.

As the shape and structure of the container containing a color-developing agent as a component of the color-developing solution, though they may be designed freely according to the demand, preferred are those having a flexible structure, like bellows, as described, for example, in JP-A-97046/1983, ibid. 50839/1988, ibid. 235950/1989, and JP-A-U-(the term "JP-A-U" as used herein means unexamined published Japanese utility model application) 45555/1988; containers having flexible partitions that are able to contain a waste, as described, for example, in JP-A-52065/1983, ibid. 246061/1987, and ibid. 134646/1987; and a structure in which two or more containers, each having a variable inner volume, are connected with each other, as described in JP-A-264950/1990.

In order to fill a processing solution tank set in the processor with a color-developing agent from these containers, the color-developing agent may be once stored in a replenishing solution tank, and then mixed with water to dilute automatically or manually in this tank, or alternatively the above-said liquid color-developing agent and water may be separately transported directly into the processing solution tank.

A structure in which a lid of the container can be opened by a touch is preferred for the above-mentioned operations. Specific examples of such a structure are described, for example, in JP-A-U-128646/1986, JP-A-265849/1991, and ibid. 240850/1992.

It is preferred to fill a container made of a material of not more than 25 ml/m<sup>2</sup> • 24 hrs • atm in terms of transmission speed of carbon dioxide, with the above-described color-developing agent at voids in the range of from 0.15 to 0.05.

Preferred materials having such a transmission speed of carbon dioxide, are polyethyleneterephthalate, polyvinyl chloride, polyvinylidene chloride, a laminated material of nylon and polyethylene or polypropylene, a laminated material of aluminum and polyethylene or polypropylene, and glass, each of which has a thickness of 300 to 2000  $\mu$ m. In particular, polyethyleneterephthalate, and a laminated material of polyethylene and nylon, each of which has a thickness of 500 to 1000  $\mu$ m, are most preferred in view of balance among the transmission of carbon dioxide, the mechanical

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strength, and the weight thereof. Further, the material of the container for use in the present invention preferably has a transmission speed of oxygen of not more than 20 ml/ $m^2 \cdot 24$  hrs  $\cdot$  atm.

The terminology "voids" as used herein means a value obtained according to the formula: [(volume (ml) of a container to be filled with a color-developing agent) - (volume (ml) of the color-developing agent)]÷[volume (ml) of the container]. The liquid color-developing agent for use in the present invention is preferably filled in the above-described container at voids of 0.15 to 0.05.

The above-described color-developing agent may be used as it is, as a color-developing solution or a replenishing solution, but preferably it is used as a mixture with water, for dilution. When the color-developing agent is used as a color-developing solution, it is preferred to add therein a starter containing a pH adjuster, a bromide, and the like, in addition to water.

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Further, when the color-developing agent is used as a replenishing solution, the color-developing agent may be mixed and diluted with water, and preliminarily stored in a replenishing solution tank, so that the diluted solution from this tank may be quantitatively replenished to a processing solution tank. Alternatively, the color-developing agent and water may be separately replenished directly to a processing solution tank at a quantitative rate, and then mixed with each other for dilution in the processing solution tank. Further, as an intermediate method that may be used in the present invention, the color-developing agent may be transported to a processing solution tank, while being successively mixed with water for dilution. In this case there can be applied known methods, such as a method in which a mixing tank is set along the path to the processing solution tank.

With regard to the processing solution having a fixing capacity, compounds and processing conditions described in JP-A-125558/1992, page 7, left lower column, line 10, to page 8, right lower column, line 19, can be applied. In particular, one or more of the compounds represented by general formula (I) or (II) described in JP-A-301169/1994 are preferably added to the processing solution having a fixing capacity, to improve preservation and the fixing rate. Further, the use of *p*-toluenesulfinic acid salt and other sulfinic acids, as described in JP-A-224762/1989, is also preferred, to improve preservation. In the processing solution having a bleaching capacity and the processing solution having a fixing capacity, ammonium ion as a cation is preferably used, to improve desilvering. However, it is desirable to suppress, or not use at all, ammonium ion, to reduce environmental contamination.

In the steps of bleaching, blixing and fixing, it is especially preferred to use a jet agitation, as disclosed in JP-A-309059/1989.

The replenishing amount of the replenishing solution in the blixing and fixing steps is generally from 100 to 1000 ml, preferably 150 to 700 ml, and particularly preferably from 200 to 600 ml, per m<sup>2</sup> of the light-sensitive material, respectively.

In the steps of blixing and fixing, it is preferred to recover silver by means of various kinds of silver recovery apparatuses, which are in-line or off-line set. By in-line setting, the processing can be carried out at the reduced silver density in the solution, which results in reduction of the replenishing amount. Further, a residual solution after off-line silver recovery treatment is preferably reused as a replenishing solution.

In the blix step and the fixing step, two or more processing tanks can be used, respectively. A countercurrent cascade system, in which these tanks are connected by a cascade piping, can be preferably adopted. In view of the size of the processor, generally a two-tank cascade system is effective, and the ratio of the processing time between the preceding tank and the subsequent tank is preferably from (0.5:1) to (1:0.5), and particularly preferably from (0.8:1) to (1:0.8)

In the blix solution or the fixing solution, it is preferable to exist a free chelating agent that has not formed a metal complex, to improve preservation of the solution. As such chelating agents, the use of at least one of the compounds represented by general formula (X) according to the present invention is especially preferred.

Especially preferably, the processing according to the present invention is subjected to an evaporation correction of the processing solution, as disclosed in <u>Kokai-giho</u>, published by Hatsumei-kyokai, Kogi: No. 94-4992. In particular, a method in which correction is carried out according to Formula-1 on page 2, based on information of the temperature and the moisture in the environment where a processor is set, is preferred. Water to be used for the evaporation correction is preferably collected from a tank for replenishment of the washing water. In this case, it is preferable to use a deionized water as a replenishing water of the washing water.

The processing according to the present invention can be carried out by means of various kinds of processors. Preferred examples of these processors include cine-type (motion picture film-type) processors manufactured by Fuji Photo Film Co., Ltd., such as Autoprocessors FNCP-300II, FNCP-600II, and FNCP-900II; cine-type processors having a leader-transportation system, which is called a "mini-lab," manufactured by Fuji Photo Film Co., Ltd., such as Autoprocessors FP-560B and FP-350; hangar-type processors manufactured by Noritsu Koki Co., Ltd., such as autoprocessors HM-55S, H8-440W-4, HM-60R, and HR6-8360; and processors having a roller-transportation system manufactured by HOPE company (U.S.A.), such as HOPE 138 and HOPE 2409V. Further, as the agitation methods and materials of the processors, those disclosed in JP-A-130432/1992 are preferred.

Preferred silver halide color photographic light-sensitive materials for use in the present invention are explained below.

Preferred examples of the silver halide color photographic light-sensitive material for use in the present invention include color reversal films and color negative films having coated on them a silver iodobromide emulsion. Color negative films are especially preferred. A color photographic material in which a magnetic recording layer is coated on a support, is most preferred of all.

Preferred light-sensitive materials having a magnetic recording layer for use in the present invention are explained below.

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The magnetic recording layer is formed by coating, on a support, an aqueous or organic solvent coating solution having dispersed particles of a magnetic substance in a binder. Examples of the magnetic substance include ferromagnetic iron oxide, such as  $\gamma \text{Fe}_2 \text{O}_3$ , Co-coated  $\gamma \text{Fe}_2 \text{O}_3$ , Co-coated magnetite, Co-doped magnetite, ferromagnetic chromium dioxide, ferromagnetic metal, ferromagnetic alloy, hexagonal system Ba ferrite, Sr ferrite, Pb ferrite, and Ca ferrite. Preferred among these magnetic substances are Co-coated ferromagnetic iron oxides, such as Co-coated  $\gamma \text{Fe}_2 \text{O}_3$ .

With respect to the form, any of an acicular, a rice grain-like, a spherical, a cubic, or a tabular form may be used. A specific surface area is preferably  $S_{BET}$  of 20 m²/g or more, particularly preferably 30 m²/g or more. Saturated magnetization ( $\sigma$ s) of the ferromagnetic substance is preferably from 3.0 x 10<sup>4</sup> to 3.0 x 10<sup>5</sup> A/m, particularly preferably from 4.0 x 10<sup>4</sup> to 2.5 x 10<sup>5</sup> A/m. The surface of the ferromagnetic substance grains may be treated with silica and/or alumina, or with an organic material. Further, the surface of the magnetic substance grains may be treated with a silane coupling agent or a titan coupling agent, as described in JP-A-161032/1994. Further, magnetic substance grains whose surfaces are coated with an inorganic material or an organic material, as described in JP-A-259911/1992 and ibid. 81652/1993, can also be used.

The following may be used as a binder for magnetic grains: these described in JP-A-219569/1992, such as thermoplastic resins, thermosetting resins, radiation-setting resins, reactive-type resins, polymers having an acid or alkali decomposability or a biodegradability, natural polymers (e.g. cellulose derivatives, sugar derivatives), and a mixture thereof. The glass transition temperature, Tg, of the above resins is generally from -40 °C to 300 °C, and the weight-average molecular weight is generally from 2,000 to 1,000,000. Examples of the above-listed materials include vinyl-based copolymers; cellulose derivatives, such as cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, and cellulose tripropionate; acrylic resins, and polyvinylacetal resins. Gelatin is also preferred. In particular, cellulose di(tri)acetate is preferred. Curing treatment of the above-enumerated binders can be carried out by adding therein epoxy-, aziridine-, or isocyanate-based crosslinking agents. Examples of the isocyanate-based crosslinking agents include isocyanates, such as tolylenediisocyanate, 4,4'-diphenylmethanediisocyanate, hexamethylenediisocyanate, and xylylenediisocyanate; reaction products of these isocyanates and polyalcohol (e.g. a reaction product of tolylenediisocyanate (3 mol) and trimethylolpropane (1 mol)); and polyisocyanates produced by the condensation of these isocyanates, as described, for example, in JP-A-59357/1994.

