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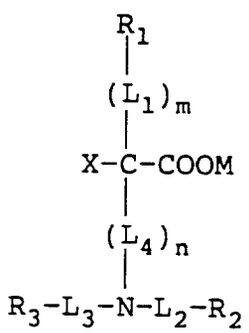
(54) Photographic processing composition and processing method.

(57) A novel photographic processing composition is provided, comprising at least one of compounds represented by the following general formula (I) or salts thereof:



(I)

wherein R_1 represents a carboxyl, aliphatic or aromatic group; R_2 and R_3 each represents a carboxyl, phosphono, sulfo or hydroxyl group; L_1, L_2, L_3 and L_4 each represents an alkylene group; X represents a hydrogen atom, aliphatic group or aromatic group; M represents a hydrogen atom or cation; and m and n each represents an integer 0 to 3. A novel method for the processing of a silver halide photographic material is also provided, which comprises the processing of a silver halide photographic material which has been imagewise exposed to light with a processing solution containing at least one of the compounds represented by the general formula (I) as defined above or salts thereof.

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FIELD OF THE INVENTION

The present invention relates to a processing composition for silver halide photographic material and a processing method with such a processing composition.

BACKGROUND OF THE INVENTION

In general, a silver halide black-and-white photographic material which has been exposed to light is then subjected to processing, including black-and-white development, fixing and rinsing. A silver halide color photographic material (hereinafter referred to as "color photographic material) which has been exposed to light is then subjected to processing including color development, desilvering, rinsing and stabilization. A silver halide color reversal photographic material which has been exposed to light black-and-white development and reversal processing followed by color development, desilvering, rinsing and stabilization.

In the color development procedure, silver halide grains which have been exposed to light are reduced to silver, with a color developing agent. An oxidation product of the color developing agent simultaneously reacts with a coupler to form image dyes.

In the subsequent desilvering procedure, the developed silver grains produced at the color development procedure are oxidized (bleached) with an oxidizing bleaching agent to silver salts which are than removed from the photographic layer (fixing) together with unused silver halide grains by a fixing agent which forms soluble silver grains. Bleach and fixing may be separately conducted as bleach procedure and fixing procedure or simultaneously conducted as blix procedure. For the details of these processing procedures and processing compositions, reference can be made to James, "The Theory of Photographic Process", 4th edition, 1977, and Research Disclosure Nos. 17643, pp. 28-29, 18716, left column to right column, p. 651, and 307105, pp. 880-881.

For the purpose of maintaining the photographic and physical qualities of dye image and the processing stability, various auxiliary procedures may be added to the foregoing basic processing procedures. Examples of these auxiliary procedures include rinsing, stabilizing, film hardening and stop procedures.

The foregoing processing operations are normally conducted in an automatic developing machine. In recent years, photographic processing has been conducted in various places ranging from lare-scale laboratory equipped with large-sized automatic developing machine to so-called minilabo, which is a photo studio equipped with small-sized automatic developing machine. This tendency has been accompanied by a drop in the processability.

One of the major causes for this trouble is a contamination of the processing solution with metallic ions.

Various metallic ions can get mixed in the processing solution through various processes. For example, calcium, magnesium or sometimes iron ions may get mixed in the processing solution via water used in the preparation of the processing solution. Further, calcium contained in gelatin incorporated in the photographic material may get mixed in the processing solution. Moreover, when the blix solution splashes, an iron chelate contained in the blix solution can get mixed in the prebath, i.e., development bath. Further, when the photographic film impregnated with a processing solution is brought over to the subsequent both, metallic ions can get mixed in the subsequent bath.

The effect of these contaminative metallic ions depends on the kind of these metallic ions and the processing solution.

The calcium and magnesium ions which have got mixed in the developer react with a carbonate used as a buffer to produce precipitates or sludges that cause troubles such as clogging of the filter in the circulation system in the automatic developing machine and processing stain on the film. Further, the contamination of the developer with a salt of a transition metal ion such as iron ion causes decomposition of a paraphenylenediamine color developing agent, a black-and-white developing agent such as hydroquinone and monole or a preservative such as hydroxylamine and sulfite that results in a remarkable deterioration of photographic properties.

Moreover, the contamination of a bleaching solution comprising hydrogen peroxide or persulfate with a transition metal ion such as iron ion causes a remarkable deterioration of the stability of the solution that results in troubles such as underbleach.

These problems can be seen in fixing solutions as well. When contaminated with a transition metal salt, a commonly used fixing solution comprising a thiosulfate suffers from a deterioration of stability that causes the generation of turbidity or sludge in the solution. This leads to the clogging of the filter in the automatic developing machine that causes a drop in the circulation rate resulting in underfixing or processing stain on the film. Such a phenomenon also occurs in the washing water in the subsequent procedure. In particular, when the used amount of the washing water is reduced, the percent exchange of solution in the tank is

lowered, making it extremely easy to cause troubles such as decomposition of thiosulfate, which is called sulfurization, and precipitation of silver sulfide. Under these conditions, fatal stain often occurs on the surface of the film.

In a stabilizing solution prepared from hard water containing a large amount of calcium and/or magnesium ions, bacteria proliferate with these ions as nutrition sources, causing liquid turbidity that gives stain on the film. Further, when the stabilizing solution is contaminated with transition metal ions, some of these ions are left in the film, causing a deterioration of the preservability of the processed film.

As mentioned above, the contamination of the processing solutions with metallic ions causes various troubles. It has thus been keenly desired to provide an effective ion hiding agent.

As an approach for eliminating these problems there has been proposed the use of a chelating agent for hiding metallic ions. Examples of cinch a chelating agent include aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid) as disclosed in JP-B-48-30496 and JP-B-44-30232 (The term "JP-B" as used herein means an "examined Japanese patent publication"), organic phosphonic acids as disclosed in JP-A-56-97347 (The term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-56-39359, and West German Patent 2,227,639, phosphonocarboxylic acids as disclosed in JP-A-52-102726, JP-A-53-42730, JP-A-54-121127, JP-A-55-126241, and JP-A-55-65956, and compounds as disclosed in JP-A-58-195845, JP-A-58-203440, and JP-B-53-40900.

Among these compounds, some have been put into practical use. However, these compounds leave much to be desired in properties. For example, ethylenediaminetetraacetic acid exhibits a great capacity of hiding calcium ions. However, when incorporated in a developer, this compound accelerates the decomposition of a developing agent or developing agent preservative in the presence of iron ions, causing a deterioration of photographic properties such as image density drop and fog increase. Further, alkylidenediphosphonic acid doesn't exert any such bad effects even in the presence of iron ions. However, this compound produces solid matters in a processing solution prepared from hard water containing much calcium ions, causing troubles in the automatic developing machine.

In recent years, as the social demand for environmental protection grows, the replenishment rate of photographic processing solutions tends to be reduced more and more. This causes the processing solutions to stay longer in the processing machine, giving a greater problem of deterioration of preservability than ever. Thus, it has been desired to develop an approach for effectively hiding metallic ions accumulated in the processing solutions without causing any troubles.

Further, it has recently been desired to render the waste liquid from the photographic processing unharmful from the standpoint of environmental protection. In particular, biodegaradable processing compositions have been desired. However, none of chelating agents which have been put into practical use can sufficiently meet the demand for biodegradability and properties.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a photographic processing composition which produces no precipitates nor sludges oven when contaminated with metallic ions and a processing method using such a photographic processing composition.

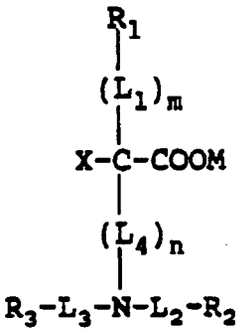
It is another object of the present invention to provide a stable processing composition which is free from the drop of effective components in the processing solution or the production of components which exert photographically adverse effects even when contaminated with metallic ions and a processing method using such a processing composition.

It is a further object of the present invention to provide a processing composition which eliminates the deterioration of image preservability caused by metallic ions in the processing components left in the processed photographic material and a processing method using such a processing composition.

It is a still further object of the present invention to provide a processing composition which produces no environmentally unharmful waste liquid and a processing method using such a processing composition.

These and other objects of the present invention will become more apparent from the following detailed description and examples.

The foregoing objects of the present invention are accomplished with a photographic processing composition for silver halide photographic material, comprising at least one of compounds represented by the following general formula (I) or salts thereof:



(I)

wherein R_1 represents a carboxyl, aliphatic or aromatic group; R_2 and R_3 each represents a carboxyl, phosphono, sulfo or hydroxyl group; L_1, L_2, L_3 and L_4 each represents an alkylene group; X represents a hydrogen atom, aliphatic group or aromatic group; M represents a hydrogen atom or cation; and m and n each represents an integer 0 to 3. The foregoing objects of the present invention are also accomplished by a processing method using such a processing composition.

DETAILED DESCRIPTION OF THE INVENTION

The compound represented by the general formula (I) will be further described hereinafter.

