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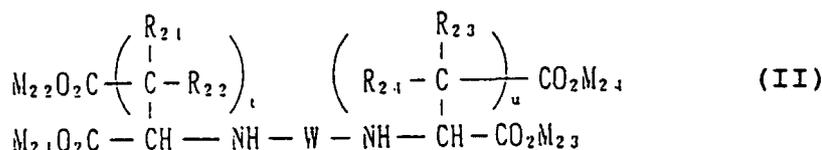
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(54) **Method for processing silver halide color photographic material and processing solution for silver halide photographic material**

(57) The present invention provides a method for processing a silver halide color photographic material which gives an excellent stability to a processing solution having a fixing ability (e.g., fixing solution, blixing solution), provides an image with little stain (particularly cyan stain), gives an excellent image stability with time after processing (particularly magenta) and causes minimized failure of color restoration. A novel method for processing a silver halide color photographic material comprising color development, desilvering, rinsing and/or processing with a stabilizer is provided, wherein the desilvering is effected with (a) a processing solution with a bleaching ability containing at least one ferric complex salt (III) of a compound represented by formula (I) and having a pH value of from 3 to 7 and (b) a processing solution with a fixing ability containing at least complex-forming agent selected from the group consisting of a compound represented by formula (II), EDTA and an organic phosphonic acid and having a pH value of from 6.1 to 8.0.



wherein R₁ represents a hydrogen atom, aliphatic hydrocarbon group, aryl group or heterocyclic group; L₁ and L₂ each represent an alkylene group; and M₁ and M₂ each represent a hydrogen atom or cation; or cation; or cation;



wherein R₂₁, R₂₂, R₂₃ and R₂₄ each represent a hydrogen atom, aliphatic hydrocarbon group, aryl group, heterocyclic group, hydroxyl group or carboxyl group; t and u each represent an integer of 0 or 1; W represents a divalent connecting group containing carbon atoms; and M₂₁, M₂₂, M₂₃ and M₂₄ each represent a hydrogen atom or cation.

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DescriptionFIELD OF THE INVENTION

5 **[0001]** The present invention relates to a method for processing a silver halide color photographic material which has been imagewise exposed to light (hereinafter merely referred to as "light-sensitive material") with a processing composition having a fixing ability. More particularly, the present invention relates to a processing composition for improving liquid stability and photographic properties and a processing method using the processing composition.

10 BACKGROUND OF THE INVENTION

[0002] A light-sensitive material which has been subjected to exposure and development is processed with a bleaching solution or fixing solution. As the fixing agent to be incorporated in the fixing solution there has conventionally been well-known a thiosulfate. Such a thiosulfate has been widely used in combination with sulfites which are used as preservatives therefor and auxiliaries such as aminopolycarboxylic acid and organic phosphonic acid described in JP-A-2-139548 (The term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-6-130567.

15 **[0003]** A processing solution having a fixing ability is liable to deterioration or affects the color forming property of dyes when its pH value is lowered. Therefore, the processing solution having a fixing ability is preferably used around pH 7. However, when the processing solution has a pH value within this range, it reacts with calcium or magnesium ion contained in water used to prepare the solution or eluate from the light-sensitive material to produce precipitates or sludge or color the light-sensitive material or accelerate the change of photographic properties with time after processing. Thus, various problems cannot necessarily be solved satisfactorily, leaving much to be desired. It is further disadvantageous in that the precision in reading magnetically recorded data from a light-sensitive material having a magnetic recording layer as described in International Patent WO90/04205 is remarkably deteriorated.

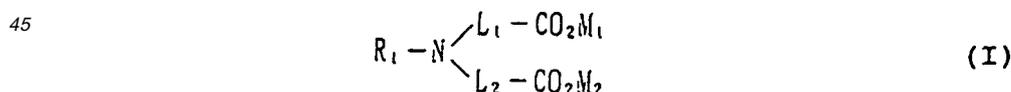
SUMMARY OF THE INVENTION

20 **[0004]** It is therefore an object of the present invention to provide a method for processing a silver halide color photographic material which gives an excellent stability to a processing solution having a fixing ability (e.g., fixing solution, bleaching solution), provides an image with little stain (particularly cyan stain), gives an excellent image stability with time after processing (particularly magenta) and causes minimized failure of color restoration.

[0005] It is another object of the present invention to provide a processing method which gives an enhanced color density (minimizes failure of color restoration) in addition to the foregoing accomplishments.

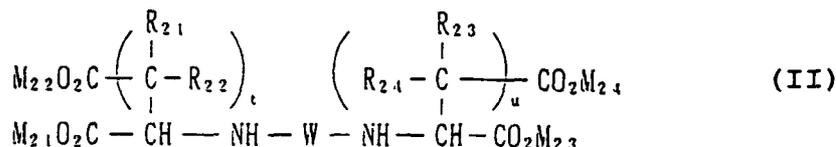
25 **[0006]** The inventors made extensive studies of solution to the foregoing problems. As a result, the following processing method was found.

[0007] The present invention lies in a method for processing a silver halide color photographic material comprising color development, desilvering, rinsing and/or processing with a stabilizer, wherein the desilvering is effected with (a) a processing solution with a bleaching ability containing at least one ferric complex salt (III) of a compound represented by formula (I) and having a pH value of from 3 to 7 and (b) a processing solution with a fixing ability containing at least complex-forming agent selected from the group consisting of a compound represented by formula (II), EDTA and an organic phosphonic acid and having a pH value of from 6.1 to 8.0.



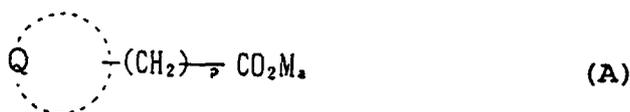
50 wherein R_1 represents a hydrogen atom, aliphatic hydrocarbon group, aryl group or heterocyclic group; L_1 and L_2 each represent an alkylene group; and M_1 and M_2 each represent a hydrogen atom or cation;

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10 wherein R_{21} , R_{22} , R_{23} and R_{24} each represent a hydrogen atom, aliphatic hydrocarbon group, aryl group, heterocyclic group, hydroxyl group or carboxyl group; t and u each represent an integer of 0 or 1; W represents a divalent connecting group containing carbon atoms; and M_{21} , M_{22} , M_{23} and M_{24} each represent a hydrogen atom or cation. In accordance with this processing, the inhibition of stain (particularly cyan stain) on the image thus formed, the improvement of stability of the image thus processed (particularly magenta) with time and the minimization of so-called failure of color restoration (phenomenon involving failure in exhibition of desired color (forming) density due to a trouble in which the production of a dye stops at an intermediate step during development process, making it impossible to produce a desired dye completely) can be remarkably accomplished, making it possible to obtain an excellent color image having a minimized change with time and hence achieve the foregoing objects.

15 [0008] When the processing solution with a fixing ability to be used in desilvering contains a compound represented by formula (A) in addition to the at least one complex-forming agent selected from the group consisting of the compound represented by formula (II), EDTA and an organic phosphonic acid, the foregoing objects of the present invention can be further accomplished. In particular, the minimization of failure of color restoration can be remarkably accomplished.



25 wherein Q represents a nonmetallic atom group required to form a heterocyclic group; p represents an integer of 0 or 1; and M_a represents a hydrogen atom or cation.

30 [0009] Accordingly, the processing solution with a fixing ability for a silver halide photographic material containing at least one complex-forming agent selected from the group consisting of the compound represented by formula (II), EDTA and an organic phosphonic acid and a compound represented by formula (A) and having a pH value of from 6.1 to 8.0 is according to the present invention. This processing solution is preferably a processing solution having a fixing ability for a color light-sensitive material.

A preferred embodiment of the processing solution according to the present invention is a fixing solution for color light-sensitive material.