In order to disperse the above-mentioned magnetic substance in the above-described binder, one or more dispersing tools, such as a kneader, a pin-type mill, and an annular-type mill, are preferably used, as disclosed in JP-A-35092/1994. Dispersing agents, as described in JP-A-88283/1993, and other known dispersing agents, can be used for the above purpose.

The thickness of the magnetic recording layer is generally from 0.1  $\mu$ m to 10  $\mu$ m, preferably from 0.2  $\mu$ m to 5  $\mu$ m, and more preferably from 0.3  $\mu$ m to 3  $\mu$ m. The ratio by weight of the magnetic substance grains and the binder is preferably from (0.5 : 100) to (60 : 100), more preferably from (1 : 100) to (30 : 100). The coating amount of the magnetic substance grains is generally from 0.005 to 3 g/m², preferably from 0.01 to 2 g/m², and more preferably from 0.02 to 0.5 g/m².

A magnetic recording layer for use in the present invention is provided with a stripe pattern or it is provided all over the surface, on the opposite side of the photographic support on which the silver halide emulsion layer is coated, by coating or printing a magnetic substance. For the coating of the magnetic recording layer, various methods, such as airdoctor, blade, air knife, squeeze, impregnation, reverse roll, transfer roll, gravure, kiss, cast, spray, dip, bar, and extrusion, can be utilized. A coating solution described in JP-A-341436/1993 is preferably used.

The magnetic recording layer may be imparted with performances, such as lubrication improvement, curling control, antistatic nature, adhesion prevention, and head abrasion, or it may be provided with another layer having these performances. It is preferred to use an abradant comprising non-spherical inorganic particles, at least one kind of which has a Mohs scale of not less than 5. Non-spherical inorganic grains are preferably composed of fine powders, such as oxides (e.g. aluminum oxide, chromium oxide, silicon dioxide, titanium dioxide), carbides (e.g. silicon carbide, titanium carbide), and diamond. The surface of these abradants may be treated with a silane coupling agent or a titanium coupling agent. These particles may be added to the magnetic recording layer, or they may be overcoated on the magnetic recording layer to form an overcoat layer (e.g. a protective layer, a lubricant-containing layer) containing them. As a binder used at this time, those described above can be used, and the same binder employed in the magnetic recording layer is preferably used. A light-sensitive material having a magnetic recording layer is described in U.S. patent No. 5,336,589, ibid. 5,250,404, ibid. 5,229,259, ibid. 5,215,874, and EP 0,466,130.

The light-sensitive material for use in the present invention is preferably a light-sensitive material for photographing, and the support thereof is preferably a polyester. Details of this material are described in <u>Kokai-giho</u>, Kogi No. 94-6023

(Hatsumei-kyokai; 1994.3.15).

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The polyester for use in the present invention is formed by a chemical reaction of a diol with an aromatic dicarboxylic acid, both of which are essential ingredients. Examples of the aromatic dicarboxylic acid include 2,6-, 1,5-, 1,4-, or 2,7-naphthalene dicarboxylic acid, terephthalic acid, isophthalic acid, and phthalic acid. Examples of the diol include diethylene glycol, triethylene glycol, cyclohexanedimethanol, bisphenol A, and bisphenol. Example thus-polymerizer polyesters include homopolymers, such as polyethylene terephthalate, polyethylene naphthalate, and polycyclohexanedimethanol terephthalate. A polyester containing 2,6-naphthalene dicarboxylic acid as a reaction component at the content ranging from 50 mol% to 100 mol%, is especially preferred. Polyethylene 2,6-naphthalate is most preferred of all. These polyesters each have an average molecular weight in the range of from 5,000 to 200,000. The Tg of these polyesters for use in the present invention is 50 °C or more, preferably 90 °C or more.

The polyester support is subjected to heat treatment at a temperature of 40 °C or more, but less than the Tg, preferably the Tg-20 °C or more, but less than the Tg, in order to suppress core set curl. The heat treatment can be performed at a constant temperature within the above-mentioned range. Alternatively, the heat treatment may be carried out during cooling. The heat treatment time is from 0.1 to 1500 hrs, more preferably from 0.5 to 200 hrs. The heat treatment of the support may be conducted in the form of a roll, or in the form of a conveying web. In order to improve the quality of the surface, unevenness may be provided to the surface of a support by, for example, coating thereon electric conductive inorganic fine particles, such as  $SnO_2$  and  $Sb_2O_5$ . Further, in the production of a support, it is desired to take, for example, a means to prevent a trouble of deformation of the support, by providing a rollette (knurling) at the both ends for the width of the support (both right and left ends towards the direction of rolling) to make the ends somewhat higher than the middle part of the support between the ends. The trouble of deformation of the support means that, when a support is wound on a core, on its second and further windings, the support follows unevenness of its cut edge of the first winding, deforming its flat film-shape. The above-mentioned heat treatment may be carried out at any stage subsequent to the production of a support (film), the surface treatment; the coating of a back layer containing an antistatic agent, a lubricant, and the like; or the coating of a subbing layer. The step subsequent to the coating of the antistatic agent is preferred.

A ultraviolet absorber may be kneaded into this polyester. Further, light-piping can be prevented by kneading into the polyester a dye or pigment for the polyester, examples of which that are commercial products are Diaresin (trade name, manufactured by Mitsubishi Chemicals Co., Ltd.) and Kayaset (trade name, manufactured by Nippon Kayaku Co., Ltd.).

The light-sensitive material for use in the present invention is, then, preferably subjected to surface treatment in order to achieve adhesion between the support and a photographic constituting layer. For the surface treatment, various surface-activation treatments can be used, such as a chemical treatment, a mechanical treatment, a corona discharge treatment, a flame treatment, an ultraviolet ray treatment, a high-frequency treatment, a glow discharge treatment, an active plasma treatment, a laser treatment, a mixed acid treatment, and an ozone oxidation treatment; and preferred are an ultraviolet ray treatment, a flame treatment, a corona treatment, and a glow treatment.

A subbing method is explained below.

A subbing layer may be a single layer or multiple layers. Examples of a binder for the subbing layer include copolymers produced by using monomers selected from vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid, maleic anhydride, and the like as a starting material; and other examples are polyethyleneimine, an epoxy resin, a graft gelatin, nitrocellulose, and gelatin. Resorcine and  $\rho$ -chlorophenol can be used in order to swell a support. The following can be used as a gelatin hardener for the subbing layer: a chromium salt (e.g. chrome alum), aldehydes (e.g. folmaldehyde, glutaric aldehyde), isocyanates, active halogen compounds (e.g. 2,4-dichloro-6-hydroxy-S-triazine), epichlorohydrin resins, and active vinylsulfone compounds. The subbing layer may contain SiO<sub>2</sub>, TiO<sub>2</sub>, inorganic fine particles, or polymethyl methacrylate or its copolymer fine particles (0.01 to 10  $\mu$ m), as a matting agent.

Further, preferably the light-sensitive material for use in the present invention contains an antistatic agent. Such an antistatic agent may be high-molecular compounds containing a carboxylic acid or its salt, or a sulfonic acid salt, cationic high-molecular compounds, and ionic surfactants.

Most preferred example antistatic agents include crystalline metal oxide fine grains having a volume resistivity of  $10^7~\Omega$  • cm or less, more preferably  $10^5~\Omega$  • cm or less, and having a grain size of 0.001 to 1.0  $\mu$ m, in which the metal oxide is at least one selected from the group consisting of ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, BaO, MoO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>, or fine grains of composite oxides of them (Sb, P, B, In, S, Si, C, etc.), and moreover fine grains of sol-like metal oxides, or composite oxides of them. The addition amount of the antistatic agent is preferably from 5 to 500 mg, and particularly preferably from 10 to 350 mg, per m<sup>2</sup> of the light-sensitive material. A ratio of the amount of electric conductive crystalline oxides or composite oxides of them to the amount of the binder is preferably from 1/300 to 100/1, more preferably from 1/100 to 100/5.

Further, preferably the light-sensitive material has a lubricating property. Preferably a lubricant-containing layer is set on the same side on which the light-sensitive layer is coated, and also on the opposite side thereof (i.e. the back surface). The preferable lubricating property is from 0.01 to 0.25 in terms of the coefficient of dynamic friction. This

value means a value obtained by conveying the light-sensitive material at the speed of 60 cm/min against a stainless steel ball of 5 mm diameter (at 25 °C, 60%RH). In this evaluation method, almost the same results are also obtained with respect to the surface on which a light-sensitive layer is coated.

Examples of available lubricants include polyorganosiloxanes, higher fatty acid amides, metal salts of higher fatty acids, and esters of higher fatty acid and higher alcohol. As the polyorganosiloxanes, polydimethylsiloxane, polydiethylsiloxane, polystyrylmethylsiloxane, polymethylphenylsiloxane, and the like can be used. As the layers to which the lubricant is added, the most outer layer on the same side on which the photographic emulsion is coated, and the backing layer, are preferred. In particular, the addition to these layers, of polydimethylsiloxane and/or an ester having a long-chain alkyl group, is preferred.

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Further, preferably the light-sensitive material contains a matting agent. The matting agent may be added to any layers on the same side on which the photographic emulsion is coated, or on the back surface, but the addition to the most outer layer on the same side on which the photographic emulsion is coated, is preferred. The matting agent may be soluble or insoluble in the processing solution. It is preferred to use both types of matting agents in combination. For example, polymethylmethacrylate, poly(methylmethacryate/methacrylic acid = 9/1 or 5/5 (molar ratio)), and polystyrene grains are preferred. A preferable grain size is from 0.8 to  $10~\mu m$ . A narrower grain size distribution is preferred. Specifically, it is preferred that not less than 90% in number of the total grains present are between 0.9 and 1.1 times as large as the average grain size.