In the general formula (I), the aromatic group having preferably 6 to 20, more preferably 6 to 12 carbon atoms, represented by R_1 or X is a monocyclic or bicyclic aromatic hydrocarbon group which may contain substituents, preferably phenyl or naphthyl group which may contain substituents, more preferably phenyl group which may contain substituents. Examples of such substituents include alkyl group having preferably 1 to 10, more preferably 1 to 4 carbon atoms (e.g., methyl, ethyl, iso-propyl), aralkyl group having preferably 7 to 13 carbon atoms (e.g., phenylmethyl), alkenyl group having preferably 2 to 10 carbon atoms (e.g., allyl), alkoxy group (having preferably 1 to 10, more preferably 1 to 3 carbon atoms (e.g., methoxy, ethoxy), aryl group having preferably 6 to 13 carbon atoms (e.g., phenyl, p-methylphenyl), acylamino group having 1 to 13, more preferably 2 to 5 carbon atoms (e.g., acetylamino), sulfonylamino group having preferably 1 to 13, more preferably 1 to 5 carbon atoms (e.g., methanesulfonylamino), ureide group having preferably 2 to 10 carbon atoms (e g., methylureide), alkoxycarbonylamino group having preferably 2 to 10, more preferably 2 to 5 carbon atoms (e.g., methoxycarbonylamino), aryloxycarbonylamino group having preferably 7 to 13 carbon atoms (e.g., phenoxycarbonylamino), aryloxy group having preferably 6 to 13 carbon atoms (e.g., phenyloxy), sulfamoyl group having preferably 0 to 10, more preferably 1 to 6 carbon atoms (e.g., methylsulfamoyl), carbamoyl group having preferably 1 to 13, more preferably 1 to 7 carbon atoms (e.g., carbamoyl, methylcarbamoyl), mercapto group, alkylthio group having preferably 1 to 10, more preferably 1 to 4 carbon atoms (e.g., methylthio, carboxylmethylthio), arylthio group having preferably 6 to 13 carbon atoms (e.g., phenylthio), sulfonyl group having preferably 1 to 13 carbon atoms (e.g., methanesulfonyl), sulfinyl group having preferably 1 to 13 carbon atoms (e.g.,methanesulfinyl), hydroxyl group, halogen atom (e.g., chlorine, bromine, fluorine), cyano group, sulfo group, carboxyl group, phosphono group, aryloxycarbonyl group having preferably 7 to 13 carbon atoms (e.g., phenyloxycarbonyl), acyl group having preferably 1 to 13 carbon atoms (e.g., acetyl, benzoyl), alkoxycarbonyl group (e.g., methoxycarbonyl), acyloxy group having preferably 2 to 13 carbon atoms (e.g., acetoxy), nitro group, and hydroxamic group.

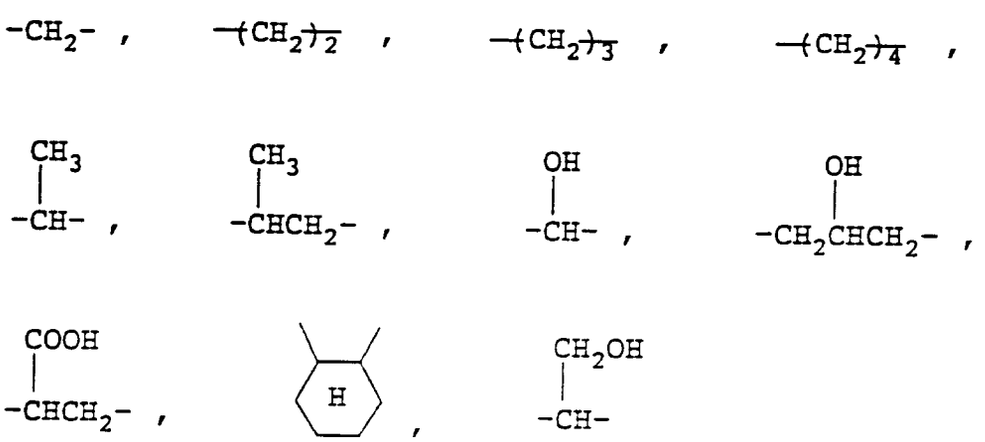
Preferred among these substituents are alkyl group, alkoxy group, sulfinyl group, hydroxyl group, halogen atom, cyano group, sulfo group, carboxyl group, phosphono group, acyl group, and nitro group. Particularly preferred among these substituents are alkoxy group, hydroxyl group, and carboxyl group.

The aliphatic group having preferably 1 to 20, more preferably 1 to 5 carbon atoms, represented by R_1 or X may be straight-chain, branched or cyclic, preferably straight-chain or branched. Examples of the aliphatic group include alkyl group, alkenyl group, and alkinyl group. Preferred among these aliphatic groups is alkyl group. The aliphatic group may be substituted by substituents. As such substituents there may be used those described with reference to the aromatic group represented by R_1 or X. Preferred among these substituents are hydroxyl group, sulfo group, carboxyl group, and phosphono group. Particularly preferred among these substituents are hydroxyl group, and carboxyl group.

R_1 is preferably a carboxyl group or aromatic group, more preferably carboxyl group. X is preferably an aliphatic group or hydrogen atom, more preferably hydrogen atom.

R_2 and R_3 each represents a carboxyl, phosphono, sulfo or hydroxyl group. Preferred among these groups are carboxyl group and hydroxyl group. Most preferred among these groups is carboxyl group.

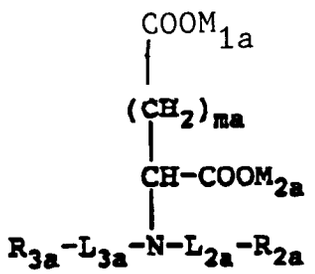
The alkylene group represented by L_1, L_2, L_3 or L_4 may be straight-chain, branched or cyclic, preferably straight-chain. The alkylene group preferably has 1 to 6 carbon atoms. The alkylene group may be substituted by substituents. As such substituents there may be used those described with reference to the aromatic group represented by R_1 or X. Preferred among these substituents are alkoxy group, sulfo group, hydroxyl group, carboxyl group, and phosphono group. Further preferred among these substituents is carboxyl group. Specific examples of L_1 to L_4 include the following groups:



Particularly preferred among these groups are methylene group and ethylene group.

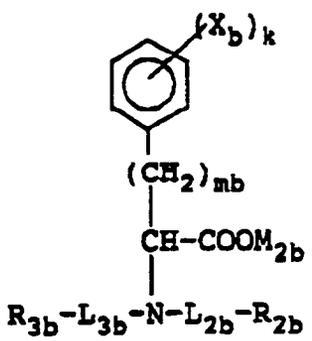
Examples of the cation represented by M include alkaline metal (e.g., lithium, potassium, sodium), ammonium (e.g., ammonium, tetraethylammonium), and pyridinium.

The general formula (I) is preferably represented by the general formula (II) or (III):



(II)

wherein L_{2a} and L_{3a} have the same meaning as L_2 end L_3 in the general formula (I), respectively; R_{2a} and R_{3a} have the same meaning as R_2 and R_3 in the general formula (I), respectively; M_{1a} and M_{2a} each has the same meaning as M in the general formula (I); and m_a represents an integer 0 to 5, preferably 0, 1 or 2, more preferably 1 or 2.



(III)

wherein L_{2b} and L_{3b} have the some meaning as L_2 and L_3 in the general formula (I), respectively; R_{2b} and R_{3b} have the same meaning as R_2 and R_3 in the general formula (I), respectively; M_{1b} and M_{2b} each has the same meaning as M in the general formula (I); m_b represents an integer 0 to 3, preferably 0, 1 or 2, more preferably 0 or 1; X_b represents a substituent. As the substituent X_b there may be used one of the substituents described with reference to the aromatic group represented by R_1 or X in the general formula (I). Preferred among these substituents are hydroxyl group and alkoxy group. The suffix k represents an integer 0 to 5, preferably 0.

In the present invention, most preferred is the general formula (II).

Specific examples of the compound represented by the general formula (I) will be given below, but the present invention should not be construed as being limited thereto.