40 DETAILED DESCRIPTION OF THE INVENTION

[0010] Examples of the complex-forming agent belonging to any of the foregoing compound represented by formula (II), EDTA (ethylenediamine-N,N,N',N'-tetraacetic acid) and the organic phosphonic acid include those included in the formulae of compound to be added to fixing solution disclosed in JP-A-1-206342, JP-A-2-139548, JP-A-4-313752, and JP-A-6-67370. However, these disclosed techniques are all intended to accelerate desilvering by a processing solution having a fixing ability or prevent the processing solution from becoming turbid. Accordingly, there are no suggestions on the effect of the present invention of improving the stability of magenta dye or minimizing failure of color restoration. The present invention exerts its effect by incorporating the compound represented by formula (I) in the processing solution having a bleaching ability. None of the above described patents has reference to the compound represented by formula (I). There is found no knowledge that such a compound is incorporated in a processing solution having a bleaching ability.

[0011] Pyridine-2,6-dicarboxylic acid, which is one of the compounds represented by formula (A), is incorporated in the fixing solution disclosed in JP-A-51-7930. However, the above described patent is intended to prevent cyan stain caused by iron chloride bleaching solution and thus differs from the present invention in purpose, process and composition of processing solution. Similarly, there is found no knowledge of the scope of the present invention.

[0012] In the present invention, the light-sensitive material is processed with a color developer, desilvered, and then rinsed and/or processed with a stabilizer.

[0013] In the desilvering step, the light-sensitive material is essentially subjected to bleaching with a processing

solution having a bleaching ability, and then subjected to fixing with a processing solution having a fixing ability. Bleaching and fixing may be separately effected. Alternatively, bleaching and fixing may be simultaneously effected with a blixing solution having both a bleaching ability and a fixing ability (blixing). These bleaching, fixing and blixing may each be effected in a single bath or two or more baths.

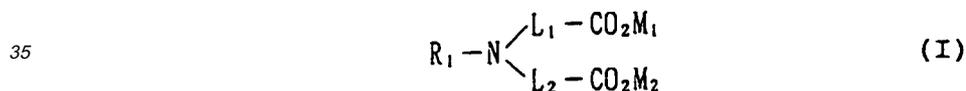
5 **[0014]** The term "processing solution having a fixing ability" as used herein means a processing solution containing a fixing agent among the processing solutions to be used in the desilvering step, particularly fixing solution and blixing solution. The term "processing solution having a bleaching ability" as used herein means a processing solution containing a bleaching agent among the processing solutions to be used in the desilvering step, particularly bleaching solution and blixing solution.

10 **[0015]** Specific embodiments of desilvering step in the present invention will be given below, but the present invention should not be construed as being limited thereto.

1. Bleaching - fixing
2. Blixing
- 15 3. Bleaching - blixing
4. Blixing - blixing
5. Bleaching - blixing - fixing
6. Bleaching - blixing - blixing
7. Bleaching - fixing - fixing
- 20 8. Bleaching - fixing - blixing
9. Blixing - fixing
10. Blixing - bleaching

[0016] A rinsing step may be provided between these processing steps. The effect of the present invention can be exerted particularly with the foregoing steps 1, 5 and 7.

[0017] The processing solution having a bleaching ability to be used in the processing method of the present invention will be described hereinafter. As the bleaching agents to be incorporated in the processing solution having a bleaching ability there are well-known an inorganic oxidizing agent such as red prussiate, ferric chloride, bichromate, persulfate, bromate and hydrogen peroxide, and organic acid ferric complex salt (III). The processing solution having a bleaching ability to be used in the present invention may contain these bleaching agents but essentially contains a compound represented by formula (I):



40 wherein R_1 represents a hydrogen atom, aliphatic hydrocarbon group, aryl group or heterocyclic group; L_1 and L_2 each represent an alkylene group; and M_1 and M_2 each represent a hydrogen atom or cation.

[0018] The compound represented by formula (I) will be further described hereinafter. The term "number of carbon atoms" as used hereinafter means the number of carbon atoms excluding those in the substituent moiety.

[0019] The aliphatic hydrocarbon group represented by R_1 is a straight-chain, branched or cyclic alkyl group (preferably having from 1 to 12 carbon atoms, more preferably from 1 to 10 carbon atoms, most preferably from 1 to 8 carbon atoms), alkenyl group (preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, most preferably from 2 to 7 carbon atoms) or alkynyl group (preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, most preferably from 2 to 7 carbon atoms) which may have substituents.

[0020] Examples of these substituents include aryl group preferably having from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, particularly preferably from 6 to 8 carbon atoms such as phenyl and p-methylphenyl, alkoxy group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methoxy and ethoxy, aryloxy group preferably having from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, particularly preferably from 6 to 8 carbon atoms such as phenyloxy, acyl group preferably having from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as acetyl, alkoxycarbonyl group preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as methoxycarbonyl, acyloxy group preferably having from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as acetoxyl, acylamino group preferably having from 1 to 10 carbon atoms, more prefer-

ably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as acetylamino, sulfonlamino group preferably having from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfonylamino, sulfamoyl group preferably having from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, particularly preferably from 0 to 4 carbon atoms such as sulfamoyl and methylsulfamoyl, carbamoyl group preferably having from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as carbamoyl and methylcarbamoyl, alkylthio group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methylthio and ethylthio, sulfonyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfonyl, sulfinyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfinyl, hydroxyl group, halogen atom such as fluorine, chlorine, bromine and iodine, cyano group, sulfo group, carboxyl group, nitro group, and heterocyclic group such as imidazolyl and pyridyl. These substituents may be further substituted. When there are two or more of these substituents, they may be the same or different.

[0021] Preferred examples of substituents on the aliphatic hydrocarbon group represented by R_1 include alkoxy group, carboxyl group, hydroxyl group, and sulfo group. Preferred among these substituents are carboxyl group and hydroxyl group.

[0022] The aliphatic hydrocarbon group represented by R_1 is preferably an alkyl group, more preferably a chain alkyl group, most preferably methyl, ethyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 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-carbamoyl-1-carboxyethyl or 4-imidazolylmethyl, particularly preferably methyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 2-hydroxyethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-phenylethyl or 1-carboxy-3-methylthiopropyl.

[0023] The aryl group represented by R_1 is preferably a C_{6-20} monocyclic or bicyclic aryl group (e.g., phenyl, naphthyl), more preferably a C_{6-15} phenyl group, most preferably a C_{6-10} phenyl group.

[0024] The aryl group represented by R_1 may have substituents. Examples of these substituents include those exemplified as the aliphatic hydrocarbon group represented by R_1 , alkyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methyl and ethyl, alkenyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as vinyl and allyl, and alkynyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as propargyl.

[0025] Preferred examples of substituents on the aryl group represented by R_1 include alkyl group, alkoxy group, hydroxyl group, and sulfo group. Preferred among these substituents are alkyl group, carboxyl group, and hydroxyl group.

[0026] Specific examples of the aryl group represented by R_1 include 2-carboxyphenyl, and 2-carboxymethoxyphenyl.

[0027] The heterocyclic group represented by R_1 is a 3- to 10-membered saturated or unsaturated heterocyclic group containing at least one of N, O and S atoms. The heterocyclic group may be monocyclic or may form a condensed ring with other rings.

[0028] The heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic group, more preferably a 5- or 6-membered aromatic heterocyclic group containing nitrogen atoms, most preferably a 5- or 6-membered heterocyclic group containing one or two nitrogen atoms.

[0029] Specific examples of the heterocyclic group include pyrrolidinyl, piperidinyl, piperadiny, imidazolyl, pyrazolyl, pyridyl, and quinolyl. Preferred among these heterocyclic groups are imidazolyl and pyridyl.

[0030] The heterocyclic group represented by R_1 may have substituents. Examples of these substituents include those exemplified as the aliphatic hydrocarbon group represented by R_1 , alkyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methyl and ethyl, alkenyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as vinyl and allyl, and alkynyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as propargyl.

[0031] Preferred examples of substituents on the heterocyclic group represented by R_1 include alkyl group, alkoxy group, hydroxyl group, and sulfo group. Preferred among these substituents are alkyl group, carboxyl group, and hydroxyl group.

[0032] The alkylene groups represented by L_1 and L_2 may be the same or different and may be chain-like, branched or cyclic. These alkylene groups may have substituents. Examples of these substituents include those exemplified as the aliphatic hydrocarbon group represented by R_1 , alkenyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as vinyl and allyl, and alkynyl group preferably having from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably

from 2 to 4 carbon atoms such as propargyl.