Further, it is also preferred to add fine grains of not larger than  $0.8 \,\mu m$  with the above-mentioned larger grains, to improve the matting property. Examples of these fine grains include polymethylmethacrylate (0.2  $\mu m$ ), poly(methylmethacrylate/methacrylic acid = 9/1 (molar ratio),  $0.3 \,\mu m$ ), polystyrene grains (0.25  $\mu m$ ), and colloidal silica (0.03  $\mu m$ ).

Preferred light-sensitive materials for use in the present invention are described in JP-A-125558/1992, page 14, left upper column, line 1, to page 18, left lower column, line 11. In particular, as a silver halide emulsion, preferred are silver iodobromide emulsions having an average silver iodide content of from 3 to 20 mol%, and preferred are those containing tabular grains having an aspect ratio of not less than 5, and those containing double-structure grains having a different halogen composition between the inner portion and the outer portion thereof. Further, the double-structure grains may have a layered structure in which the inner portion is clearly distinguished from the outer portion for the halogen composition. The aspect ratio is more preferably from 5 to 20, still more preferably 6 to 12.

Further, it is preferred to use a monodispersed emulsion, as described in U.S. patent Nos. 3,574,628 and 3,655,394.

The light-sensitive material for use in the present invention is preferred to have a layer containing a light-insensitive, fine-grained silver halide having an average grain size of 0.02 to 0.2  $\mu$ m. The fine-grained silver halide is preferably a silver bromide containing a silver iodide of 0.5 to 10 mol%.

Other additives that are used in the light-sensitive material according to the present invention are described below.

Additive	RD 17643	RD 18716	RD 307105
1. Chemical Sensitizer	p. 23	p. 648, right column	p. 866
2. Sensitivity Increasing Agent		ditto	
3. Spectral Sensitizer, Super-sensitizer	pp. 23-24	p. 648, right column to p. 649, right column	pp. 866-868
4. Brightening Agent	p. 24	p. 647, right column	p. 868
5. Light Absorber, Filter Dye, Ultraviolet ray Absorber	pp. 25-26	p. 649, right column to p. 650, left column	p.873
6. Binder	p. 26	p. 651, left column	pp. 873-874
7. Plasticizer, Lubricant	p. 27	p. 650, right column	p. 876
8. Coating Aid, Surface Active Agent	pp. 26-27	p. 650, right column	pp. 875-876
9. Antistatic Agent	p. 27	p. 650, right column	pp. 876-877
10. Matting Agent			pp. 878-879

Various kinds of dye-forming couplers can be used for the light-sensitive material according to the present invention. The following couplers are especially preferred.

Yellow coupler: couplers represented by formulae (I) and (II) of EP 502,424A; couplers represented by formulae (1) and (2) of EP 513,496A (especially Y-28 on page 18); couplers represented by formula (I), described in claim 1 of EP 568,037A; couplers represented by general formula (I) of U.S. 5,066,576, column 1, lines 45 to 55; couplers repre-

sented by general formula (I) in paragraph 0008 of JP-A-274425/1992; couplers described in claim 1 on page 40 of EP 498,381A1 (especially D-35, on page 18); couplers represented by formula (Y) on page 4 of EP 447,969A1 (especially Y-1 (page 17) and Y-54 (page 41)); couplers represented by formulae (II) to (IV) of U.S. 4,476,219, column 7, lines 36 to 58 (especially II-17, II-19 (column 17), and II-24 (column 19)).

Magenta coupler: L-57 (page 11, right lower column), L-68 (page 12, right lower column), and L-77 (page 13, right lower column) of JP-A-39737/1991; [A-4]-63 (page 134), [A-4]-73, -75 (page 139) of EP 456257; M-4, -6 (page 26), and M-7 (page 27) of EP 486,965; M-45 (page 19) of EP 571,959A; (M-1) (page 6) of JP-A-204106/1993; M-22 in the paragraph 0237 of JP-A-362631/1992.

Cyan coupler: CX-1, 3, 4, 5, 11, 12, 14, 15 (pages 14 to 16) of JP-A-204843/1992; C-7, 10 (page 35), 34, 35 (page 37), (I-1), and (I-17) (pages 42 to 43) of JP-A-43345/1992; couplers represented by general formula (Ia) or (Ib) in claim 1 of JP-A-67385/1994.

Polymer coupler: P-1 and P-5 (page 11) of JP-A-44345/1990.

Preferred as couplers that develop a dye having a moderate diffusibility, are those described in U.S. patent No. 4,366,237, British patent No. 2,125,570, EP 96,873B, and German patent No. 3,234,533.

Preferred examples of a coupler that can be used for correcting unnecessary absorption of a developed dye include yellow-colored cyan couplers represented by formulae (CI), (CII), (CIII), and (CIV) described on page 5 of EP 456,257A1 (especially YC-86 on page 84); yellow-colored magenta couplers ExM-7 (page 202), EX-1 (page 249), and EX-7 (page 251) of EP 456,257A1; magenta-colored cyan couplers CC-9 (column 8) and CC-13 (column 10) of U.S. patent No. 4,833,069; coupler (2) (column 8) of U.S. patent No. 4,837,136; and colorless masking couplers, represented by formula (A) in claim 1 of WO 92/11575 (especially exemplified compounds on pages 36 to 45).

The package (patrone; magazine) encasing the light-sensitive material to be processed by the process of the present invention is explained below. A main material of the patrone to be used may be a metal or a synthetic plastic, and preferred are such plastics as polystyrene, polyethylene, polypropylene, and polyphenylether.

Further, the partone for use in the present invention may contain various kinds of antistatic agents, and preferred are carbon black, metal oxide grains, nonionic-, anionic-, cationic-, or betain-type surfactants, polymers, and the like. The patrones containing these antistatic agents are described in JP-A-312537/1989 and ibid. 312538/1989. The resistivity of the patrone is preferably  $10^{12}~\Omega$  or less at 25 °C, 25%RH. The plastic patrone is usually made of a plastic that has carbon black or other pigments kneaded therein, for shielding from light. The size of the patrone may be the current 135 size as it is. In accordance with the miniturization of cameras, it is also beneficial to change the diameter of the 135-size cartridge from 25 mm to 22 mm or less. The volume of the patrone is not more than 30 cm³, and preferably not more than 25 cm³. The weight of plastic that is used for the patrone and its case is preferably from 5 g to 15 g.

Further, the patrone may have a structure in which a film is sent out therefrom by rotation of a spur, or a structure in which the end of a film is encased in the body of the patrone, and the end of the film is sent out from a port section of the patrone by a rotation of the spur axis in the same direction. These structures are disclosed in U.S. patent Nos. 4,834,306 and 5,226,613.

The processed light-sensitive material may be encased in a patrone again. In this case, the patrone to be used may be the same or different from that for use in the unprocessed light-sensitive material.

According to the present invention, a processing method that is excellent in not only the adhesive property and the wet-heat fading of the processed light-sensitive material but also the magnetic output capacity of the light-sensitive material having a magnetic recording layer, can be provided.

The present invention is described in more detail with reference to the following examples, but the present invention is not limited thereto.

#### Example 1

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Layers, each having the compositions described below, were multi-coated on a cellulose triacetate film base (support) having on it an subbing layer, to prepare a color negative film, Sample 101.

(Compositions of Photosensitive Layers)

Main materials used in each layer are classified as follows:

ExC: Cyan coupler
ExM: Magenta coupler
ExY: Yellow coupler
ExS: Sensitizing dye

UV: Ultraviolet ray absorbent
HBS: High-boiling organic solvent
H: Gelatin hardening agent

Figures corresponding to each component represents the coating amount in terms of  $g/m^2$ , and for silver halide in terms of silver. With respect to sensitizing dyes, the coating amount is shown in mol per mol of silver halide in the same layer.

First Layer (Halation-preventing layer)		
Black colloidal silver	silver	0.09
Gelatin		1.60
ExM-1		0.12
ExF-1		2.0 x 10 <sup>-3</sup>
Solid disperse dye ExF-2		0.030
Solid disperse dye ExF-3		0.040
HBS-1		0.15
HBS-2		0.02

Second Layer (Intermediate layer)			
Silver bromoiodide emulsion M	silver	0.065	
ExC-2		0.04	
Polyethyl acrylate latex		0.20	
Gelatin		1.04	

Third Layer (Low sensitivity red-sensitive emulsion layer)		
Silver bromoiodide emulsion A	silver	0.25
Silver bromoiodide emulsion B	silver	0.25
ExS-1		6.9 x 10 <sup>-5</sup>
ExS-2		1.8 x 10 <sup>-5</sup>
ExS-3		3.1 x 10 <sup>-4</sup>
ExC-1		0.17
ExC-3		0.030
ExC-4		0.10
ExC-5		0.020
ExC-6		0.010
Cpd-2		0.025
HBS-1		0.10
Gelatin		0.87

Fourth Layer (Medium sensitivity red-sensitive emulsion layer)		
Silver bromoiodide emulsion C	silver	0.70
ExS-1		3.5 x 10 <sup>-4</sup>
ExS-2		1.6 x 10 <sup>-5</sup>
ExS-3		5.1 x 10 <sup>-4</sup>
ExC-1		0.13
ExC-2		0.060
ExC-3		0.0070
ExC-4		0.090
ExC-5		0.015
ExC-6		0.0070
Cpd-2		0.023
HBS-1		0.10
Gelatin		0.75