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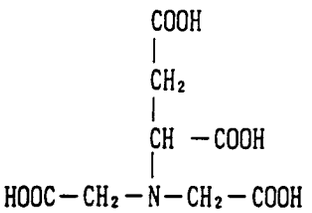

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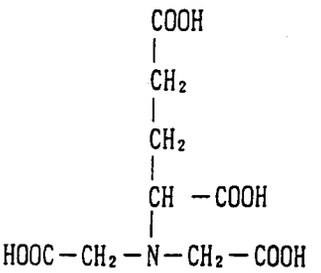

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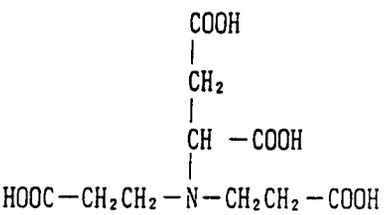

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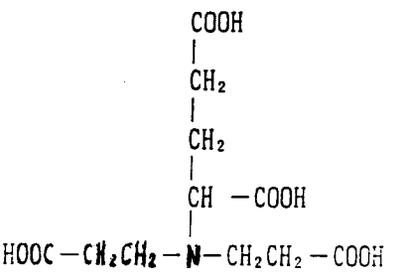

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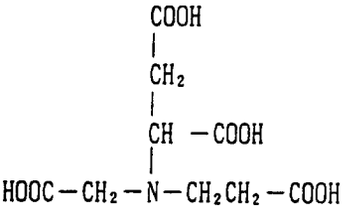

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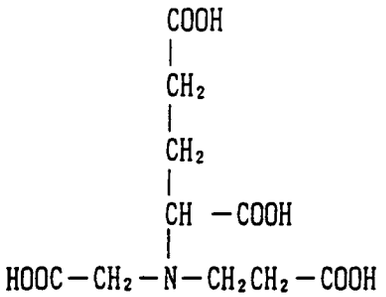

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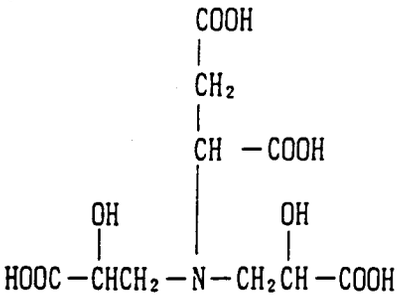

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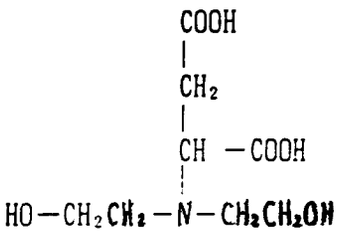

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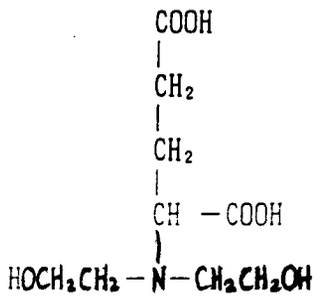

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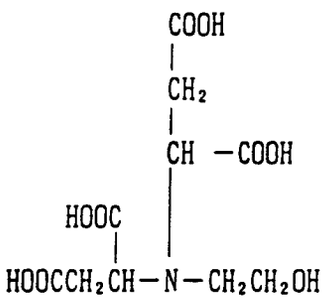

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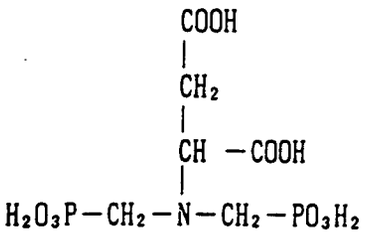

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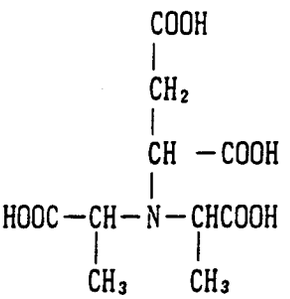

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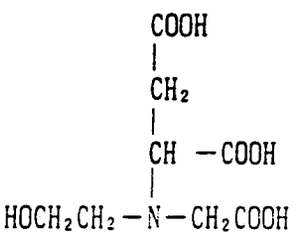

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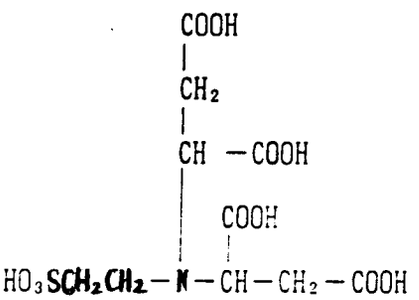

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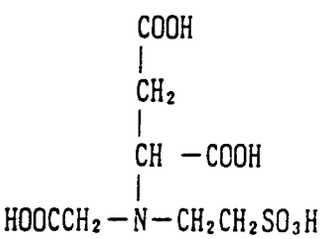

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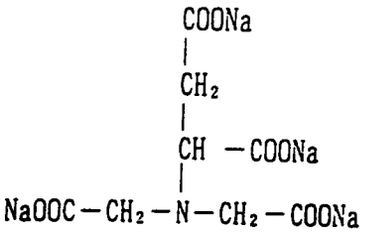

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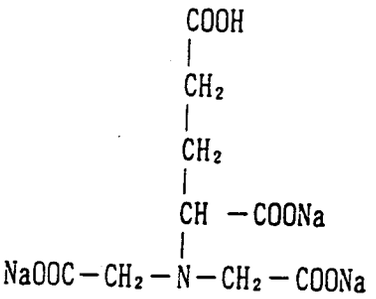

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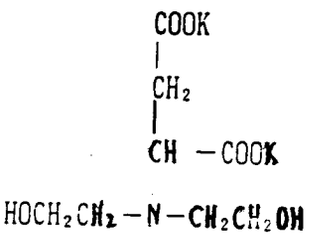

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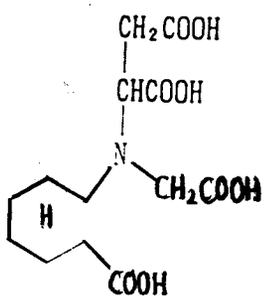

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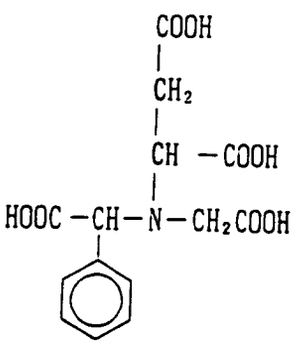

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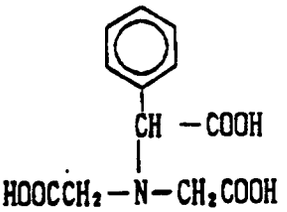

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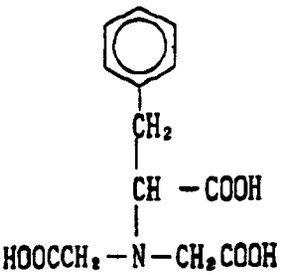

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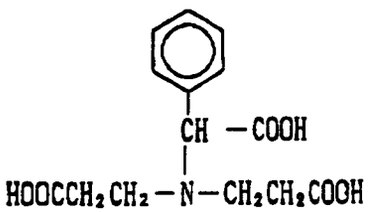

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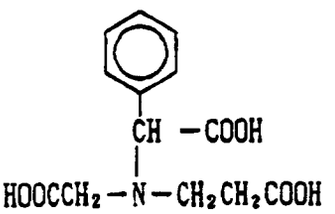

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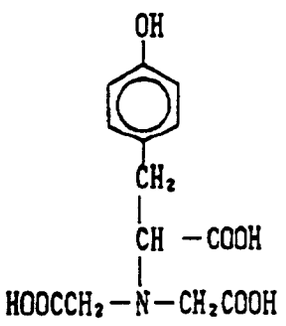

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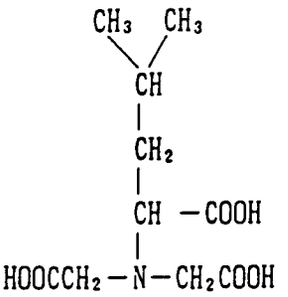

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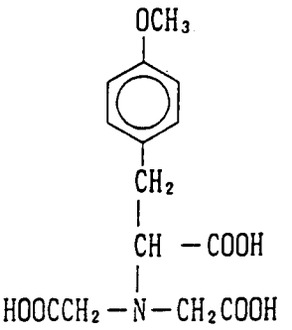

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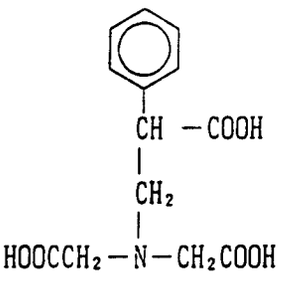

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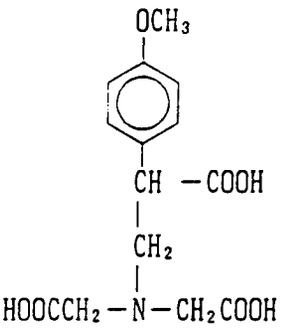

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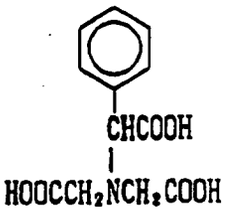

D form

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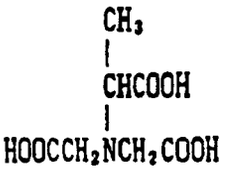

L form

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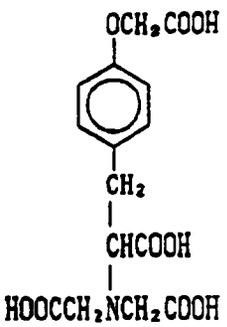