[0033] Preferred examples of substituents on the alkylene groups represented by L_1 and L_2 include aryl group, alkoxy group, hydroxyl group, carboxyl group, and sulfo group. Preferred among these substituents are aryl group, carboxyl group, and hydroxyl group.

5 **[0034]** The alkylene groups represented by L_1 and L_2 are each preferably an alkylene group having an alkylene moiety having from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms, most preferably a substituted or unsubstituted methylene or ethylene.

10 **[0035]** Specific preferred examples of the alkylene group include methylene, ethylene, trimethylene, methymethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1,2-cyclohexylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, 2-hydroxyethylmethylene, carbamoylmethylmethylene, phenylmethylene, benzylmethylene, 4-imidazolylmethylmethylene, and 2-methylthioethylmethylene. Preferred among these alkylene groups are methylene, ethylene, methymethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, benzylmethylene, 4-imidazolylmethylmethylene, and 2-methylthioethylmethylene. Particularly preferred among these alkylene groups are methylene, ethylene, methymethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, hydroxymethylmethylene, and benzylmethylene.

15 **[0036]** The cations represented by M_1 and M_2 each are an organic or inorganic cation. Examples of these cations include alkali metal ions (e.g., Li^+ , Na^+ , K^+ , Cs^+), alkaline earth metal ions (e.g., Mg^+ , Ca^+), ammonium ions (e.g., ammonium ion, trimethylammonium ion, triethylammonium, tetramethylammonium ion, tetraethylammonium ion, tetrabutylammonium ion, 1,2-ethanediammonium ion), pyridinium ion, imidazolium ion, and phosphonium ions (e.g., tetrabutylphosphonium ion). M_1 and M_2 are preferably alkali metal ions or ammonium ions, more preferably Na^+ , K^+ or NH_4^+ .

[0037] Preferred among the compounds represented by formula (I) is one represented by formula (I-a):



35 **[0038]** In the foregoing general formula (I-a), L_1 and M_1 have the same meaning as defined in formula (I). The preferred range of L_1 and M_1 are also the same as in formula (I). M_{a1} and M_{a2} have the same meaning as M_2 in formula (I).

[0039] In formula (I-a), it is more preferable that L_1 be a substituted or unsubstituted methylene or ethylene and M_1 , M_{a1} and M_{a2} be any of hydrogen atom, alkali metal and ammonium. It is most preferable that L_1 be a substituted or unsubstituted methylene and M_1 , M_{a1} and M_{a2} be any of hydrogen atom, alkali metal and ammonium. It is particularly preferable that L_1 be a substituted or unsubstituted methylene having from 1 to 10 carbon atoms in total, including substituents, and M_1 , M_{a1} and M_{a2} be any of hydrogen atom, Na^+ , K^+ and NH_4^+ .

40 **[0040]** When the compound represented by formula (I) has asymmetric carbon atoms in its molecule, at least one asymmetric carbon atom is preferably in S-form. When there are two or more asymmetric carbon atoms, it is preferred that the asymmetric carbon moiety have more S-forms.

45 **[0041]** In order to prevent the reduction of magnetic output, it is preferred that the processing method of the present invention use the compound represented by formula (I).

[0042] Specific examples of the compound represented by formula (I) will be given below, but the present invention should not be construed as being limited thereto.

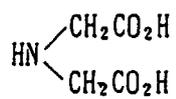
[0043] The symbol (S) indicates that the marked asymmetric carbon moiety is in S-form. The unmarked compounds each are a mixture of R-form and S-form.

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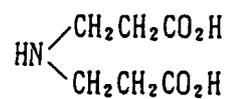
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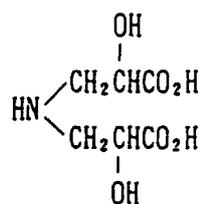
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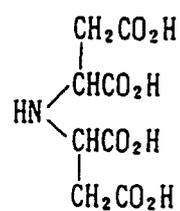
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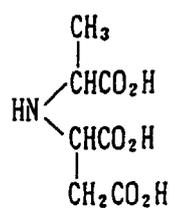
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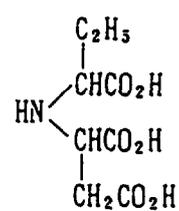
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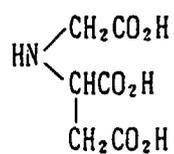
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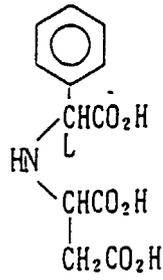
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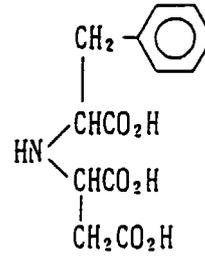
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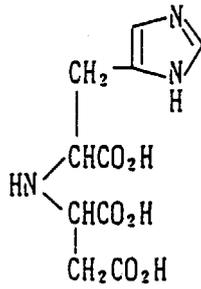
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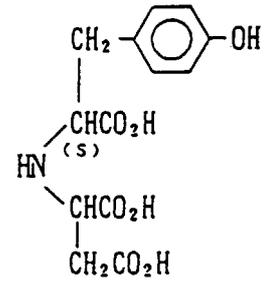
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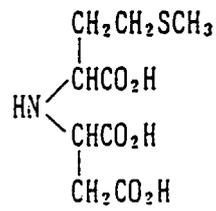
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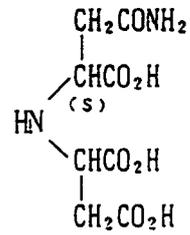
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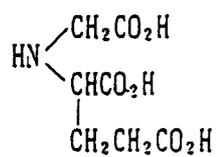
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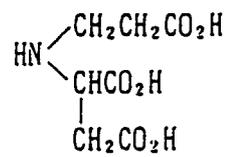
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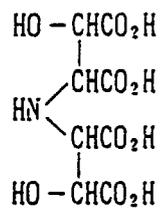
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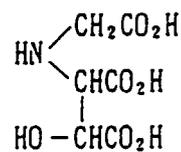
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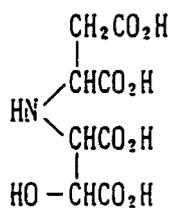
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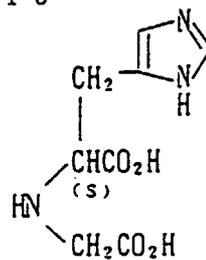
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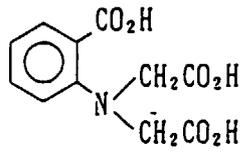
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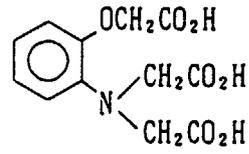
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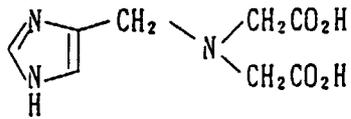
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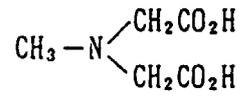
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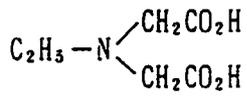
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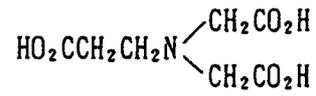
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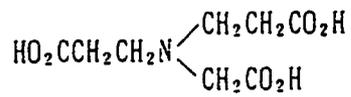
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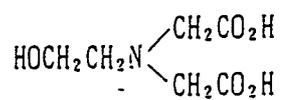
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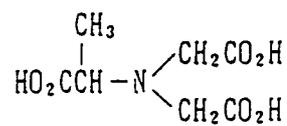
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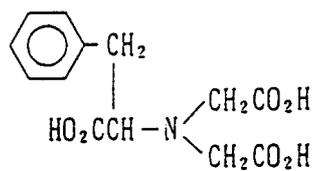
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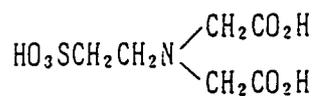
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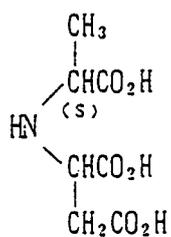
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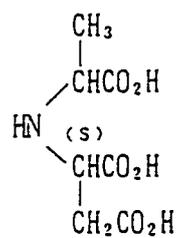
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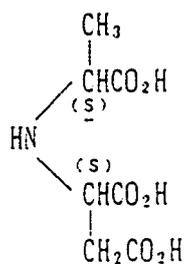
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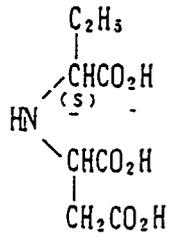