Fifth Layer (High sensitivity red-sensitive emulsion layer) Silver bromoiodide emulsion D silver 1.40 2.4 x 10<sup>-4</sup> ExS-1 1.0 x 10<sup>-4</sup> ExS-2 3.4 x 10<sup>-4</sup> ExS-3 ExC-1 0.10 ExC-3 0.045 ExC-6 0.020 ExC-7 0.010 Cpd-2 0.050 HBS-1 0.22 HBS-2 0.050 Gelatin 1.10

Sixth Layer (Intermediate layer)	
Cpd-1	0.090
Solid disperse dye ExF-4	0.030
HBS-1	0.050
Polyethyl acrylate latex	0.15
Gelatin	1.10

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Seventh Layer (Low sensitivity green-sensitive emulsion layer)		
Silver bromoiodide emulsion E	silver	0.15
Silver bromoiodide emulsion F	silver	0.10
Silver bromoiodide emulsion G	silver	0.10
ExS-4		3.0 x 10 <sup>-5</sup>
ExS-5		2.1 x 10 <sup>-4</sup>
ExS-6		8.0 x 10 <sup>-4</sup>
ExM-2		0.33
ExM-3		0.086
ExY-1		0.015
HBS-1		0.30
HBS-3		0.010
Gelatin		0.73

Eighth Layer (Medium sensitivity green-sensitive emulsion layer)		
Silver bromoiodide emulsion H	silver	0.80
ExS-4		3.2 x 10 <sup>-5</sup>
ExS-5		2.2 x 10 <sup>-4</sup>
ExS-6		8.4 x 10 <sup>-4</sup>
ExC-8		0.010
ExM-2		0.10
ExM-3		0.025
ExY-1		0.018
ExY-4		0.010
ExY-5		0.040
HBS-1		0.13
HBS-3		4.0 x 10 <sup>-3</sup>
Gelatin		0.80

Ninth Layer (High sensitivity green-sensitive emulsion layer)		
Silver bromoiodide emulsion I	silver	1.25
ExS-4		3.7 x 10 <sup>-5</sup>
ExS-5		8.1 x 10 <sup>-5</sup>
ExS-6		3.2 x 10 <sup>-4</sup>
ExC-1		0.010
ExM-1		0.020
ExM-4		0.025
ExM-5		0.040
Cpd-3		0.040
HBS-1		0.25
Polyethyl acrylate latex		0.15
Gelatin		1.33

Tenth Layer (Yellow filter layer)				
Yellow colloidal silver silver	0.015			
Cpd-1	0.16			
Solid disperse dye ExF-5	0.060			
Solid disperse dye ExF-6	0.060			
Oil-soluble dye ExF-7	0.010			
HBS-1	0.60			
Gelatin	0.60			

Eleventh Layer (Low sensitivity blue-sensitive emulsion layer)		
Silver bromoiodide emulsion J	silver	0.09
Silver bromoiodide emulsion K	silver	0.09
ExS-7		8.6 x 10 <sup>-4</sup>
ExC-8		7.0 x 10 <sup>-3</sup>
ExY-1		0.050
ExY-2		0.22
ExY-3		0.50
ExY-4		0.020
Cpd-2		0.10
Cpd-3		4.0 x 10 <sup>-3</sup>
HBS-1		0.28
Gelatin		1.20

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Twelfth Layer (High sensitivity blue-sensitive emulsion layer)		
Silver bromoiodide emulsion L	silver	1.00
ExS-7		4.0 x 10 <sup>-4</sup>
ExY-2		0.10
ExY-3		0.10
ExY-4		0.010
Cpd-2		0.10
Cpd-3		1.0 x 10 <sup>-3</sup>
HBS-1		0.070
Gelatin		0.70

Thirteenth Layer (First protective layer)			
UV-1	0.19		
UV-2	0.075		
UV-3	0.065		
HBS-1	5.0 x 10 <sup>-2</sup>		
HBS-4	5.0 x 10 <sup>-2</sup>		
Gelatin	1.8		

Fourteenth Layer (Second protective layer)					
Silver bromoiodide emulsion M	silver	0.10			
H-1		0.40			
B-1 (diameter: 1.7 μm)		5.0 x 10 <sup>-2</sup>			
B-2 (diameter: 1.7 μm)		0.15			
B-3		0.05			
S-1		0.20			
Gelatin		0.70			

Further, in order to improve preservability, processability, pressure resistance, antimold and antibacterial properties, antistatic property, and coating property, compounds of W-1 to W-3, B-4 to B-6, and F-1 to F-17, and salts of iron, lead, gold, platinum, palladium, iridium, and rhodium were suitably added in each layer.

Details of emulsions used in this Example are shown in Table 1.

Table 1

5		Average Agl	Deviation coeffi-	Average	Deviation	Diameter of	Ratio of
5		content (%)	cient of Agl content	sphere- equivalent	coefficient concerning	projected area assumed to be	Diame- ter/Thickness
			between grains	grain diame-	grain diame-	a circle (μm)	101, 111101411000
			(%)	ter (µm)	ter (%)		
10	Emulsion A	1.7	10	0.46	15	0.56	5.5
	В	3.5	15	0.57	20	0.78	4.0
	С	8.9	25	0.66	25	0.87	5.8
	D	8.9	18	0.84	26	1.03	3.7
15	Е	1.7	10	0.46	15	0.56	5.5
	F	3.5	15	0.57	20	0.78	4.0
	G	8.8	25	0.61	23	0.77	4.4
20	н	8.8	25	0.61	23	0.77	4.4
	I.	8.9	18	0.84	26	1.03	3.7
	J	1.7	10	0.46	15	0.50	4.2
	К	8.8	18	0.64	23	0.85	5.2
25	L	14.0	25	1.28	26	1.46	3.5
	М	1.0	-	0.07	15	-	1

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In Table 1,

- (1) Emulsions J to L were subjected to a reduction sensitization using thiourea dioxide and thiosulfonic acid, at the preparation of grains, according to the Example described in JP-A No. 191938/1990.
- (2) Emulsions A to I were subjected to a gold sensitization, a sulfur sensitization and a selenium sensitization under the presence of respective sensitizing dyes described in each layer and sodium thiocyanate, according to Example described in JP-A No. 237450/1991.
- (3) At the preparation of tabular grains, low-molecular-weight gelatin was used according to Example described in JP-A No. 158426/1989.
- (4) Dislocation lines as described in JP-A No. 237450/1991 were observed in the tabular grains under a high-voltage electron microscope.
- (5) Emulsion L contained double-structure grains, which grain had a core high in iodide content, as described in JP-A No. 143331/1985.
- 45 Preparation of a dispersion of an organic solid disperse dye

ExF-2 as described below was dispersed according to the following method. That is, water (21.7 ml), a 5% aqueous solution of sodium  $\rho$ -octylphenoxyethoxyethoxyethanesulfonate (3 ml), and a 5% aqueous solution of  $\rho$ -octylphenoxypolyoxyethylene ether (polymerization degree 10) (0.5 g) were added to a pot mill (700 ml), and Dye ExF-2 (5.0g) and zirconium oxide beads (diameter 1 mm) (500 ml) were further added thereto, and then the mixture was dispersed for 2 hours. For the dispersion, a BO-type vibration ball mill, manufactured by Chuo Koki Co., Ltd., was employed. After the dispersion, the mixture was taken out and added to 8 g of a 12.5% aqueous gelatin solution, and then the beads were removed by filtration, to obtain a gelatin dispersion of the dye. The average grain size of the dye in the form of fine grains was 0.44  $\mu$ m.

In the similar manner, solid dispersions of ExF-3, ExF-4, and ExF-6 were obtained. The average grain size of these dyes in the form of fine grains was 0.24  $\mu$ m, 0.45  $\mu$ m, and 0.52  $\mu$ m, respectively. On the other hand, ExF-5 was dispersed according to the dispersion method comprising microprecipitation, as described in Example 1 of EP 549,489A1. The average grain size of the dye was 0.06  $\mu$ m.

 $E \times C - 1$ 

$$E \times C - 2$$

OH 
$$CONHC_{12}H_{25}(n)$$

OH  $NHCOCH_3$ 
 $OCH_2CH_2O$ 
 $N=N$ 
 $NaOSO_2$ 
 $SO_3Na$ 

$$E \times C - 3$$

$$E \times C - 4$$

OH 
$$CONH(CH_2)_3O$$
  $C_5H_{11}(t)$  (i)  $C_4H_9OCNH$ 

 $E \times C - 5$ 

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OH CH3 C9H19(n)
CONHCH2CHOCOCHC7H15(n)

CH3
CONH2
CH3
CONH2
CH3
CONH2
CONH2

 $E \times C - 6$ 

 $E \times C - 7$ 

OH 
$$CONH(CH_2)_3O \longrightarrow C_5H_{11}(t)$$
  $C_5H_{11}$   $C_5H_{21}$ 

 $E \times C - 8$ 

 $E \times M - 1$ 

$$\begin{array}{c|c} & C_2H_5 \\ \hline \\ & -0CHCONH \\ \hline \\ & C_5H_{11}(t) \\ \hline \\ & -CONH \\ \hline \\ & N \\ \hline \\ & -OCH_3 \\ \hline \\ & -OCH_3 \\ \hline \\ & C_1 \\ \hline \\ & C_1 \\ \hline \end{array}$$

 $E \times M - 2$ 

 $E \times M - 3$ 

$$C_{15}H_{31}$$

$$C_{15}H_{31}$$

$$NH$$

$$N=N$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{2}$$

$$C_{1}$$

$$E \times M - 4$$

CH<sub>3</sub> C1

N NH

O(CH<sub>2</sub>)<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>

C<sub>5</sub>H<sub>11</sub>(t)