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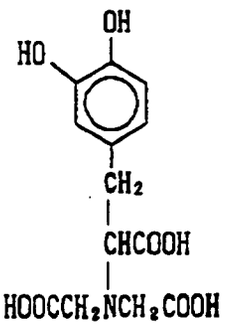

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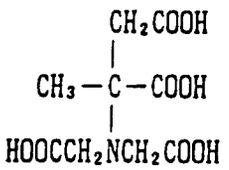

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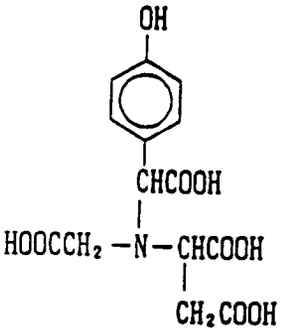

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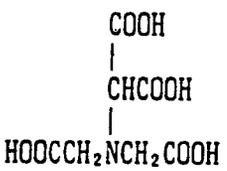

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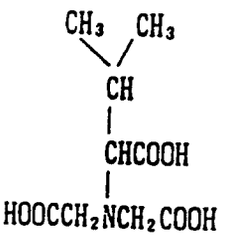

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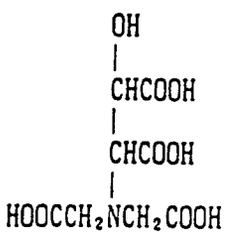

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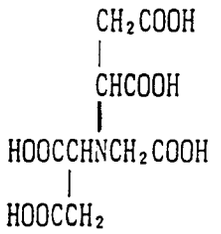

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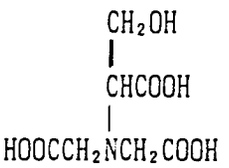

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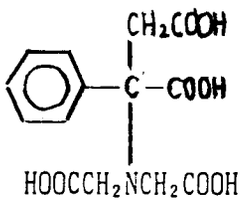


The compound represented by the general formula (I) may be in the form of ammonium salt (e.g., ammonium salt, tetraethylammonium salt) or alkaline metal salt (e.g., lithium salt, potassium salt, sodium salt).

Typical examples of synthesis of the compound of the present invention will be given below.

The compound of the present invention can be synthesized by synthesis methods as disclosed in "Bulletin of the Chemical Society of Japan", vol. 42, pp. 2835-2840, 1969, (Aspartic-N,N-diacetic acid), "Inorganic Chemistry", 34 (1974), West German Patent 3,739,610, and JP-A-63-267751 or analogous synthesis methods.

SYNTHESIS EXAMPLE 1: Synthesis of Compound (1)

Into a 1-ℓ three-necked flask were charged 26.0 g (0.195 mol) of L-aspartic acid and 200 ml of water. 35.0 g (0.417 mol) of sodium hydrogencarbonate was gradually added to the material with vigorous stirring. On the other hand, 47.4 g (0.501 mol) of monochloroacetic acid was dissolved in 200 ml of water. The acid solution was then neutralized with 42.0 g (0.501 mol) of sodium hydrogencarbonate. The aqueous solution was added to the material in the three-necked flask which was then heated to a temperature of 70 to 80 °C over a hot water bath. A solution of 18.0 g (0.450 mol) of sodium hydroxide in 50 ml of water was added dropwise to the aqueous solution. During this process, the pH value of the system was kept to 9 to 11. After the completion of the dropwise addition, the system was further heated for 1 hour to complete the reaction. After cooled, the material was adjusted with concentrated sulfuric acid to pH 2. The material was then distilled off under reduced pressure until the volume thereof was halved. The resulting salt was recovered by filtration. The filtrate was distilled off under reduced pressure to remove the solvent. The resulting salt was recovered by filtration. To the salt thus recovered was added a small amount of acetone. The material

was then allowed to stand in a refrigerator for 2 weeks. The resulting white powder was recovered by filtration, and then recrystallized from a 1 : 1 mixture of acetone and water. Yield: 11.5 g (4.62×10^{-2} mol) (23.7%)

m.p.: 177 °C (gradually decomposed beyond this point)

Elementary analysis for $C_8H_{11}O_8N$:			
	H	C	N
Calculated (%)	5.49	38.22	4.37
Found (%)	5.63	38.52	4.41

SYNTHESIS EXAMPLE 2: Synthesis of Compound (2)

Into a 1-ℓ three-necked flask were charged 40.0 g (0.214 mol) of sodium L-glutamate monohydrate and 200 ml of water. 18.0 g (0.214 mol) of sodium hydrogen-carbonate was gradually added to the material with vigorous stirring. On the other hand, 52.0 g (0.550 mol) of monochloroacetic acid was dissolved in 200 ml of water. The acid solution was then neutralized with 46.2 g (0.550 mol) of sodium hydrogencarbonate. The aqueous solution was added to the material in the three-necked flask which was then heated to a temperature of 70 to 80 °C over a hot water bath. A solution of 21.0 g (0.52 mol) of sodium hydroxide in 50 ml of water was added dropwise to the aqueous solution. During this process, the pH value of the system was kept to 9 to 11.

After the completion of the dropwise addition, the system was further heated for 1 hour to complete the reaction. After cooled, the material was adjusted with concentrated sulfuric acid to pH 2. The material was then distilled off under reduced pressure until the volume thereof was halved. The resulting salt was recovered by filtration. The filtrate was distilled off under reduced pressure to remove the solvent. The resulting salt was recovered by filtration. To the salt thus recovered was added a small amount of acetone. The material was then allowed to stand in a refrigerator for 1 month. The resulting white powder was recovered by filtration, and then recrystallized from a 1 : 1 mixture of acetone and water. Yield: 15.3 g (5.81×10^{-2} mol) (27.2%)

Elementary analysis for $C_9H_{13}O_8N$:			
	H	C	N
Calculated (%)	4.98	41.07	5.32
Found (%)	5.09	40.98	5.22

^{1}H NMR (D_2O + NaOD)δppm
δ1.78 (m 2H)
δ2.14 (t 2H)
δ3.15 (t 1H)
δ3.20 (q 4H)

SYNTHESIS EXAMPLE 3: Synthesis of Compound (21)

To 25.3 g (0.167 mol) of L-phenylglycine and 30 ml of water was added 15 ml of an aqueous solution of 6.68 g (0.167 mol) of sodium hydroxide to make a solution. To the solution were then added 58.4 g (0.501 mol) of sodium chloroacetate and 200 ml of water. The material was then heated to a temperature of 50 to 55 °C. 40 ml of an aqueous solution of 20.0 g (0.500 mol) of sodium hydroxide was slowly added dropwise to the material with stirring in such a manner that the pH value of the system was kept to 9 to 10. After the completion of the dropwise addition, the system was further heated for 2 hours with stirring. The material was then allowed to cool to room temperature. To the material was then added 67.6 g (0.667 mol) of concentrated sulfuric acid. The resulting solid matter was recovered by filtration, and then recrystallized from water to obtain 30.3 g (0.113 mol) of the desired compound (21). Yield: 68%

m.p.: 219 - 221 °C (decomposition)

Elementary analysis for $C_{12}H_{13}NO_6$:			
	H	C	N
Calculated (%)	4.90	53.93	5.24
Found (%)	4.91	53.68	5.32

^{1}H NMR (D_2O + NaOD) δppm
δ3.01 (d 2H)
δ3.13 (d 2H)
δ4.50 (s 1H)
δ7.40 (s 5H)

SYNTHESIS EXAMPLE 4: Synthesis of Compound (22)

To 25.4 g (0.154 mol) of L-phenylaranine and 30 ml of water was added 15 ml of an aqueous solution of 6.16 g (0.154 mol) of sodium hydroxide to make a solution. To the solution were then added 43.0 g (0.369 mol) of sodium chloroacetate and 200 ml of water. The material was then heated to a temperature of 50 to 55 °C. 40 ml of an aqueous solution of 14.8 g (0.370 mol) of sodium hydroxide was slowly added dropwise to the material with stirring in such a manner that the pH value of the system was kept to 9 to 10. After the completion of the dropwise addition, the system was further heated for 2 hours with stirring. The material was then allowed to cool to room temperature. To the material was then added 53.0 g (0.523 mol) of concentrated sulfuric acid. The resulting solid litter was recovered by filtration, and then recrystallized from water to obtain 29.2 g (0.101 mol) of the desired compound (22)of 1/2 hydrate. Yield: 65%
m.p.: 139 - 141 °C (decomposition)

Elementary analysis for $C_{13}H_{15}NO_6 \cdot \frac{1}{2}H_2O$:			
	H	C	N
Calculated (%)	5.56	53.79	4.83
Found (%)	5.38	53.98	4.89