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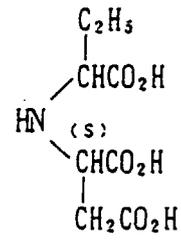
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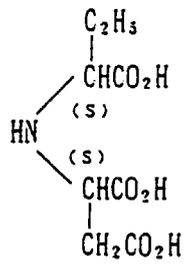
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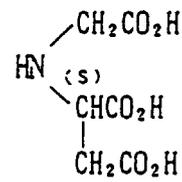
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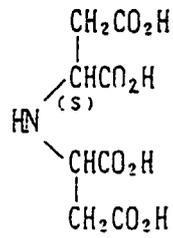
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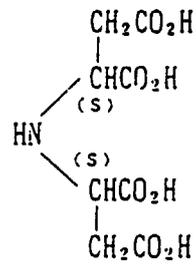
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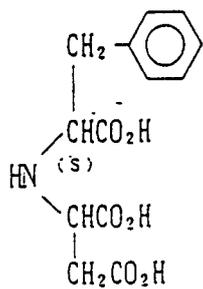
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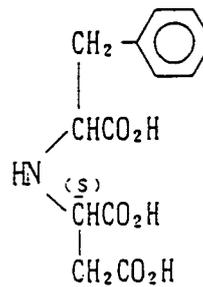
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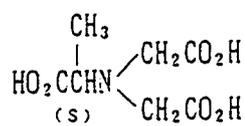
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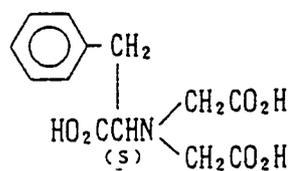
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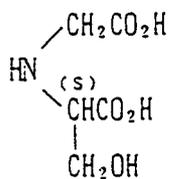
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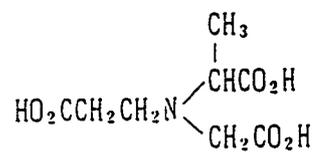
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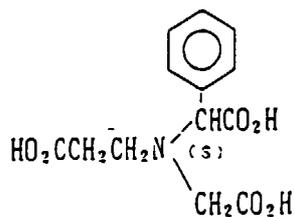
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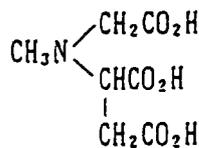
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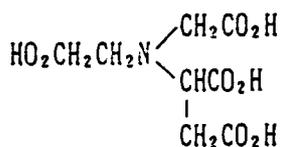
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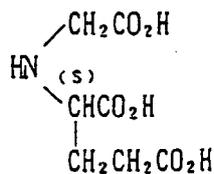
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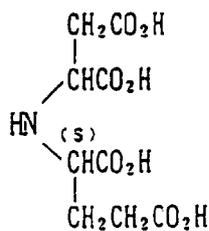
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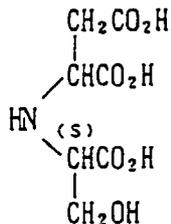
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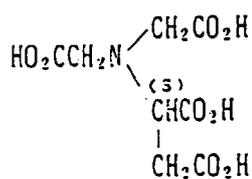
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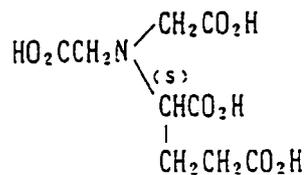
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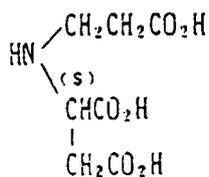
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I - 5 3



I - 5 4



[0044] Preferred among these exemplified compounds are Compounds (I-7), (I-14), (I-15), (I-44) and (I-54). Particularly preferred among these compounds are Compounds (I-44) and (I-54).

[0045] The foregoing compounds may have a cation substituted for hydrogen atom in the carboxyl group. The cat-

ion has the same meaning as M₁ or M₂ in formula (I).

[0046] The synthesis of the compound of the present invention represented by formula (I) can be accomplished by any proper method as described in "Journal of Inorganic and Nuclear Chemistry", Vol. 35, page 523, 1973, Swiss Patent 561,604, German Patents 3912551A1, 3939755A1 and 3939756A1, JP-A-5-265159, JP-A-6-59422 (The synthesis of Exemplary Compounds I-42, I-43, I-46, I-52 and I-53 in L-form is described in Synthesis Examples 1, 2, 3, 4 and 6), JP-A-6-95319 (The synthesis of Exemplary Compounds I-8, I-11, I-37, I-38 and I-40 in L-form is described in Synthesis Examples 2 to 6), JP-A-6-161054, JP-A-6-161065, "Helvetica Chimica Acta", Vol. 38, page 2,038, 1955 (The synthesis of Exemplary Compound I-54 is described), and "Journal of American Chemical Society", Vol. 74, page 1,942, 1952 (The synthesis of Exemplary Compound I-15 in D-form and L-form in admixture is described).

[0047] The compound group having as a partial structure an aspartic acid or glutamic acid structure such as Compounds I-15 and I-54 can be synthesized by subjecting aspartic acid or glutamic acid and an acrylic acid derivative or acrylonitrile derivative to addition reaction. (When an acrylonitrile derivative is used, it is necessary that N-(2-cyanoalkyl)-amino acid produced by the addition reaction be subjected to hydrolysis.) For details, reference can be made to JP-A-9-120129, pp. 69 - 70.

[0048] The aspartic acids and glutamic acids to be used as starting materials are not specifically limited. Those industrially available can be used. These aspartic acids and glutamic acids may be in the form of metal salt such as alkali metal salt (e.g., Li salt, Na salt, K salt, Rb salt, Cs salt), alkaline earth metal salt (e.g., Ca salt, Mg salt, Ba salt) and transition metal salt (e.g., Zn salt), tertiary ammonium salt such as triethylammonium salt, quaternary ammonium salt such as tetrabutylammonium salt or pyridinium salt. It goes without saying that these aspartic acids and glutamic acids may be in the form of free acid. These acids may also be in the form of solid, slurry or aqueous solution.

[0049] The asymmetric carbon moiety may be in S-form, R-form or mixture thereof, preferably S-form.

[0050] In the present invention, the ferric complex (III) of compound represented by formula (I) may be added in the form of ferric complex (III) previously obtained. Alternatively, a compound represented by formula (I) and a ferric salt (III) (e.g., ferric nitrate (III), ferric chloride) may be present in the processing solution to cause complex-formation therein.

[0051] Compounds of the present invention represented by formula (I) may be used singly or in combination of two or more thereof.

[0052] In the present invention, the compound represented by formula (I) may be used in slight excess of the amount required for complex-forming of ferric ion (III) (e.g., 0.5 mols, 1 mol, 2 mols per mol of ferric ion (III)). It is usually preferred that the excess be from 0.01 to 15 mol-%.

[0053] The organic acid ferric complex salt(III) to be incorporated in the processing solution having a bleaching ability of the invention may be used in the form of metal salt or ammonium salt. Examples of the alkali metal salt include lithium salt, sodium salt, and potassium salt. Examples of the ammonium salt include ammonium salt, and tetraethylammonium salt. In the present invention, the ammonium ion concentration of the processing solution having a bleaching ability is preferably from 0 to 2.0 mol/l, particularly preferably from 0 to 1.0 mol/l.