CH<sub>3</sub> NHCOCHO — C<sub>5</sub>H<sub>11</sub>(t)

# $E \times M - 5$

 $\begin{array}{c|c} O(CH_2)_2O & N \\ \hline \\ N \\ N \\ \hline \\ CH_2 NHSO_2 \\ \hline \\ CH_3 \\ \hline \\ NHCOCHO \\ \hline \\ C_5H_{11}(t) \\ \hline \\ C_2H_5 \\ \hline \end{array}$ 

# $E \times Y - 1$

CH<sub>3</sub>
C<sub>12</sub>H<sub>25</sub>OCOCHOOC
COOCHCOOC<sub>12</sub>H<sub>25</sub>
COOCHCOOC<sub>12</sub>H<sub>25</sub>
COOCHCOOC
CI
N
N
COOCHCOOC
COOCHC

$$E \times Y - 2$$

$$CH_3O \longrightarrow COCHCONH \longrightarrow C$$

$$E \times Y - 3$$

$$E \times Y - 4$$

$$SO_{2}NH - COCHCONH - CI$$

$$CI$$

$$N - COCHCONH - CO_{2}CH_{2}CO_{2}C_{5}H_{11}(i)$$

$$E \times Y - 5$$

$$H_{3}C - C - COCHCONH - NHCO(CH2)3O - C5H11(t)$$

$$C_{1}$$

$$N - N - N - S$$

$$C_{1}$$

$$C_{2}$$

$$C_{3}$$

$$C_{4}$$

$$C_{5}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{2}$$

$$C_{3}$$

$$C_{4}$$

$$C_{5}$$

$$C_{1}$$

$$C_{5}$$

$$C_{5}$$

$$C_{5}$$

$$C_{5}$$

$$C_{5}$$

$$C_{5}$$

$$C_{5}$$

$$C_{7}$$

$$C_{$$

$$E \times F - 1$$

 $E \times F - 2$ 

COOH

$$\begin{array}{c|c} CH_3 & CH-CH=CH-CH=CH\\ \hline \\ N & HO \\ \hline \end{array}$$

COOH

$$E \times F - 3$$

$$\begin{array}{c} CH_3 \\ CH - CH = C - CH = CH \\ \hline N \\ H \end{array}$$

$$E \times F - 4$$

CH<sub>3</sub> CH-CH=CH CH<sub>3</sub>

N =0 HO N

COOH

COOH

 $E \times F - 5$ 

 $E \times F - 6$ 

 $E \times F - 7$ 

$$Cpd-1$$

OH NHCOCHC<sub>8</sub>H<sub>17</sub>(n)

NHCOCHC<sub>8</sub>H<sub>17</sub>(n)

NHCOCHC<sub>8</sub>H<sub>17</sub>(n)

C<sub>6</sub>H<sub>13</sub>(n)

Cpd-2

$$(t)C_4H_9 \xrightarrow{OH} CH_2 \xrightarrow{OH} C_4H_9(t)$$

$$CH_3 \qquad CH_3$$

$$C p d - 3$$

$$UV-1$$

$$(C_2H_5)_2NCH = CH - CH = C < CO_2C_8H_{17}$$
 $SO_2 - CO_2C_8H_{17}$ 

UV-2

$$\begin{array}{c|c}
N & OH \\
\hline
(t)C_4H_9
\end{array}$$

$$UV-3$$

$$\begin{array}{c|c}
N & OH \\
\hline
 & C_4H_9 \text{ (sec)} \\
\hline
 & (t)C_4H_9
\end{array}$$

$$HBS-1$$
 Tricresyl phosphate

$$HBS-2$$
 Di-n-butyl phthalate

HBS-3 
$$(t)C_5H_1$$
  $(t)C_5H_1$   $(t)C_5H_1$   $(t)C_5H_1$ 

$$HBS-4$$
 Tri(2-ethylhexyl) phosphate

 $E \times S - 1$ 

$$\begin{array}{c|c}
C_2H_5 \\
\hline
O \\
C \\
CH - C = CH \\
\hline
O \\
CH_2)_3SO_3Na
\end{array}$$

$$\begin{array}{c|c}
C_2H_5 \\
CH_2)_4SO_3 \\
CH_2$$

$$E \times S - 2$$

$$\begin{array}{c} C_2H_5 \\ S \\ -CH = C - CH \\ \end{array}$$

$$\begin{array}{c} C_2H_5 \\ S \\ (CH_2)_3SO_3\Theta \end{array}$$

$$\begin{array}{c} C_2H_5 \\ (CH_2)_3SO_3H \cdot N(C_2H_5)_3 \end{array}$$

 $E \times S - 3$ 

$$C_{2}H_{5}$$

$$C-CH = C - CH$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{3}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{1}$$

$$C_{2}H_{2}$$

$$C_{3}SO_{3}H \cdot N$$

 $E \times S - 4$ 

$$\begin{array}{c|c}
C_2H_5 \\
\hline
CH_3
\end{array}$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_2$$

$$CH_2$$

$$CH_2$$

$$CH_3$$

$$CH_3$$

 $E \times S - 5$ 

$$\begin{array}{c|c} C_2H_5 \\ \hline \\ O \\ -CH = C - CH \\ \hline \\ (CH_2)_4SO_3 \\ \hline \\ CH_2CH_2CH(CH_3)SO_3N_2 \\ \hline \end{array}$$

$$E \times S - 6$$

Br 
$$C_2H_5$$
 $C_2H_5$ 
 $C_2H_5$ 

$$E \times S - 7$$

C1 
$$CH_2$$
  $CH_3$   $CH_3$   $CH_2$   $CHCH_3$   $CH_2$   $CHCH_3$   $CH_2$   $CHCH_3$   $CH_2$   $CHCH_3$   $CH_3$   $CH_4$   $CH_5$   $CH_$ 

$$S-1$$

$$0 = \begin{pmatrix} H & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$$

H-1

5  $CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$  $CH_2 = CH - SO_2 - CH_2 - CONH - \dot{C}H_2$ 

B-1

10

15

20

25

: ca.35,000

B-2

 $\begin{array}{c|c} CH_3 & CH_3 \\ \hline -(-CH_2-C - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} \\ \hline \end{array}$  x/y=40/60 (weight ratio) average molecular weight : ca.20,000 B - 3

 $(CH_3)_3SiO \xrightarrow{CH_3} (CH_3)_3$   $(CH_2)_2g \xrightarrow{CH_3} (SiCH_3)_3$   $(CH_2)_2g \xrightarrow{CH_3} (molar ratio)$   $(CH_3-CH) \xrightarrow{CH_3} (cH_3)_3$   $(CH_3-CH) \xrightarrow{CH_3} (cH_3-CH)$   $(CH_3-CH) \xrightarrow$ 30 35 : ca.8,000

B-4

average molecular weight : ca.750,000 45

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B-5

B - 6

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W - 1

C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub> $\stackrel{\bigoplus}{N}$ (CH<sub>3</sub>)<sub>3</sub>
CH<sub>3</sub> $\longrightarrow$ SO<sub>3</sub> $\stackrel{\bigoplus}{\sim}$ 

W-2

$$C_8 H_{17} \longrightarrow C_8 CH_2 CH_2 \longrightarrow SO_3 Na$$

$$D = 2 \sim 4$$

W - 3

NaO<sub>3</sub> S C<sub>4</sub>H<sub>9</sub> (n)

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5

F-1

F - 2

15

10

F - 3

20

25

30

50

55

$$F - 5$$

F - 7

$$F-4$$

F - 6

F - 8

F-9

F - 10

5

10

F - 11

F - 12

15

20

CH<sub>3</sub> N N

25

F - 1 3

F - 14

30

$$\langle \bigcirc \rangle$$
—SO<sub>2</sub>SNa

F - 15

F - 16

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OCH2CH2OH

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F - 17

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The above Sample 101 was cut into 135-type film size (corresponding to the international standard, ISO 1007), and the cut film was exposed to light through wedge. Then, the exposed film, light-sensitive material, of 9 m<sup>2</sup> per day by two months was carried out the processings under the conditions shown below. The employed processor was Autoprocessor FNCP-300 II, manufactured by Fuji Photo Film Co., Ltd. The temperature of each processing solutions had been set and kept to the following processing temperature during the testing period.

Tank Volume

82 liter 118 liter

20 liter

20 liter 77 liter

40 liter

40 liter 40 liter

	Processing step	Processing step Processing		Replenisher*
5		time	temperature	
	Color developing	3 min 15 sec	38.0 °C	550 ml/m <sup>2</sup>
	Bleaching	3 min 00 sec	38.0 °C	150 ml/m <sup>2</sup>
10	Washing (1)	15 sec	24.0 °C	counter-current piping system from tank (2) to tank (1)
	Washing (2)	15 sec	24.0 °C	200 ml/m <sup>2</sup>
	Fixing	3 min 00 sec	38.0 °C	400 ml/m <sup>2</sup>
15	Washing (3)	30 sec	24.0 °C	counter-current piping system from tank (4) to tank (3)
	Washing (4)	30 sec	24.0 °C	1000 ml/m <sup>2</sup>
	Stabilizing	30 sec	38.0 °C	300 ml/m <sup>2</sup>
20	Drying	4 min 20 sec	55 °C	

Note:

The composition of each processing solution was as follows, respectively:

## (Color-developer)

	Tank Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	1.0	1.2
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.2
Sodium sulfite	4.0	4.8
Potassium carbonate	30.0	39.0
Potassium bromide	1.4	0.3
Potassium iodide	1.5 mg	_
Hydroxylamine sulfate	2.0	3.0
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfonate	4.5	6.0
Water to make	1,000 ml	1,000 ml
рН	10.05	10.15

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<sup>\*</sup> Replenisher amount (ml) per m<sup>2</sup> of photographic material.