^{1}H NMR (D_2O + NaOD) δppm
δ2.77-3.02 (m 2H)
δ3.12 (d 2H)
δ3.26 (d 2H)
δ3.47 (dd 1H)
δ7.19-7.50 (m 5H)

SYNTHESIS EXAMPLE 5: Synthesis of Compound (30)

To 25.3 g (0.167 mol) of D-phenylglycine and 30 ml of water was added 15 ml of an aqueous solution of 6.68 g (0.167 mol) of sodium hydroxide to make a solution. To the solution were then added 58.4 g (0.501 mol) of sodium chloroacetate and 200 ml of water. The material was then heated to a temperature of 50 to 55 °C. 40 ml of an aqueous solution of 20.0 g (0.500 mol) of sodium hydroxide was slowly added dropwise to the material with stirring in such a manner that the pH value of the system was kept to 9 to 10. After the completion of the dropwise addition, the system was further heated for 2 hours with stirring. The material was then allowed to cool to room temperature. To the material was then added 67.6 g (0.667 mol) of concentrated sulfuric acid. The resulting solid matter was recovered by filtration, and then recrystallized from water to obtain 33.9 g (0.127 mol) of the desired compound (30). Yield: 76%
m.p.: 219 - 221 °C (decomposition)

Elementary analysis for $C_{12}H_{13}NO_6$:			
	H	C	N
Calculated (%)	4.90	53.93	5.24
Found (%)	4.90	53.65	5.25

^{1}H NMR (D_2O + NaOD) δppm
δ3.09 (d 2H)
δ3.30 (d 2H)
δ4.57 (s 1H)
δ7.50 (s 5H)

SYNTHESIS EXAMPLE 6: Synthesis of Compound (31)

To 19.1 g (0.214 mol) of L-α-aranine, 1.49 g (0.01 mol) of sodium iodide and 30 ml of water was added 15 ml of an aqueous solution of 8.5 g (0.214 mol) of sodium hydroxide to make a solution. To the solution were then added 74.8 g (0.642 mol) of sodium chloroacetate and 200 ml of water. The material was then heated to a temperature of 50 to 55 °C. 40 ml of an aqueous solution of 25.6 g (0.641 mol) of sodium hydroxide was slowly added dropwise to the material with stirring in such a manner that the pH value of the system was kept to 9 to 10. After the completion of the dropwise addition, the system was further heated for 2 hours with stirring. The material was then allowed to cool to room temperature. To the material was then added 95.3 g (0.941 mol) of concentrated sulfuric acid. The resulting solid matter was recovered by filtration, and then recrystallized from water to obtain 28.5 g (0.139 mol) of the desired compound (31). Yield: 65%

m.p.: 213 - 215 °C (decomposition)

Elementary analysis for $C_{12}H_{13}NO_6$:			
	H	C	N
Calculated (%)	5.40	40.98	6.83
Found (%)	5.27	40.72	6.89

^{1}H NMR (D_2O + NaOD) δppm
δ1.60 (d 3H)
δ4.09 (d 2H)
δ4.18 (d 2H)
δ4.34 (q 1H)

Other compounds of the present invention can be synthesized in the same manner as mentioned above.

The compound of the present invention can be applied to all processing compositions for processing silver halide black-and-white photographic materials or silver halide color photographic materials. For processing compositions for black-and-white photographic light-sensitive materials, the compound of the present invention can be applied to general black-and-white developer, lith film infectious developer, fixing solution, washing water, etc. For processing compositions for color photographic light-sensitive materials, the compound of the present invention can be applied to color developer, bleaching solution, fixing solution, blix solution, adjustor, stop solution, film hardener, washing water, stabilizing solution, rinsing solution, fogging solution, toner, etc. However, the present invention is not limited to these applications.

The amount of the compound of the present invention to be incorporated in the system depends on the processing composition to be added and is normally in the range of 10 mg to 50 g per ℓ of processing composition.

More specifically, if added to a black-and-white developer or color developer, the amount of the compound of the present invention is preferably in the range of 0.5 to 10 g, particularly 0.5 to 5 g per ℓ of processing solution.

If added to a bleaching solution, the amount of the compound of the present invention is preferably in the range of 0.1 to 20 g, particularly 0.1 to 5 g per ℓ of bleaching solution.

If added to a fixing solution or blix solution, the amount of the compound of the present invention is preferably in the range of 1 to 40 g, particularly 1 to 20 g per ℓ of processing solution.

If added to a stabilizing solution, the amount of the compound of the present invention is preferably in the range of 50 mg to 1 g, particularly 50 to 300 mg per ℓ of stabilizing solution.

Compounds of the present invention may be used singly or in combination. Various chelating agents may be used so far as the effects of the compound of the present invention are not impaired.

Preferred examples of chelating agents to be used in combination with the compound of the present invention include aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, transcyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, glycoletherdiaminetetraacetic acid, iminodiacetic acid, methyliminodiacetic acid, carbamoylmethyliminodiacetic acid, hydroxyethyliminodiacetic acid and ethylenediamine-N-(β-hydroxyethyl)-N,N',N'-triacetic acid, organic phosphonio acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid and ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and hydrolyzate of maleic anhydride polymers as disclosed in European Patent 345172A1.

The black-and-white developer preferably comprises a hydroquinone developing agent such as hydroquinone, bromohydroquinone, methylhydroquinone and 2,5-dichlorohydroquinone as a developing agent. As an auxiliary developing agent to be used in combination with the developing agent there may be preferably used a p-aminophenolic developing agent such as N-methyl-p-aminophenol or 3-pyrazolidone developing agent such as 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone. As a preservative there may be preferably used a sulfite compound such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium metabisulfite and formaldehyde sodium bisulfite.

The pH value of the black-and-white developer is preferably in the range of 9 to 13. Examples of an alkaline agent to be used for the adjustment of pH value include sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. The developer may further comprise a pH buffer such as boric acid, borax, silicate, tribasic sodium phosphate and tribasic potassium phosphate. The developer may comprise a development inhibitor such as potassium bromide and potassium iodide, an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol and methanol, and a fog inhibitor such as indazole compound, benzimidazole compound and benztriazole compound. Further, the developer may comprise a development accelerator as disclosed in Research Disclosure No. 17643, vol. 176, Chapter XXI, December 1978. Moreover, the developer may comprise an amine compound as disclosed in U.S. Patent 4,269,929, JP-A-61-267759, and Japanese Patent Application No. 1-29418. The developer may further comprise a color toner, a surface active agent, a film hardener, etc. as necessary. Further, the developer may comprise a silver stain inhibitor as disclosed in JP-A-56-24347. The developer may further comprise an amino compound such as alkanolamine as disclosed in European Patent 136582, British Patent 958678, U.S. Patent 3,232,761, and JP-A-56-106244 for the purpose of enhancing contrast.

The black-and-white fixing solution is an aqueous solution having a pH value of 4.2 to 7.0 containing a thiosulfate as a fixing agent. Examples of such a thiosulfate include sodium thiosulfate and ammonium thiosulfate. In addition to such a thiosulfate, a mesoionic compound as disclosed in JP-A-57-150842 may be preferably used. The fixing solution may contain a film hardener (e.g., water-soluble aluminum salt), tartaric acid, citric acid, gluconic acid, derivative thereof, a preservative (e.g., sulfite, bisulfite), a pH buffer (e.g., acetic acid, boric acid), and a pH adjustor (e.g., sulfuric acid).

The color developer is an alkaline aqueous solution having a pH value of 9 to 12 containing an aromatic primary amine color developing agent as a main component. As such a color developing agent there may be used an aminophenolic compound, preferably p-phenylenediamine compound. Typical examples of such a p-phenylenediamine compound include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamideethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline, and sulfates, hydrochlorides and p-toluenesulfonates thereof. The color developer normally contains a carbonate of alkaline metal (e.g., potassium carbonate), a pH buffer such as borate and phosphate, and a development inhibitor or fog inhibitor such as chloride (e.g., potassium chloride), bromide (e.g., potassium bromide), iodide (e.g., potassium iodide), benzimidazole, benzotriazole, benzothiazole and mercapto compound. As necessary, the color developer may contain various preservatives such as hydroxylamine (e.g., hydroxylamine, diethylhydroxylamine, bis-(sulfonateethyl)hydroxylamine) and sulfite (e.g., sodium sulfite, sodium bisulfite), organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salt and amine, dye-forming couplers, competing couplers, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, nucleating agents such as sodium boron

hydride and hydrazine compound, thickening agents, fluorescent brightening agents such as 4,4'-diamino-2,2'-disulfostilbene compound, various surface active agents such as alkylsulfonic acid, arylsulfonic acid, aliphatic carboxylic acid and aromatic carboxylic acid, etc.

Examples of the bleaching agent to be incorporated in the bleaching solution or blix solution include compounds of polyvalent metals such as ferric iron(III), peracids, quinones, and iron salts. Typical examples of the bleaching agents include iron chloride, ferricyanides, bichromates, organic complex salts of ferric iron(III) (e.g., complex salts of metal with aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid and 1,3-diaminopropanetetraacetic acid), and persulfates. The bleaching solution or blix solution containing a ferric complex of aminopolycarboxylic acid is used in the pH range of 3.5 to 8.