[0054] In the present invention, other bleaching agents may be used in combination with the ferric complex (III) of compound represented by formula (I). Examples of these bleaching agents to be used in combination with the ferric complex (III) of compound represented by formula (I) include bleaching agents described in JP-A-4-121739, lower right column, page 4 - lower left column, page 5, including ferric complex salt (III) of organic acid such as ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid, N-methyliminodiacetic acid, N-(hydroxyethyl)iminodiacetic acid and glycoletherdiaminetetraacetic acid and ferric complex salt (III) of 1,3-propanediamine-N,N,N',N'-tetraacetic acid, carbamoyl-based bleaching agents described in European Patent Publication No. 461,413, heterocyclic bleaching agents described in JP-A-4-174432, bleaching agents described in European Patent Publication No. 520457, including ferric complex salt (III) of N-(2-carboxyphenyl)iminodiacetic acid, bleaching agents described in European Patent Publication No. 530828, including ferric complex salt (III) of ethylenediamine-N-(2-carboxyphenyl)-N,N',N'-triacetic acid, bleaching agents described in European Patent Publication No. 567126, including ferric complex salt (III) of N,N'-bis-(1,2-dicarboxyethyl)ethylenediamine, bleaching agents described in European Patent Publication No. 588289, including ferric complex salt (III) of N-(1-carboxy-2-phenylethyl)aspartic acid, bleaching agents described in European Patent Publication No. 591934, including ferric complex salt (III) of N-(1-carboxyethyl)iminodiacetic acid, bleaching agents described in European Patent Publication No. 501479, bleaching agents described in European Patent Publication No. 461670, bleaching agents described in European Patent Publication No. 430000, and ferric complex salt (III) of aminopolycarboxylic acid described in JP-A-3-144446.

[0055] The ferric complex salt (III) of compound represented by formula (I) preferably accounts for 10% or more of all the bleaching agents. All the bleaching agents may be constituted by the ferric complex salt (III) of compound represented by formula (I). Preferably, the ferric complex salt (III) of compound represented by formula (I) accounts for 10% to 100% of all the bleaching agents and the ferric complex salt (III) of aminopolycarboxylic acid other than the compound represented by formula (I) accounts for 90% or less of all the bleaching agents. More preferably, the ferric complex salt (III) of compound represented by formula (I) accounts for 30% to 100%, most preferably 50% to 100% of all

the bleaching agents.

[0056] In the present invention, the concentration of the ferric complex salt (III) of compound represented by formula (I) in the processing solution having a bleaching ability is preferably from 0.003 to 3.00 mols/l, more preferably from 0.02 to 2.00 mols/l, most preferably 0.05 to 1.00 mols/l, particularly preferably from 0.08 to 0.5 mols/l. In the case where the inorganic oxidizing agent as mentioned above is used as well, the total concentration of ferric complex salt (III) is preferably from 0.005 to 0.030 mols/l.

[0057] In the present invention, the bleaching solution preferably comprises a pH buffer incorporated therein. Preferred examples of the pH buffer include organic acids with little odor such as glycolic acid, succinic acid, maleic acid, malonic acid and glutaric acid. Particularly preferred among these pH buffers are glycolic acid, malonic acid, and succinic acid. The concentration of pH buffer is preferably from 0 to 3 mols/l, particularly preferably from 0.2 to 1.5 mols/l.

[0058] The pH value of the processing solution having a bleaching ability of the present invention is preferably from 3.0 to 7.0. The pH value of the bleaching solution is preferably from 3.5 to 5.0 in particular. On the other hand, the pH value of the blixing solution is preferably from 4.0 to 6.5 in particular. When the pH value of the processing solution having a bleaching ability exceeds the above described range, the deterioration of liquid stability is apprehended. On the contrary, when the pH value of the processing solution having a bleaching ability falls below the above described range, the increase in occurrence of stain and the occurrence of precipitation are apprehended. In order to provide such a pH range, it is preferable herein that the organic acid as mentioned above be added as a buffer. Preferred examples of the alkali agent to be used to adjust pH include aqueous ammonia, potassium hydroxide, sodium hydroxide, potassium carbonate, and sodium carbonate.

[0059] In order to adjust the pH value of the processing solution having a bleaching ability of the invention to the above defined range, the foregoing alkali agent and a well-known acid (inorganic acid, organic acid) can be used.

[0060] The processing with the processing solution having a bleaching ability of the invention is preferably effected immediately after color development. In the case of reversal process, it is normally effected via processing with adjusting bath (or bleach accelerating bath). Such an adjusting bath may contain an image stabilizer described later.

[0061] In the present invention, the solution having a bleaching ability may comprise re-halogenating agents, pH buffers, well-known additives, aminopolycarboxylic acids and organic phosphonic acids described in JP-A-3-144446, page (12), incorporated therein besides bleaching agent. Preferred examples of the re-halogenating agent employable herein include sodium bromide, potassium bromide, ammonium bromide, and potassium chloride. The content of the re-halogenating agent is preferably from 0.1 to 1.5 mols, more preferably from 0.1 to 1.0 mols, particularly preferably from 0.1 to 0.8 mols per l of processing solution having a bleaching ability.

[0062] However, the solution having a bleaching ability, if it is a blixing solution, doesn't need to comprise a re-halogenating agent incorporated therein.

[0063] In the present invention, the solution having a bleaching ability preferably comprises a nitric acid compound such as ammonium nitrate and sodium nitrate incorporated therein. In the present invention, the concentration of nitric acid compound per l of the solution having a bleaching ability is preferably from 0 to 0.3 mols, more preferably from 0 to 0.2 mols.

[0064] In general, a nitric acid compound such as ammonium nitrate and sodium nitrate is added to prevent the corrosion of stainless steel. In the present invention, even when such a nitric acid compound is used in a small amount, corrosion can hardly take place, and desilvering can be fairly effected.

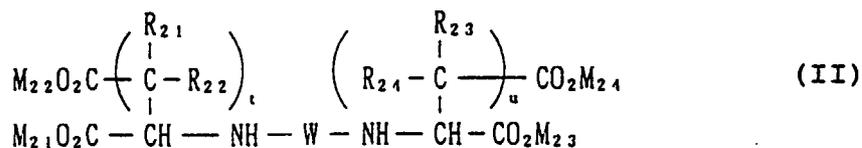
[0065] In this case, also, the solution having a bleaching ability, if it is a blixing solution, doesn't need to comprise a re-halogenating agent incorporated therein.

[0066] The replenishment rate of the solution having a bleaching ability is preferably from 30 to 600 ml, more preferably from 50 to 400 ml per m² of light-sensitive material.

[0067] The processing time with the bleaching solution is preferably 7 minutes or less, particularly preferably from 10 seconds to 5 minutes, most preferably from 15 seconds to 3 minutes.

[0068] The processing solution having a fixing ability will be further described hereinafter. The processing solution having a fixing ability to be used in the present invention comprises as an essential component a complex-forming agent selected from the group consisting of a compound represented by formula (II), EDTA and phosphonic acids incorporated therein.

[0069] The compound represented by formula (II) will be further described hereinafter.



[0070] In formula (II), the aliphatic hydrocarbon group, aryl group and heterocyclic group represented by R_{21} , R_{22} , R_{23} and R_{24} have the same meaning as those represented by R_1 in formula (I). The preferred range of R_{21} , R_{22} , R_{23} and R_{24} are also the same as in formula (I).

[0071] R_{21} , R_{22} , R_{23} and R_{24} are each preferably a hydrogen atom or hydroxyl group, more preferably hydrogen atom.

[0072] The suffixes t and u each represent an integer of 0 or 1, preferably 1.