# (Bleaching solution)

5		Tank solution	Replenisher
	Compound (as shown in Table 2)	0.17 mol	0.25 mol
	Irom (III) nitrate nonahydrate	65.0 g	100.0 g
10	Ammonium bromide	80.0 g	120.0 g
	Glycolic acid	50.0 g	75.0 g
	Compound J according to this invention (as shown in Table 2)	0.04 mol	0.05 mol
15	Water to make	1,000 ml	1,000 ml
	рН	4.3	3.8
	(pH was adjusted by aqueous ammonia and nitric acid)		

## (Fixing solution)

	Tank	Replenisher
	solution (g)	(g)
Sodium thiosulfate	0.7 mol	1.0 mol
Sodium sulfite	0.2 mol	0.3 mol
Compound 28 according to this invention	5.0	7.0
Acetic acid (90%).	3.0	4.0
Water to make	1,000 ml	1,000 ml
рН	6.2	6.4
(pH was adjusted by NaOH and acetic acid	d)	

#### (Stabilizing solution)

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O:

Δ:

5	(Both tank solution and replenisher)	(g)
	p-Nonylphenoxy polyglycidol (av. polymerization degree of glycidol: 10)	0.2
	Ethylenediaminetetraacetatic acid	0.05
10	1,2,4-Triazole	0.5
70	1,4-Bis(1,2,4-triazole-1-ylmethyl)pyperazine	0.35
	Glycolic acid	0.02
	Compound according to this invention (as shown in Table 2)	0.05
15	Water to make	1.0 liter
	На	8.5
	(pH was adjusted by aqueous ammonia and nitric acid)	

With respect to the light-sensitive material thus processed by the above-described method, adhesive property of the light-sensitive material was evaluated by the method described below. Further, light-fading was also evaluated.

Adhesive property: Samples at the termination of the whole processings were cut into strips of 23 cm in length, and each strip was encased in Fuji Color nega sheets (SP roll of solid color (plain)/trade name, manufactured by Fuji Color Hanbai Co., Ltd.). After that, two sheets of mounts were put on both surfaces of the nega sheet, and then weighting of 1 kg/25 cm<sup>2</sup> was charged thereon at the wetheat condition (60 °C/60%). They were maintained at the same condition for 4 weeks, and the

adhesive property between the samples and the nega sheets was evaluated.

the level at which the sample can be quickly picked out from the nega sheet, and no scratch is

found on the sample. the level at which adhesion between the sample and the nega sheet is slightly appreciated, but

the sample can be picked out.

**X** : the level at which adhesion between the sample and the nega sheet is strong, and marks of

adhesion are observed on the picked sample.

Wet-heat fading: Density measurement was carried out with respect to each of the processed samples, and

D<sub>max</sub> measured by blue light (B light) was read from a characteristic curve. Subsequently, the thus measured light-sensitive material was stored at the condition described below, and  $D_{max}$ with the lapse of time was measured in the same manner. A change of D<sub>max</sub> of the yellow dye

due to the lapse of time was measured according to the following formula. Storage condition: Temperature, 60 °C; Relative humidity, 80%; 2 weeks

[Change of D  $_{max}$  with the lapse of time ( $\Delta D_{max}(B)$ )] = (D  $_{max}$  before storage) - (D  $_{max}$  after storage)

The thus-obtained results are shown in Table 2.

Table 2

5	Compound in bleaching solution	Compound according to this invention J	Compound in stabilizer	Adhesion	∆Dmax(B)	Remarks
	PDTA	-	-	Δ	0.54	Comparative Example
	EDDS	-	-	Δ	0.65	"
10	4	-	-	Х	0.71	"
10	5	-	-	Х	0.67	"
	7	-	-	Х	0.69	"
	PDTA	-	A-38	Δ	0.55	"
15	EDDS	-	"	Х	0.64	"
	4	-	"	0	0.44	This invention
	5	-	"	0	0.42	"
20	7	-	"	0	0.38	"
20	15	-	"	0	0.43	"
	23	-	"	0	0.47	"
	25	-	"	0	0.46	"
25	37	-	"	0	0.36	"
	38	-	"	0	0.39	"
	40	-	"	0	0.40	"
30	42	-	"	0	0.45	"
	54	-	"	0	0.35	"
	7	-	A-1	0	0.40	"
	,,	-	A-7	0	0.46	"
35	,,	-	A-18	0	0.45	"
	,,	-	A-20	0	0.41	"
	"	-	A-22	0	0.43	"
40	,,	-	A-26	0	0.42	"
	5	-	A-39	0	0.41	"
	"	-	A-40	0	0.40	"
	,,	-	B-1	0	0.39	"
45	7	J-6	A-38	0	0.33	"
	"	J-7	"	0	0.31	"
	,,	J-48	"	0	0.35	"
50	54	J-7	"	0	0.28	"
	PDTA: 1,3-propaned	liamine-N,N,N',N'-tetraac	etic acid		•	<u> </u>

PDTA: 1,3-propanediamine-N,N,N',N'-tetraacetic acid EDDS: N,N'-bis-(1,2-dicarboxyethyl)ethylenediamine

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As is apparent from the results in Table 2, it is found that the samples processed by the processing method of the present invention had minimized adhesion and were excellent in wet-heat fading.

### Example 2

The support of the light-sensitive material and the backing layer were prepared as described below, and the light-sensitive layers as described in Example 1 of this application were coated on the support, to prepare light-sensitive material Sample 102.

### 1) Support

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The support that was used in the present example was prepared as follows:

100 weight parts of polyethylene-2,6-naphthalate polymer, and 2 weight parts of Tinuvin P. 326 (trade name, manufactured by Ciba-Geigy Co.), as an ultraviolet absorbing agent, were dried, then melted at 300 °C; subsequently they were extruded through a T-type die, and stretched 3.3 times in the lengthwise direction at 140 °C, and then 3.3 times in the width direction at 130 °C; and further they were thermally fixed for 6 seconds at 250 °C, and PEN film having a thickness of 90  $\mu$ m was obtained. To the PEN film, appropriate amounts of a blue dye, a magenta dye, and a yellow dye (I-1, I-4, I-6, I-24, I-26, I-27, II-5, as described in Kokai Giho: Kogi No. 94-6023) were added. Further, this film was wound around a stainless steel core (spool) having a diameter of 20 cm, and thermal history was imparted thereto at 110 °C for 48 hours, to obtain a support having suppressed core-set-curl.

#### 2) Coating of a subbing layer

2) Coating of a subbing i

A subbing layer having the composition mentioned below was coated on each side of the above support, after both surfaces of the support were subjected to corona discharge, UV discharge, and glow discharge treatments (10 cc/m², a bar coater was used). The subbing layer was provided on the side that was heated at a higher temperature at the time of stretching. Drying was carried out at 115 °C for 6 minutes (the roller and the transportation apparatus in the drying zone all were set at 115 °C).

Composition of Coating Solution for the Subbing Layer:			
Gelatin	0.1 g/m <sup>2</sup>		
Sodium $\alpha$ -sulfo-di-2-ethylhexylsuccinate	0.01 g/m <sup>2</sup>		
Salicylic acid	0.04 g/m <sup>2</sup>		
ρ-Chlorophenol	0.2 g/m <sup>2</sup>		
(CH <sub>2</sub> =CHSO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCO) <sub>2</sub> CH <sub>2</sub>	0.012 g/m <sup>2</sup>		
Polyamide-epichlorohydrin polycondensation product	0.02 g/m <sup>2</sup>		

#### 3) Coating of a backing layer

An antistatic layer, a magnetic recording layer, and a lubricant layer, each having the compositions mentioned below, were coated on the other side of the above support coated with the subbing layer, as a backing layer.

#### 3-1) Coating of an antistatic layer

A layer having the following composition was coated:

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5	A dispersion of fine grain powder of a composite of stannic oxide-antimony oxide having an average grain size of 0.005 $\mu$ m, and the specific resistance of 5 $\Omega$ • cm (secondary aggregation grain size about 0.08 $\mu$ m)	0.2 g/m <sup>2</sup>
	Gelatin	0.05 g/m <sup>2</sup>
	(CH <sub>2</sub> =CHSO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCO) <sub>2</sub> CH <sub>2</sub>	0.02 g/m <sup>2</sup>
40	Polyoxyethylene- $p$ -nonylphenol (polymerization degree: 10)	0.005 g/m <sup>2</sup>
10	Resorsine	1.0 g/m <sup>2</sup>

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#### 3-2) Coating of a magnetic recording layer

3-Poly(polymerization degree: 15)oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated Co- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (specific surface area, 43 m²/g; major axis, 0.14 µm; minor axis, 0.03 µm; saturation magnetization, 89 emu/g, Fe²+/Fe³+ = 6/94; the surface was treated with 2 wt% respectively, based on Fe<sub>2</sub>O<sub>3</sub>, of aluminum oxide and silicon oxide; a dispersion of the iron oxide was carried out by an open kneader and a sand mill) (0.06 g/m²), diacetylcellulose (1.2 g/m²), and the hardener C<sub>2</sub>H<sub>5</sub>C(CH<sub>2</sub>OCONH-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)NCO)<sub>3</sub> (0.3 g/m²) were coated using acetone, methylethylketone, and cyclohexanone, as solvents, by means of a bar coater, to obtain a magnetic recording layer having a thickness of 1.2 µm. Silica grains (0.3 µm), as a matting agent, and 3-poly(polymerization degree: 15) oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated aluminum oxide (0.15 µm), as an abrasive, were each added thereto, to give a coverage of 10 mg/m². Drying was conducted at 115 °C for 6 min (the roller and the transportation apparatus in the drying zone all were set at 115 °C). The increment of the color density of D<sup>B</sup> of the magnetic recording layer was about 0.1 when X-light (blue filter) was used. The saturation magnetisation moment of the magnetic recording layer was 4.2 emu/g, the coercive force was 7.3 x 10<sup>4</sup> A/m, and the squareness ratio was 65%.