The bleaching solution or blix solution may comprise any known additive such as rehalogenating agent (e.g., ammonium bromide, sodium bromide, potassium bromide, ammonium chloride), pH buffer (e.g., ammonium nitrate) and metal corrosion inhibitor (e.g., ammonium sulfate) incorporated therein.

Besides these compounds, the bleaching solution or blix solution may comprise an organic acid for the purpose of inhibiting bleach stain. A particularly preferred organic acid is a compound having an acid dissociation constant (pKa) of 2 to 5.5. Specific examples of such a compound include acetic acid, glycolic acid, and propionic acid.

Examples of the fixing agent to be incorporated in the fixing solution or blix solution for color photographic light-sensitive materials include thiosulfate, thiocyanate, thioether compound, thiourea, mesoionic compound, and iodide (used in a large amount). A thiosulfate is normally used. In particular, ammonium thiosulfate can be most widely used. Such a thiosulfate may be preferably used in combination with thiocyanate, thioether compound, thiourea, etc.

The fixing solution or blix solution may contain a sulfite, a bisulfite, a carbonyl-bisulfurous acid adduct, a preservative such as sulfinic compound as disclosed in European Patent 294769A, various fluorescent brightening agents, an antifoaming agent, a surface active agent, polyvinylpyrrolidone, methanol, a buffer such as imidazole, a bleach accelerator such as mercapto- or disulfide-containing compound as disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630, etc.

The washing water or stabilizing solution may contain an inorganic phosphoric acid, isothiazolone compound, thiabendazole, chlorine germicide such as chlorinated sodium isocyanurate, metallic salt such as magnesium salt, aluminum salt and bismuth salt, surface active agent, film hardener, etc. Further, the washing water and/or stabilizing solution may contain various bactericides or mildewproofing agents for the purpose of inhibiting the generation of fur or the proliferation of mildew in the photographic light-sensitive material after processing. Examples of such bactericides or mildewproofing agents include thiazolylbenzimidazole compounds as disclosed in JP-A-57-157244 and JP-A-58-105145, isothiazolone compounds as disclosed in JP-A-54-27424 and JP-A-57-8542, chlorophenolic compounds represented by trichlorophenol, bromophenolic compounds, organic tin compounds, organic zinc compounds, thiocyanic compounds, isothiocyanic compounds, acid amide compounds, diazine compounds, triazine compounds, thiourea compounds, benzotriazolealkylguanidine compounds, quaternary ammonium salts represented by benzalconium chloride, antibiotics represented by peniciline, and general-purpose anti-fungas agents as disclosed in "Journal Antibacteria And Antifungas Agents", vol. 11, No. 5, pp. 207-223, 1983. Two or more of these bactericides and mildewproofing agents can be used in combination. Further, various germicides as disclosed in JP-A-48-83820 can be used as well.

As a dye stabilizer to be incorporated in the stabilizing solution there may be normally used formaldehyde. From the standpoint of safety in the working atmosphere, N-methylolazole, hexamethylenetetramine, formaldehyde-bisulfurous acid adduct, dimethylolurea, azolylmethylamine derivatives, etc. may be preferably used. These dye stabilizers are further described in JP-A-2-153348, and JP-A-4-270344. In particular, the combined use of an azole such as 1,2,4-triazole and an azolylmethylamine derivative such as 1,4-bis(1,2,4-triazole-1-ilmethyl)piperazine (as disclosed in JP-A-4-359249) provides a high image stability and a low formaldehyde vapor pressure to advantage. The stabilizing solution may further contain a pH adjusting buffer such as boric acid and sodium hydroxide, a sulfurization inhibitor such as alkanolamine, a fluorescent brightening agent, etc.

Examples of photographic materials which can be processed with the processing composition according to the present invention include ordinary black-and-white silver halide photographic materials (e.g., black-and-white photographic material for picture taking, X-ray black-and-white photographic material, black-and-white photographic material for printing), ordinary multi-layer silver halide color photographic materials (e.g., color negative film, color reversal film, color positive film, color negative film for motion picture, color photographic paper, reversal color photographic paper, direct positive color photographic material), infrared-sensitive photographic materials for laser scanner, and diffusion transfer photographic materials (e.g., silver

diffusion transfer photographic material, color diffusion transfer photographic material). The photographic material according to the present invention may have various layer configurations (e.g., silver halide emulsion layers sensitive to red, green and blue, respectively, undercoating layer, antihalation layer, filter layer, interlayer, surface protective layer) on one or both, sides thereof depending on the purpose.

The support for the photographic material of the present invention, the coating method, the kind of silver halide grains to be coated on the silver halide emulsion layer, surface protective layer, etc. (e.g., silver bromoiodie, silver bromochloroiodide, silver bromide, silver bromochloride, silver chloride), the crystal form thereof (e.g., cube, tabular, sphere), the size thereof, the size flutuation coefficient, the crystalline structure thereof (e.g., core/shell structure, polyphase structure, uniform phase structure), the preparation method thereof (e.g., single jet process, double jet process), the binder to be incorporated therein (e.g., gelatin), the film hardener to be incorporated therein, the fog inhibitor to be incorporated therein, the metal doping agent to be incorporated therein , the silver halide solvent to be incorporated therein, the thickening agent to be incorporated therein, the emulsion precipitant to be incorporated therein, the dimensional stabiliser to be incorporated therein, the adhesion inhibitor to be incorporated therein, the stabilizer to be incorporated therein, the color stain inhibitor to be incorporated therein, the dye stabilizer to be incorporated therein, the stain inhibitor to be incorporated therein, the chemical sensitizer to be incorporated therein, the spectral sensitizer to be incorporated therein, the sensitivity improver to be incorporated therein, the supersensitizer to be incorporated therein, the nucleating agent to be incorporated therein, the coupler to be incorporated therein (e.g., pivaloylacetanilide type or benzoylacetanilide type yellow coupler, 5-pyrazolone type or pyrazoloazole type magenta coupler, phenol type or naphthol type cyan coupler, DIR coupler, bleach accelerator-releasing coupler, competing coupler, colored coupler), the coupler dispersion method (e.g., oil-in-water dispersion method using a high boiling solvent), the plasticizer to be incorporated therein, the antistatic agent to be incorporated therein, the lubricant to be incorporated therein, the coating aid to be incorporated therein, the surface active agent to be incorporated therein, the brightening agent to be incorporated therein, formalin scavenger to be incorporated therein, the light scattering agent to be incorporated therein, the matting agent to be incorporated therein, the light absorbent to be incorporated therein, the ultraviolet absorbent to be incorporated therein, the filter dye to be incorporated therein, the irradiation dye to be incorporated therein, the development improver to be incorporated therein, the delusterant to be incorporated therein, the preservative to be incorporated therein (e.g., 2-phenoxyethanol), and the mildewproofing agent to be incorporated therein are not specifically limited. For these items, reference can be made to Product Licensing, vol. 92, pp. 107-110, December 1971, Research Disclosure - (hereinafter referred as "RD") Nos. 17643 (December 1978), 18716 (November 1979), and 307105 (November 1989), JP-A-4-34548, line 1, lover left column, page 15 - line 3, lover right column, page 20, JP-A-4-184432, line 32, right column, page 7 - line 26, right column, page 9, and JP-A-4-274237, line 30, right column, page 6 - line 49, right column, page 9.

The processing solution containing the compound of the present invention exhibits minimized oxidation or decomposition of components of the processing solution due to metallic ions, maintains desired properties for a prolonged period of time, and shows no precipitation even due to the accumulation of metallic ions. Accordingly, the processing solution according to the present invention causes no troubles such as film stain and clogging in the filter in the automatic developing machine. Further, the compound of the present invention is biodegradable and thus contributes to environmental protection.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

EXAMPLE 1

The following processing solutions were prepared.

Color developer

Diethylenetriaminepentaacetic acid	1.0 g
Chelate compound (set forth in Table 1)	0.01 mol
Sodium sulfite	4.0 g
Potassium carbonate	30.0 g
Potassium bromide	1.4 g
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water to make	1,000 ml
pH	10.05

To the foregoing color developer were then added ferric chloride as ferric ion in an amount of 5 ppm and calcium nitrate as calcium ion in an amount of 150 ppm to prepare Specimens 101 to 113. These specimens were each packed into a hard vinyl chloride container having a length of 10 cm, a width of 25 cm and a depth of 30 cm in an amount of 5 ℓ. The solution in the container was continuously circulated at a rate of 3 ℓ per minute by means of a pump while being kept to a temperature of 38 °C for 30 days for ageing test.

In the container, the liquid surface was covered by a floating cover by 200 cm^2 and left open to the air by 50 cm^2.