[0073] The divalent connecting group represented by W is preferably represented by formula (W):

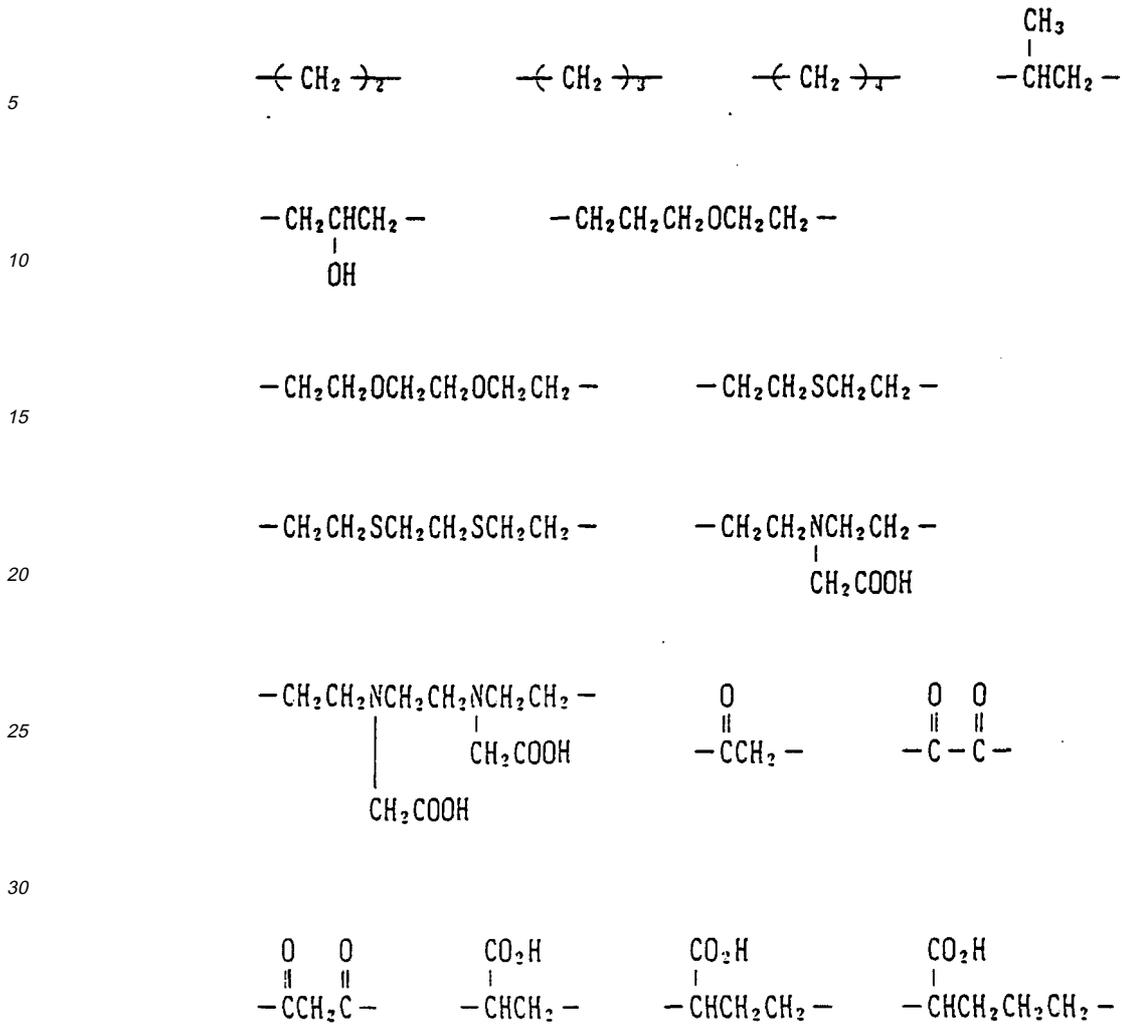


[0074] In formula (W), W^1 and W^2 may be the same or different and each represent a C_{2-8} straight-chain or branched alkylene group such as ethylene, propylene and trimethylene, C_{5-10} cycloalkylene group such as 1,2-cyclohexylene, C_{6-10} arylene group such as *o*-phenylene, C_{7-10} aralkylene group such as *o*-xylylenyl, divalent nitrogen-containing heterocyclic group or carbonyl group. The divalent nitrogen-containing heterocyclic group is preferably a 5- or 6-membered heterocyclic group having nitrogen atoms as heteroatoms, more preferably a heterocyclic group having cycles connected to each other via adjacent carbon atoms such as imidazolyl group. D represents $-\text{O}-$, $-\text{S}-$ or $-\text{N}(\text{R}_w)-$. R_w represents a hydrogen atom or a C_{1-3} alkyl group (e.g., methyl) or C_{6-10} aryl group (e.g., phenyl) which may be substituted by carboxyl group, phosphono group, hydroxyl group or sulfo group.

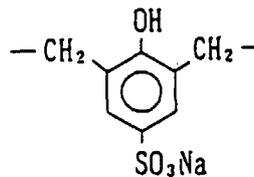
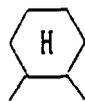
[0075] W_1 and W_2 each are preferably a C_{2-4} alkylene group.

[0076] The suffix v represents an integer of from 0 to 3. When v is 2 or 3, the plurality of $(\text{W}^1 - \text{D})$'s may be the same or different. The suffix w is preferably 0 to 2, more preferably 0 or 1, particularly preferably 0. The suffix w represents an integer of from 1 to 3. When w is 2 or 3, the plurality of W_2 's may be the same or different. The suffix w is preferably 1 or 2.

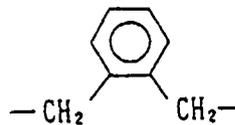
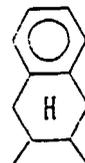
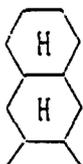
[0077] Examples of W will be given below.



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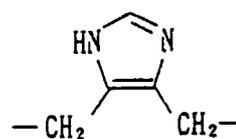
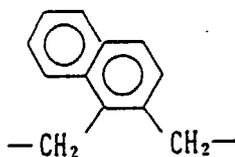
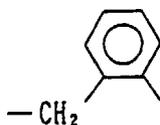


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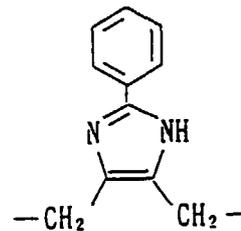
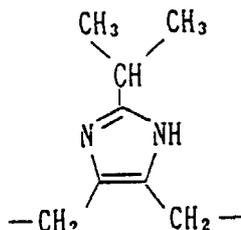
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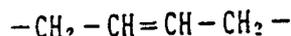
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[0078] Preferred among the groups represented by W are ethylene, propylene, trimethylene, and 2,2-dimethyltrimethylene. Particularly preferred among these groups are ethylene, and trimethylene.

45 **[0079]** M_{21} , M_{22} , M_{23} and M_{24} each represent a hydrogen or cation, and has the same meaning as in as defined in M_1 and M_2 in formula (I).

[0080] Preferred among the compounds represented by formula (II) are those wherein R_{22} and R_{24} each are a hydrogen atom and t and u each are 1. Particularly preferred among these compounds are those wherein R_{21} , R_{22} , R_{23} and R_{24} each are a hydrogen atom and t and u each are 1.

50 **[0081]** Most desirable among the compounds represented by formula (II) are those wherein R_{21} , R_{22} , R_{23} and R_{24} each are a hydrogen atom, t and u each are 1, W is ethylene and M_{21} , M_{22} , M_{23} and M_{24} each are selected from the group consisting of hydrogen atom, Na^+ , K^+ and NH_4^+ and those wherein R_{21} , R_{22} , R_{23} and R_{24} each are a hydrogen atom, t and u each are 1, W is trimethylene and M_{21} , M_{22} , M_{23} and M_{24} each are selected from the group consisting of hydrogen atom, Na^+ , K^+ and NH_4^+ .

55 **[0082]** When the compound represented by formula (II) has asymmetric carbon atoms in its molecule, at least one asymmetric carbon atom is preferably in S-form. When there are two or more asymmetric carbon atoms, it is preferred that the asymmetric carbon moiety have more S-forms.

[0083] Specific examples of the compound represented by formula (II) will be given below, but the present invention

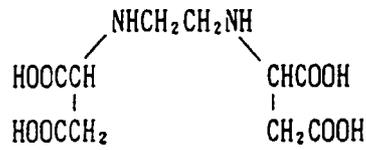
should not be construed as being limited thereto.