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### 3-3) Preparation of a lubricant layer

A lubricant layer was prepared by coating the following composition so that the solid part of the coating amount became the following amount, and the layer was dried at 115 °C for 6 minutes, to prepare a lubricant layer (the roller and the transportation apparatus in the drying zone all were set at 115 °C).

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Diacetyl Cellulose	25 mg/m <sup>2</sup>
${ m C_6H_{13}CH(OH)C_{10}H_{20}COOC_{40}H_{81}}$ (Compound a)*	6 mg/m <sup>2</sup>
$C_{50}H_{101}O(CH_2CH_2O)_{16}H$ (Compound b)*	9 mg/m <sup>2</sup>

\* A mixture

The mixture of Compound a/Compound b (6/9) was dissolved in a solution of xylene and propyleneglycol monomethylether (1/1) at 105 °C, and this solution was poured into a 10-fold volume of propyleneglycol monomethylether (25 °C) and finely dispersed. This was further dispersed in acetone, and the obtained dispersion (average grain diameter: 0.01 μm) was added to the coating solution. Silica grains (0.3 μm), as a matting agent, and 3-poly(polymerization degree, 15) oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated aluminum oxide (0.15 μm), as an abrasive, were each added thereto, to give a coverage of 15 mg/m². The lubricant layer showed excellent performances of the coefficient of dynamic friction: 0.06 (a stainless steel hard ball of 5 mmØ, diameter, load: 100 g, speed: 6 cm/min), and of the static friction coefficient: 0.07 (clip method). The sliding property of the lubricant layer with the surface of the emulsion, which will be described below, was also excellent, such that the coefficient of dynamic friction was 0.12.

The thus-prepared Sample 102 was cut into a strip having a length of 160 cm and a width of 24 mm. Two perforations of 2 mm square were made at intervals of 5.8 mm, located at the position of 0.7 mm in the width direction and at one side in the lengthwise direction of the light-sensitive material, respectively. Further, sets of such two perforations were made at intervals of 32 mm. The sample was encased in a plastic film cartridge, as illustrated in Fig. 1 to Fig. 7 of U.S. patent No. 5,296,887.

The sample 102 was wedge-exposed to light, and then set in a camera with a built-in magnetic recording device

having a headgap of 5  $\mu$ m, a turn number of 50, and made of permalloy. A digital saturation recording was conducted using a recording wavelength of 50  $\mu$ m.

The sample 102, having magnetic information recorded as mentioned above, was processed with sample 101, which was cut, processed and exposed to light in the same manner as in Example 1, according to the same method described in Example 1, except that the developing solution, the bleaching solution, and the fixing solution were replaced by the following solutions. At this time, the ratio of processing amounts between sample 101 and sample 102 was 5:1.

Tank

Solution (g)

1.0

2.0

4.0

30.0

1.4

5.0

4.5

10.05

1.5 mg

1,000 ml

Replenisher

(g)

1.2

2.2

4.8

39.0

0.3

6.0

6.0

1,000 ml

10.15

(Color-developer)

Diethylenetriaminepentaacetic acid

Sodium sulfite

Potassium carbonate

Hydroxylamine sulfate

Potassium bromide

Potassium iodide

Water to make

рΗ

1-Hydroxyethylidene-1,1-diphosphonic acid

 $4-(N-ethyl-N-\beta-hydroxyethylamino)-2-methylaniline sulfonate$ 

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(Bleaching solution)

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	Tank solution	Replenisher
Compound (as shown in Table 3)	0.17 mol	0.25 mol
Irom (III) nitrate nonahydrate	65.0 g	100.0 g
Sodium bromide	40.0 g	60.0 g
Glycolic acid	60.0 g	90.0 g
Compound J according to this invention (as shown in Table 3)	20 mg	30 mg
Water to make	1,000 ml	1,000 ml
На	4.3	3.8
(pH was adjusted by NaOH and nitric acid)		

(Stabilizing solution)

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J	

(Both tank solution and replenisher)	(g)
p-Nonylphenoxy polyglycidol (av. polymerization degree of glycidol: 10)	0.2
1,2,4-Triazole	1.3
1,4-Bis(1,2,4-triazole-1-ylmethyl)pyperazine	0.75
Glycolic acid	0.02
Compound according to this invention (as shown in Table 3)	0.10
Water to make	1.0 liter
pH	8.5

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After the termination of the processings under their respective conditions, the adhesive property and the wet-heat fading of sample 101 were examined in the same manner as in Example 1. Moreover, with respect to sample 102 of 150 m portion from the point terminated the processing to the point retroactively from the termination point of the processing, the output signal level of the isolated frequency was measured by means of a magnetic regeneration head having headgap of 2.5  $\mu$ m, a turn number of 2000, and made of sendust. The results thus obtained are shown in Table 3. With respect to the results of magnetic output, an average of output from the beginning of the measurement to 1 m was defined as 100, and the average output of the final 1 m portion to the above 100 was shown by %.

Table 3

30	Compound in bleaching solution	Compound J according to this invention	Compound according to this invention in stabi-	Adhesion	∆Dmax(B)	Magnetic output	Remarks
			lizer				
35	PDTA	-	-	Δ	0.57	81%	Comparative Example
	EDDS	-	-	Δ	0.64	73%	11
	5	-	-	Х	0.69	69%	"
	7	-	-	Х	0.70	75%	"
40	PDTA	-	A-38	Δ	0.56	77%	"
	EDDS	-	"	Х	0.66	71%	"
	5	-	"	0	0.40	89%	This invention
45	7	-	"	0	0.35	91%	"
	15	-	"	0	0.41	87%	"
	40	-	"	0	0.39	88%	"
	54	-	"	0	0.33	90%	"
50	7	-	A-40	0	0.39	89%	"
	"	-	B-1	0	0.37	92%	"
	"	J-6	A-38	0	0.31	97%	**
55	"	J-7	"	0	0.30	99%	**
	54	**	"	0	0.26	99%	"

PDTA: 1,3-propanediamine-N,N,N',N'-tetraacetic acid

EDDS: N,N'-bis-(1,2-dicarboxyethyl)ethylenediamine

As is shown in Table 3, the present invention is also excellent in magnetic output.

### Example 3

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The processings and evaluation of Samples were conducted in the similar manner as Example 2, except that the bleaching and stabilizing solutions were replaced with those mentioned below.

### (Bleaching solution)

	Tank solution	Replenisher		
Exemplified Compound 7	0.17 mol	0.25 mol		
Iron (III) nitrate nonahydrate	65.0 g	100.0 g		
Sodium bromide	40.0 g	60.0 g		
Glycolic acid	60.0 g	90.0 g		
(Exemplified Compound J-7)	0.03 mol	0.05 mol		
(Exemplified Compound A-38)	0.02 g	0.03 g		
Water to make	1,000 ml	1,000 ml		
рН	4.3	3.8		
(pH was adjusted by NaOH and nitric acid)				

#### (Stabilizing solution)

[	(Both tank solution and replenisher)	(g)
	p-Nonylphenoxy polyglycidol (av. polymerization degree of glycidol: 10)	0.2
	1,2,4-Triazole	1.3
	1,4-Bis(1,2,4-triazole-1-ylmethyl)pyperazine	0.75
	Water to make	1.0liter
	рН	8.5
	(pH was adjusted by aqueous ammonia and nitric acid)	

After the termination of the processings under their respective conditions, the light fading and the magnetic output were measured in the same manner as in Example 2. Consequently it was confirmed that excellent effects were obtained by the present invention.

### Example 4

The sample 102 as described in Example 2 was cut, processed exposed to light, and magnetic information was recorded on the sample 102. After that, the sample was mixed with the sample 101 as described in Example 1. A total of 6 m<sup>2</sup> per day of the light-sensitive materials had been processed under the conditioned described below for three (3) months. At this time, it was adjusted so that the ratio of processing amounts between sample 101 and sample 102 was 5:2. As a processor, an autoprocessor FP-560B (manufactured by Fuji Photo Film Co., Ltd.) was used, but the auto-

processor was remodeled so that an overflow solution from the bleaching bath would not flow to the next bath but would be discharged to a waste tank. Further, the autoprocessor FP-560B has a means for correcting evaporation, as described in <u>Kokai-goho</u> No. 94-4992 (Hatsumei-Kyokai).

The processing steps and the composition of processing solutions used in this example are shown below.

Processing step	Processing		Replenisher*	Tank Volume
	time	temperature		
Color developing	3 min 5 sec	37.8°C	400 ml	17 liter
Bleaching	50 sec	38.0°C	100 ml	5 liter
Fixing (1)	50 sec	38.0°C	-	5 liter
Fixing (2)	50 sec	38.0°C	300 ml	5 liter
Washing	30 sec	38.0°C	500 ml	3.5 liter
Stabilizing (1)	20 sec	38.0°C	-	3 liter
Stabilizing (2)	20 sec	38.0°C	500 ml	3 liter
Drying	1 min 30 sec	60°C		

Note:

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Stabilizing and fixings was carried out in a countercurrent mode from tank (2) to tank (1). Overflow solutions from washing were all introduced into fixing bath (2). Further, the carried over amount of color developer to the bleaching step, the carried over amount of bleaching solution to the fixing step, the carried over amount of fixing solution to the washing step, and the carried over amount of washing water to the stabilizing step were respectively 65 ml, 50 ml, 50 ml, and 50 ml, per m<sup>2</sup> of the light-sensitive material of a 35 mm width. Each crossover time was 6 sec and is included in the processing time of the preceding step.