A multi-layer color photographic material specimen 101 described in Example 1 of JP-A-4-274236 was cut into strips having a width of 35 mm, and then wedgewise exposed to light with 5CMS at a color temperature of 4,800 °K. The photographic sensitive material specimen was then processed with the color developer specimens 101 to 113 which had been just prepared (fresh solution) or the same color developer specimens which had been aged in accordance with the following procedures:

Processing step	Processing time	Processing temperature (°C)
Color development	3 min. 15 sec.	37.8
Bleach	50 sec.	38.0
Fixing	1 min. 40 sec.	38.0
Rinse (1)	30 sec.	38.0
Rinse (2)	20 sec.	38.0
Stabilization	20 sec.	38.0

Bleaching solution

Ferric ammonium 1,3-propanediaminetetraacetate	0.55 mol
Ammonium bromide	85 g
Ammonium nitrate	20 g
Glycolic acid	55 g
Water to make	1,000 ml
pH	4.0

Fixing solution

Dibasic ammonium ethylenediaminetetraacetate	1.7 g
Ammonium sulfite	14.0 g
Aqueous solution of ammonium thiosulfate (700 g/ℓ)	260.0 ml
Water to make	1,000 ml
pH	7.0

Washing water

Tap water was passed through a mixed bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B produced by Rohm & Haas) and an OH type anion exchange resin (Amberlite IR-400) so that the calcium and magnesium ion concentrations were each reduced to 3 mg/ℓ or less. To the solution were then added 20 mg/ℓ of dichlorinated sodium isocyanurate and 150 mg/ℓ of sodium sulfate. The pH range of the solution was from 6.5 to 7.5.

Stabilizing solution

Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10)	0.2 g
Disodium ethylenediaminetetraacetate	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazole-1-ilmethyl) piperazine	0.75 g
Water to make	1,000 ml
pH	8.5

At the exposure such that the specimen which has been processed with the fresh solution exhibits B density of 2.5 when measured with blue light, the specimen which had been processed with the aged solution was measured for B density by means of a Type X Light 310 photographic densitometer to determine a difference ΔD_B from that of the fresh solution. Further, the percent residue of developing agent and hydroxylamine after ageing were determined by analysis. Moreover, the color developers which had been aged were visually examined for the presence of precipitate. The results are set forth in Table 1.

TABLE 1

No.	Chelate compound	ΔDmax	% Residue of developing agent (%)	% Residue of hydroxylamine** (%)	Precipitate*
101	None	-0.5	60	20	BBB
102	Ethylenediaminetetraacetic acid	-0.4	62	30	G
103	Ethylenediaminetetramethylene-phosphonic acid	-0.05	88	70	B
104	Exemplary Compound 1	-0.04	91	75	G
105	" 2	-0.05	87	72	G
106	" 3	-0.07	84	70	G
107	" 4	-0.08	80	68	G
108	" 7	-0.05	88	74	G
109	" 13	-0.06	85	70	G
110	" 21	-0.08	82	69	G
111	" 22	-0.06	84	70	G
112	" 30	-0.08	81	68	G
113	" 31	-0.05	87	71	G

* G: No precipitate observed
B: The more number of B marks, the more precipitates
** : After oxidized with iodine, hydroxylamine turned to red with the addition of sulfonic acid and α-naphthylamine. The percent residue of hydroxylamine was determined by spectrophotometry.

Table 1 shows that the use of conventional chelating agents leaves much to be desired in the prevention of precipitate and the maintenance of solution stability while the use of the compound of the present invention provides great effects.

EXAMPLE 2

To the fixing solution of Example 1 were added the present compounds 1, 2, 3, 4, 7, 13, 21, 22, 30 and 31, respectively, in an amount of 3 g/ℓ, and ferric ions corresponding to those brought over from the prebath bleaching solution to prepare Specimens 201 to 210. These specimens were aged at a temperature of 38 °C with an opening value of 0.1 cm^{-1} for 30 days, and then observed for turbidity. The specimens free of compound of the present invention showed a remarkable turbidity after ageing while the specimens comprising the compound of the present invention incorporated therein all stayed transparent, showing no precipitation.

EXAMPLE 3

The stabilizing solution of Example 1 was used as Comparative Specimen 301. To the same stabilizing solution were added Exemplary Compounds 1, 2, 3, 4, 7, 13, 21, 22, 30 and 31, respectively, in an amount of 100 mg/ℓ to prepare Specimens 302 to 311. With these specimens as stabilizing solutions, the multi-layer color photographic light-sensitive material specimen 101 was then processed with the fresh form of the color developer as used for Specimen 101 in Example 1. The multi-layer color photographic light-sensitive material specimen 101 which had been thus processed was then aged at a temperature of 45 °C and a relative humidity of 70% for 1 week. The magenta stain increase (ΔDmin) from before ageing to after ageing was then determined.

The results are set forth in Table 2.

TABLE 2

No.	Chelate Compound	ΔDmin	Remarks
301	None	0.25	Comparative
302	Exemplary Compound 1	0.07	Present Invention
303	" 2	0.09	"
304	" 3	0.11	"
305	" 4	0.12	"
306	" 7	0.09	"
307	" 13	0.11	"
308	" 21	0.12	"
309	" 22	0.11	"
310	" 30	0.13	"
311	" 31	0.10	"

Table 2 shows that the use of the stabilizing solution of the present invention containing the compound of the present invention inhibits the stain increase and improves the image preservability.

EXAMPLE 4

The following color developer was prepared.

Color Developer

Water	600 ml
Potassium bromide	0.015 g
Potassium chloride	3.1 g
Triethanolamine	10.0 g
Potassium carbonate	27 g
Fluorescent brightening agent (WHITEX•4B, available from Sumitomo Chemical Co., Ltd.)	1.0 g
Preservative (disodium-N,N-bis(sulfonateethyl)hydroxylamine)	45 mmol
N-ethyl-N-(β-methanesulfoneamideethyl)-3-methyl-4-aminoanilinesulfate	5.0 g
Water to make	1,000 ml
pH (25 °C)	10.05

The foregoing color developer was used Specimen 401. To the same color developer were added the compounds of the present invention and comparative compounds in amounts set forth in Table 3, respectively, to prepare Specimens 402 to 408. To these color developers were then added ferric ion in an amount of 5 ppm and calcium ion in an amount of 150 ppm, respectively. These color developers were then aged in a beaker with an opening value of 0.10 cm^{-1} at a temperature of 38 °C for 20 days.

Specimen 103 described in JP-A-4-145433 was subjected to gradation exposure through a three-color separation filter for sensitometry. The exposure was effected in such a manner that an exposure of 250CMS reached for 0.1 second. The photographic light-sensitive material thus exposed was then processed with the foregoing color developer which had been just prepared (fresh solution) and the same color developer which had been aged (aged solution) in accordance with the following procedures:

Processing step	Temperature (°C)	Time (sec.)
Color development	38	45
Blix	35	25
Rinse 1	35	20
Rinse 2	35	20
Rinse 3	35	20
Drying	80	60

Blix solution

Water	400 ml
Ammonium thiosulfate (700 g/ℓ)	100 ml
Sodium sulfite	17 g
Ferric ammonium ethylenediaminetetraacetate	55 g
Disodium ethylenediaminetetraacetate	5 g
Ammonium bromide	40 g
Water to make	1,000 ml
pH (25 °C)	6.8

Rinsing solution

Ion-exchanged water (calcium and magnesium concentrations: 3 ppm or less each)

With respect to the minimum yellow density (Dmin) and magenta sensitivity (log E of exposure which gives a density of 0.5) obtained with the fresh solution, the increase (ΔDmin) of the minimum yellow density and the change (ΔS) of the magenta sensitivity obtained with the aged solution were determined. Further, the percent residue of developing agent in the aged solution was determined by high speed liquid chromatography. Moreover, the aged solution was observed for the presence of precipitate.

TABLE 3

No.	Chelating agent (added amount)	Yellow ΔDmin	Magenta ΔS	% Residue of developing agent	Precipitation*	Remarks
401	None	+0.07	-0.11	61	BBB	Comparative
402	Sodium hexametaphosphate (1 g/ℓ)	+0.04	-0.07	78	BB	"
403	1-Hydroxyethylidene-1,1-diphosphonic acid (60%) (1.6 g/ℓ)	+0.04	-0.05	80	BB	"
404	Ethylenediaminetetraacetic acid (1 g/ℓ)	+0.06	-0.08	65	G	"
405	Nitrilotrimethylenephosphonic acid (1 g/ℓ)	+0.05	-0.07	75	B	"
406	Exemplary Compound 1 (1 g/ℓ)	+0.02	-0.02	89	G	Present Invention
407	Exemplary Compound 2 (1 g/ℓ)	+0.03	-0.04	83	G	"
408	Exemplary Compound 21 (1 g/ℓ)	+0.03	-0.02	87	G	"

* G: No precipitation observed

B: Precipitation observed (The more number of B marks, the more precipitates)

Table 3 shows that the use of the compound of the present invention provides small ΔDmin and ΔS values, showing reduced flutuations of photographic properties. Further, the use of the compound of the present invention provides a great improvement in the inhibition of precipitation as compared to the comparative compounds. In particular, the comparative compounds which exert a great effect of inhibiting precipitation exhibit a poor preservability of developing agent while the comparative compounds which

cause little decomposition of developing agent leave much to be desired in the inhibition of precipitation. On the contrary, the compound of the present invention provides a stable developer free from precipitation.