[0084] The symbol (S) indicates that the marked asymmetric carbon moiety is in S-form. The unmarked compounds each are a mixture of R-form and S-form.

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II-1

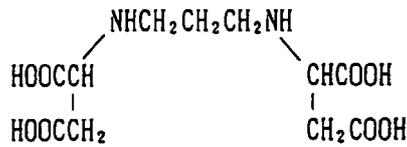
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II-2

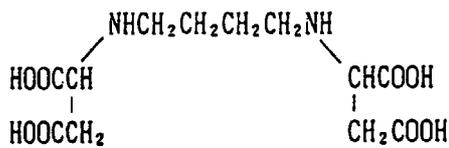
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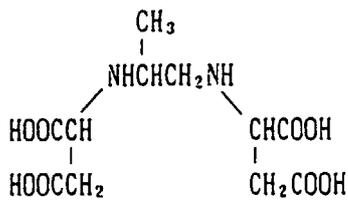
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II-4

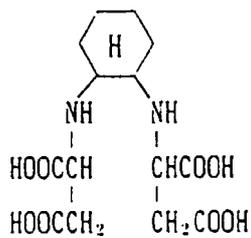
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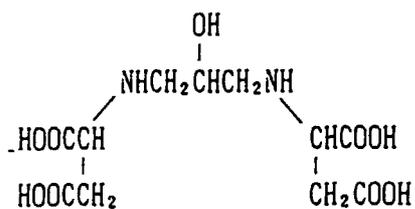
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II-6

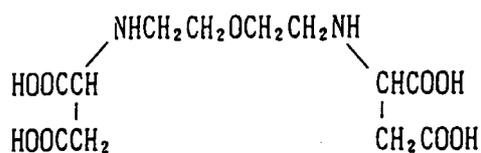
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II-7

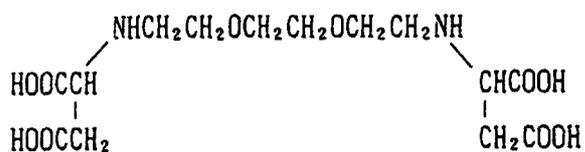
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II-8

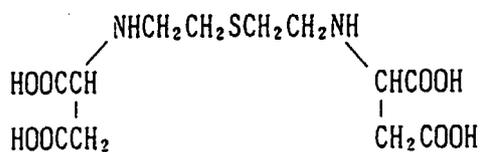
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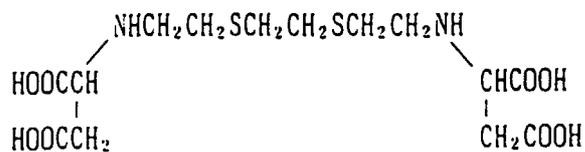
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II-10

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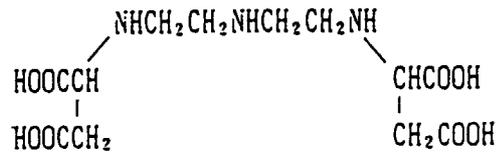


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II-11

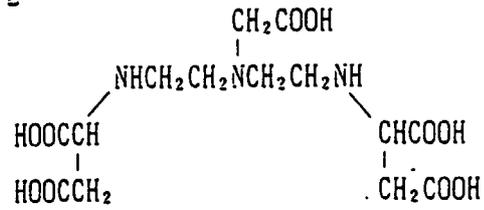
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II-12

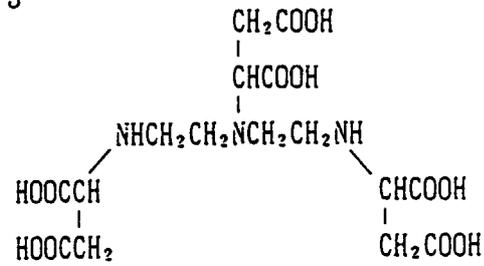
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II-13

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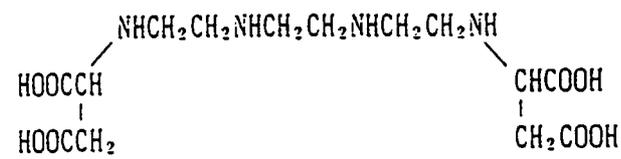


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II-14

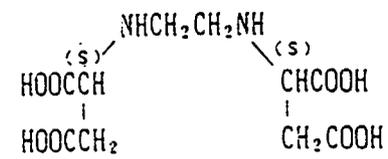
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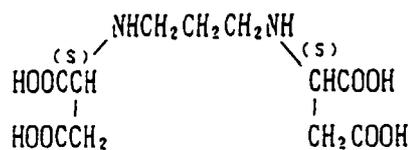
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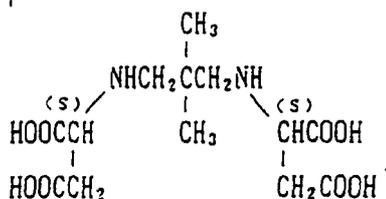
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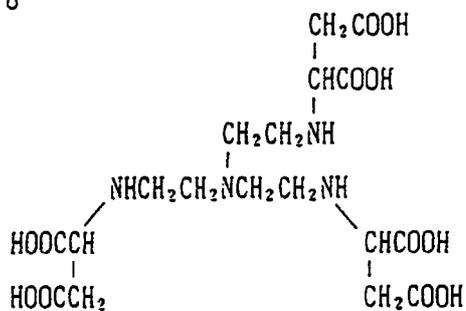
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II-18

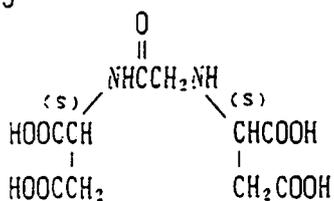
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II-19

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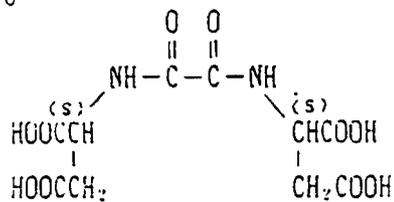


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II-20

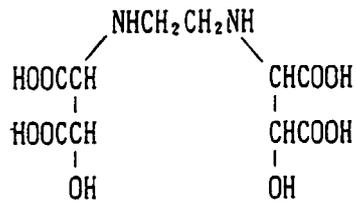
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II-2 1

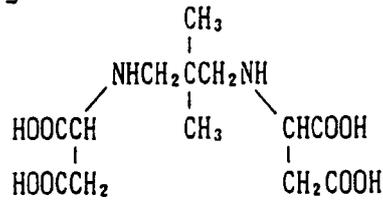
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II-2 2

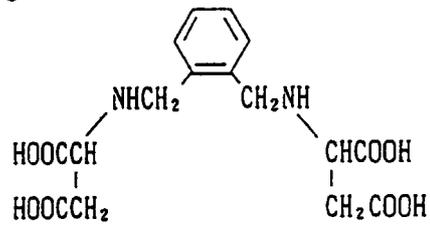
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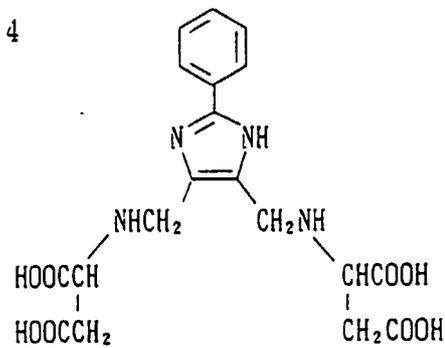
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II-2 4

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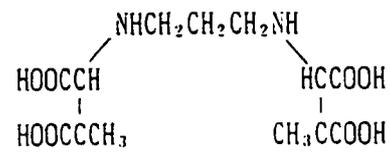