Each opening area in the processor were 100 cm<sup>2</sup> for the color-developer, 120 cm<sup>2</sup> for the bleaching solution, and about 100 cm<sup>2</sup> for other processing solutions, respectively.

By using the tank volumes and opening areas in the processor, opening ratios for each of processing solutions can be calculated as defined in the above description.

The composition of each processing solution was as follows, respectively:

<sup>\*</sup> Replenisher amount (ml) per m<sup>2</sup> of light-sensitive material.

Tank

Solution (g)

3.0

0.3

3.9

39.0

5.0

1.3

1.3 mg

1.0 liter

0.05

4.5

10.05

Replenisher

Replenisher

(g)

3.0

0.3

5.3

39.0

6.5

6.5

1.0 liter

10.21

### (Color-developer)

Diethylenetriaminepentaacetic acid

4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene

(pH was adjusted by potassium hydroxide and

 $2-Methyl-4-[N-ethyl-N-(\beta-hydroxyethyl)amino]aniline sulfate$ 

Disodium catecol-3,5-disulfonate

Sodium sulfite

Potassium carbonate

Hydroxylamine sulfate Potassium bromide

Potassium iodide

Water to make

рΗ

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### (Bleaching solution)

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	solution (g)	(g)			
Exemplified Comound 40	0.25 mol	0.38 mol			
Iron (III) nitrate nonahydrate	0.24 mol	0.36 mol			
Ammonium bromide	70.0	105.0			
(Exemplified Compound J-7)	8.0	12.0			
(Exemplified Compound A-38)	0.03	0.05			
Succinic acid	20.0	30.0			
Glycolic acid	60.0	90.0			
Water to make	1,000 ml	1,000 ml			
рН	4.6	4.0			
(pH was adjusted by aqueous ammonia and nitric acid)					

Tank

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Aqueous ammonium thiosulfate solution (750 g/liter)

(pH was adjusted by aqueous ammonia and acetic acid)

Ammonium methanethiosulfonate

Ammonium methanesulfinate

1-Hydroxymethyl-1,2,4-triazole

1,2,4-Triazole

Imidazole

рΗ

Water to make

Ethylenediaminetetraacetic acid

Tank

solution (g)

240.0 ml

5.0

10.0

13.0

7.0

7.4

1,000 ml

Replenisher

(g) 720.0 ml

15.0

30.0

39.0

21.0

7.5

1,000 ml

(g)

4.0

1.0

(Fixing solution)

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(Washing water)

(Both tank solution and replenisher)

Tap water was treated by passage through a mixed bed ion-exchange column filled with H-type strong acidic cation exchange resin (Amberlite IR-120B, trade name, made by Rohm & Haas) and OH-type strong basic anion exchange resin (Amberlite IRA-400, the same as the above) so that the concentrations of Ca ions and Mg ions in water were both made to decrease to below 3 mg/liter, followed by adding 20 mg/liter of sodium dichlorinated isocyanurate and 150 mg/liter of sodium sulfate. The pH of this water was in the range of 6.5 to 7.5.

(Both tank solution and replenisher)

(Stabilizing solution)

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Polyoxyethylene-p-monononylphenylether (av. polymerization degree: 10) 0.2
(Exemplified Compound B-1) 0.02
Water to make 1.0 liter
pH 7.0

(pH was adjusted by aqueous ammonia and nitric acid)

As a result of the processings, it was confirmed that the processing method of the present invention provided excellent effects on the adhesive property, the wet-heat fading, and the magnetic output of the processed light-sensitive material, as were seen in Example 2.

#### Claims

1. A method for processing a silver halide color photographic light-sensitive material, which method comprises steps of color developing a silver halide color photographic light-sensitive material, and then desilvering, and further washing and/or stabilizing it, wherein a processing solution having a bleaching capacity in the desilvering step contains a ferric complex salt of at least one compound represented by general formula(X), and wherein a processing solution used in the desilvering step or subsequent steps therefrom contains at least one compound represented

by general formulae (A) to (I), or at least one aminoglycoside selected from the group consisting of gentamicins, amikacin, tobramicin, dibekacin, albekacin, micronomicin, isepamicin, sisomicin, netilmicin, and astromicin: general formula (X)

$$R-N \begin{pmatrix} L_1 - CO_2 M_1 \\ L_2 - CO_2 M_2 \end{pmatrix}$$

wherein R represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group;  $L_1$  and  $L_2$  each represent an alkylene group; and  $M_1$  and  $M_2$  each represent a hydrogen atom or a cation: general formulae (A) to (I)

formula (A)

$$\left(\begin{array}{c}
R_2 \\
| \\
R_1 - N - R_3 \\
| \\
R_4
\end{array}\right) \stackrel{\bigoplus}{Y}$$

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formula(C) formula (D)

$$\begin{array}{c} \text{NH} \\ \text{R}_7 - \text{NH} + \begin{pmatrix} \text{NH} \\ \text{C} - \text{NH} \end{pmatrix}_{\underline{m}} R_8 \end{array} \qquad \begin{array}{c} \text{NH} \\ + L_3 - \text{NH} + \begin{pmatrix} \text{C} - \text{NH} \end{pmatrix}_{\underline{m}} \end{pmatrix}_{\underline{k}} \end{array}$$

formula (F) formula (E)

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formula (H). formula (G)

$$R_{14}$$
 $R_{15}$ 
 $N-R_{16}$ 
HO
 $CO_2R_1$ 

formula (I)

$$\sim$$
 0-L<sub>4</sub> -OH

wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>7</sub>, and R<sub>8</sub> each represent a hydrogen atom, an alkyl group, or an aryl group; R<sub>6</sub> represents a hydrogen atom, an alkyl group, an aryl group, a nitro group, a carboxyl group, a sulfo group, a sulfamoyl group, a hydroxyl group, a halogen atom, an alkoxy group, or a thiazolyl group;  $L_3$  and  $L_4$  each represent an alkylene group or an arylene group; R<sub>9</sub>, R<sub>10</sub>, and R<sub>11</sub> each represent a halogen atom or an alkyl group; R<sub>12</sub> and R<sub>13</sub> each represent a hydrogen atom, an alkyl group, an aryl group, or a nitrogen-containing heterocyclic residue

group;  $R_{14}$  and  $R_{15}$  each represent a hydrogen atom, a halogen atom, an alkyl group, or an aryl group, with the proviso that  $R_{14}$  and  $R_{15}$  may bond together to form a benzene ring;  $R_{16}$  represents a hydrogen atom or an alkyl group;  $R_{17}$  represents an alkyl group or an aryl group; Y represents a halogen atom;  $Z_1$  represents a group of non-metallic atoms necessary to complete a thiazolyl ring;  $Z_2$  represents a group of non-metallic atoms necessary to complete a 6-membered hydrocarbon ring; n is 0 or 1; m is 1 or 2; and k is an integer of 3 to 20.

- 2. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, wherein the processing solution having a bleaching capacity contains at least one compound represented by general formula (J):
- general formula (J)

wherein Q represents a group of non-metallic atoms necessary to complete a heterocyclic ring; p is 0 or 1; and Ma represents a hydrogen atom or a cation.

- 3. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, wherein the processing solution containing at least one compound of general formula (A), (B), (C), (D), (E), (F), (G), (H) or (I), or at least one aminoglycoside, is a processing solution having a bleaching capacity, an washing water, or a stabilizing solution.
- 4. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, wherein R in general formula (X) represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms.
- 5. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 4, wherein R in general formula (X) represents a hydrogen atom.
  - 6. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, wherein the compound represented by general formula (X) is a compound represented by general formula (1-a): general formula (1-a)

$$H-N = \begin{bmatrix} L_1 - CO_2M_1 \\ CH - CO_2M_2 \end{bmatrix}$$

$$CH_2 - CO_2M_2$$

wherein  $L_1$  represents an alkylene group;  $M_1$  represents a hydrogen atom or a cation; and  $Ma_1$  and  $Ma_2$  each represent a hydrogen atom or a cation.

- 7. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, wherein the ferric complex salt of at least one compound represented by general formula (X) is contained in a bleaching solution.
- **8.** The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, 4, 5, 6 or 7 wherein the silver halide color photographic light-sensitive material is a color negative film.
- 9. The method for processing a silver halide color photographic light-sensitive material as claimed in claim 1, 2, 3, 4, 5, 6, 7 or 8 wherein the silver halide color photographic light-sensitive material has a magnetic recording layer.
  - **10.** The method for processing a silver halide color photographic light-sensitive material as claimed in claim 9, wherein the magnetic recording layer contains Co-coated ferromagnetic iron oxide.

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# **EUROPEAN SEARCH REPORT**

Application Number EP 96 10 9200

1		DERED TO BE RELEVAN	T	
Category	Citation of document with in of relevant pa	dication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	August 1994	I PHOTO FILM CO LTD) 24 - page 15, line 15 * line 17 * line 7 *	1,3-5, 7-10 2,6	G03C7/42 G03C7/30
Υ		P-479), 23 July 1986 ONISHIROKU PHOTO IND CO	2	
Υ	* abstract *	•	2	
Υ		I PHOTO FILM CO LTD) 23	2,6	
Υ	March 1994 * page 3, line 3 - * page 24, line 30 * claims *		2,6	
D,A		JAPAN P-1766), 7 July 1994 ONICA CORP), 8 April	9,10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	12 September 199	6   Ph	ilosoph, L
X: par Y: par doc A: tec O: no	CATEGORY OF CITED DOCUME ticularly relevant if taken alone ticularly relevant if combined with an unent of the same category hnological background newritten disclosure ermediate document	E : earlier patent do after the filing d	cument, but pullate in the application for other reason	blished on, or on s