EXAMPLE 5

A color developer (A) was prepared having the composition as mentioned below. Further, a color developer (B) was prepared by replacing disodium ethylenediaminetetraacetate in the color developer (A) by Exemplary Compound 3 in the equimolecular amount. The two color developers were aged at a temperature of 40 °C for 4 days. Specimen B-6 of an example in JP-A-3-174148 was then subjected to running processing with the color developers, respectively. As a result, the color developer (B) showed some improvement in the inhibition of precipitation. The percent residue of hydroquinone and potassium sulfite in the developer and the pH value of the developer after ageing were determined. As a result, it was found that the use of the compound of the present invention provides minimum loss of hydroquinone and potassium sulfite by air oxidation and hence a reduced rise of pH.

Developer (A)

Hydroquinone	45.0 g
N-methyl-p-aminophenol 1/2 sulfate	0.8 g
Sodium hydroxide	18.0 g
Potassium hydroxide	55.0 g
5-Sulfosalicylic acid	45.0 g
Boric acid	25.0 g
Potassium sulfite	110.0 g
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	6.0 g
5-Methylbenztriazole	0.6 g
n-Butyl-diethanolamine	15.0 g
Water to make	1 ℓ
pH	11.6

EXAMPLE 6

The compounds of the present invention and a comparative compound were subjected to a biodegradability test in accordance with an amended SCAS method defined in PECD chemical test guide line. The results are set forth in Table 4.

TABLE 4

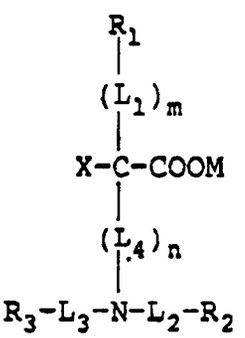
No.	Chelating agent		% Decomposition	Remarks
501	Ethylenediamine-tetraacetic acid		0	Comparative
502	Exemplary Compound	1	76	Present Invention
503	"	2	72	"
504	"	3	85	"
505	"	8	80	"
506	"	13	73	"
507	"	21	68	"
508	"	22	70	"
509	"	31	72	"

Table 4 shows that the compound of the present invention exhibits an excellent biodegradability.

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

Claims

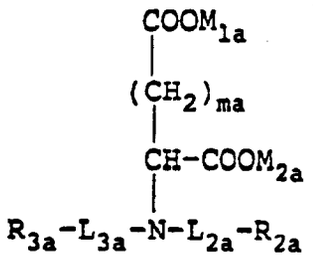
1. A photographic processing composition, comprising at least one of compounds represented by the following general formula (I) or salts thereof:



(I)

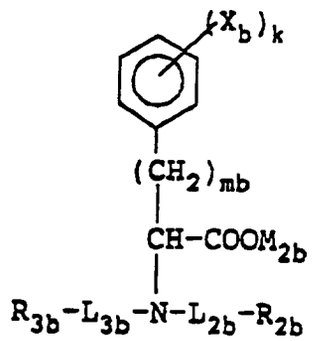
wherein R_1 represents a carboxyl, aliphatic or aromatic group: R_2 and R_3 each represents a carboxyl, phosphono, sulfo or hydroxyl group; L_1, L_2, L_3 and L_4 each represents an alkylene group; X represents a hydrogen atom, aliphatic group or aromatic group; M represents a hydrogen atom or cation; and m and n each represents an integer 0 to 3.

2. A photographing processing composition as claimed in claim 1, wherein the compound of formula (I) is a compound of formula (II) or (III):



(II)

wherein L_{2a} and L_{3a} have the same meaning as L_2 and L_3 in the general formula (I), respectively; R_{2a} and R_{3a} have the same meaning as R_2 and R_3 in the' general formula (I), respectively; M_{1a} and M_{2a} each has the same meaning as M in the general formula (I); and m_a represents an integer 0 to 5.



(III)

wherein L_{2b} and L_{3b} have the same meaning as L_2 and L_3 in the general formula (I), respectively; R_{2b} and R_{3b} have the same meaning as R_2 and R_3 in the general formula (I), respectively; M_{1b} and M_{2b} each has the same meaning as M in the general formula (I); m_b represents an integer 0 to 3; X_b represents a substituent.

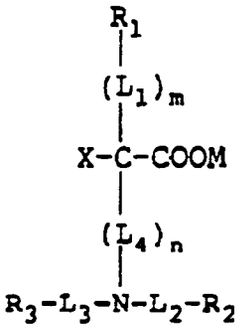
3. A photographing processing composition as claimed in claim 1, wherein the salts of the compound represented by formula (I) are an ammonium salt or an alkali metal salt.

4. A photographing processing composition as claimed in claim 1, wherein the compound of formula (I) is applied to black-and-white developer, or color developer.

5. A photographing processing composition as claimed in claim 1, wherein the compound of formula (I) is applied to fixing solution.

6. A photographing processing composition as claimed in claim 1, wherein the compound of formula (I) is applied to stabilizing solution.

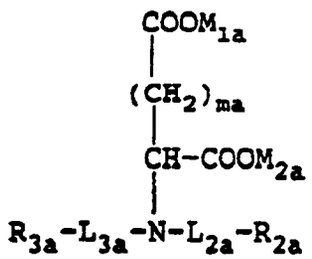
7. A method for the processing of a silver halide photographic material, which comprises the processing of a silver halide photographic material which has been imagewise exposed to light with a processing solution containing at least one of the compounds represented by the general formula (I) or salts thereof:



(I)

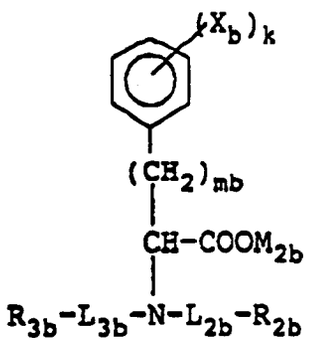
wherein R_1 represents a carboxyl, aliphatic or aromatic group; R_2 and R_3 each represents a carboxyl, phosphono, sulfo or hydroxyl group; L_1, L_2, L_3 and L_4 each represents an alkylene group; X represents a hydrogen atom, aliphatic group or aromatic group; M represents a hydrogen atom or cation; and m and n each represents an integer 0 to 3.

8. A method as claimed in claim 7, wherein the compound of formula (I) is a compound of formula (II) or (III):



(II)

wherein L_{2a} and L_{3a} have the same meaning as L_2 and L_3 in the general formula (I), respectively; R_{2a} and R_{3a} have the same meaning as R_2 and R_3 in the general formula (I), respectively; M_{1a} and M_{2a} each has the same meaning as M in the general formula (I); and m_a represents an integer 0 to 5.



(III)

wherein L_{2b} and L_{3b} have the same meaning as L_2 and L_3 in the general formula (I), respectively; R_{2b} and R_{3b} have the same meaning as R_2 and R_3 in the general formula (I), respectively; M_{1b} and M_{2b} each has the same meaning as M in the general formula (I); m_b represents an integer 0 to 3; X_b represents a substituent.

9. A method as claimed in claim 7, wherein the salts of the compound of formula (I) are an ammonium salt or an alkali metal salt.

10. A method as claimed in claim 7, wherein the compound of formula (I) is applied to black-and-white developer, or color developer.

11. A method as claimed in claim 7, wherein the compound of formula (I) is applied to fixing solution.

12. A method as claimed in claim 7, wherein the compound of formula (I) is applied to stabilizing solution.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 6104

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X Y	EP-A-0 486 909 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * claim 1 *	1-3,5, 7-9,11 4,6,10, 12	G03C5/305 G03C5/26 G03C7/30 G03C5/38 G03C7/413
P,X	EP-A-0 556 782 (KONICA CORPORATION) *Page 5,compounds A-I-4,5,6* * page 18, line 14 - line 17 *	1-3	G03C7/42
E	EP-A-0 563 571 (KONICA CORPORATION) *Page 9,compound A-I-13* * page 40, line 32 - line 35 *	1-3	
Y	EP-A-0 206 148 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * page 3, line 5 - page 4, line 15 *	6,12	
Y	GB-A-1 006 878 (EASTMAN KODAK COMPANY) * page 1, line 80 - line 85 * * page 2, line 4 - line 43 *	4,10	
A	DE-A-37 39 610 (BASF AG) * page 4, line 68 - page 5, line 5; claim 1 *	4,10	TECHNICAL FIELDS SEARCHED (Int.Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 January 1994	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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