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II-2 5

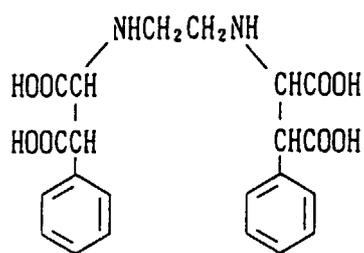
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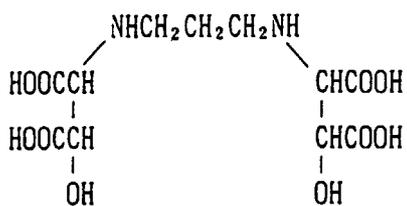
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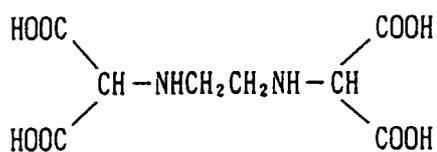
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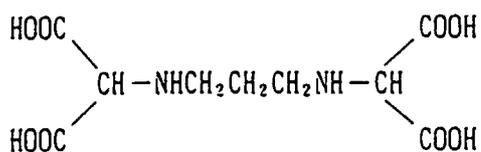
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II-29

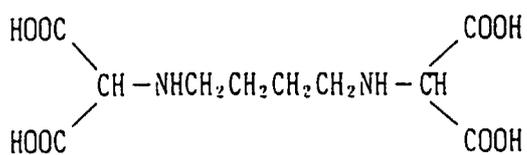
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II-30

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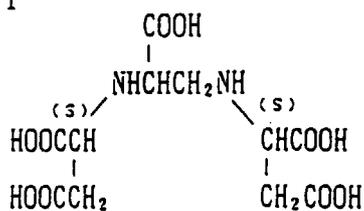


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II-3 1

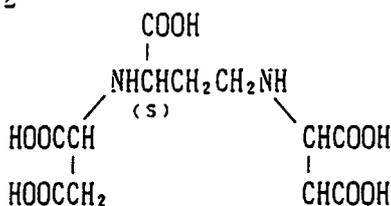
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II-3 2

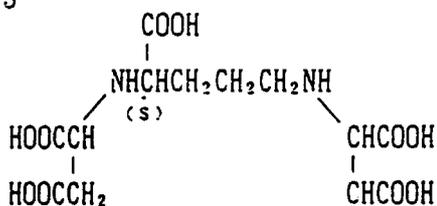
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II-3 3

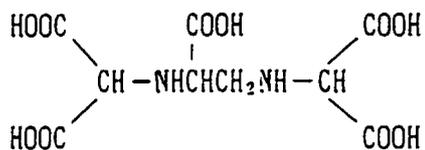
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II-3 4

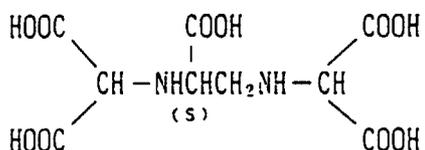
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II-3 5

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[0085] Preferred among the foregoing exemplified compounds are Compounds II-1, II-2, II-6, II-15 and II-16. Particularly preferred among these compounds are Compounds II-15 and II-16.

[0086] The foregoing compounds may have a cation substituted for hydrogen atom in the carboxyl group. The cation has the same meaning as in M_1 or M_2 in formula (I).

[0087] There can be found many commercially available compounds represented by formula (II). Further, the com-

pounds represented by formula (II) can be synthesized by any proper method described in JP-A-63-199295, JP-A-3-173857, "Bulletin of Chemical Society of Japan", Vol. 46, page 884, 1973, and "Inorganic Chemistry", Vol. 7, page 2,405, 1968 (The synthesis of Exemplary Compound II-15 in S,S-form is described).

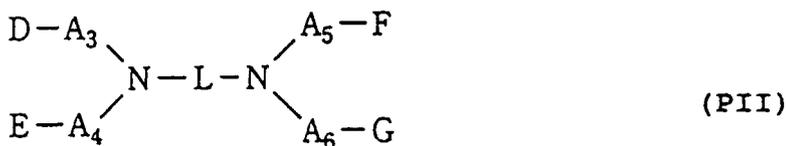
[0088] The compounds represented by formula (II), EDTA or phosphonic acids of the present invention each may be used singly or in combination of two or more thereof. Alternatively, compounds represented by formula (II), EDTA and phosphonic acids may be used in combination with each other.

[0089] The compound represented by formula (II) may be used in the form of alkali metal salt or ammonium salt. Examples of the alkali metal salt include lithium salt, sodium salt, and potassium salt. Examples of the ammonium salt include ammonium salt, and tetraethylammonium salt. In the present invention, the ammonium ion concentration of the processing solution having a bleaching ability is preferably from 0 to 2.0 mol/l, particularly preferably from 0.2 to 1.0 mol/l.

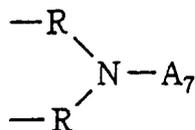
[0090] In the present invention, the concentration of the compound represented by formula (II) is preferably from 0.001 to 1.00 mols/l, more preferably from 0.005 to 0.9 mols/l, most preferably from 0.01 to 0.8 mols/l.

[0091] The compound represented by formula (P) will be further described hereinafter.

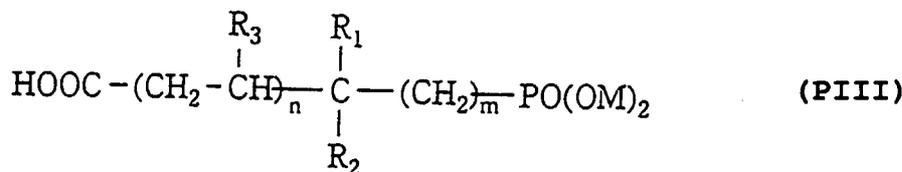
[0092] As the organic phosphonic acid to be used herein there may be used any organic phosphonic acid such as alkylphosphonic acid, phosphonocarboxylic acid and aminopolyphosphonic acid. Particularly preferred among these organic phosphonic acids are alkylphosphonic acid and aminopolyphosphonic acid. The formulae of organic phosphonic acids employable herein will be given below in formula.



wherein A₁ to A₆ each represent a C₁₋₃ substituted or unsubstituted alkylene group; Z represents a C₁₋₃ alkylene group, cyclohexane group, phenylene group, -R-O-R, -ROROR-,



or >N-A₇ (in which R is a C₁₋₃ alkylene group, and A₇ is a hydrogen atom, C₁₋₃ hydrocarbon group, lower aliphatic carboxylic acid group or lower alcohol group); B, C, D, E, F and G each represent -OH, -COOM or -PO₃M₂ (in which M is a hydrogen atom, alkali metal atom or ammonium group), with the proviso that at least one of B, C, D, E, F and G is -PO₃M₂; and L has the same meaning as Z in formula (PI).

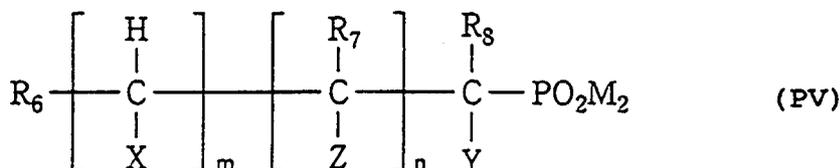


wherein R₁ represents -COOM or -PO(OM)₂; R₂ represents a hydrogen atom, C₁₋₄ alkyl group, -(CH₂)_n or COOM; R₃ represents a hydrogen atom or -COOM; M represents a hydrogen atom, alkali metal atom or ammonium group; m represents an integer of 0 or 1; n' represents an integer of from 1 to 4; and q represents an integer of 0 or 1, with the proviso

that when m is 0, R₁ is -PO(OM)₂.



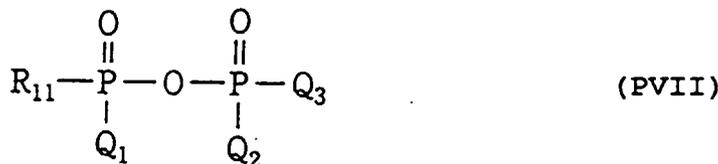
5 wherein R₄ represents a C₁₋₆ substituted or unsubstituted alkyl group, C₆₋₁₂ substituted or unsubstituted aryl group, aralkyl group or nitrogen-containing 6-membered ring (Examples of substituents on these groups include -OH, -OR₅ (in which R₅ is a C₁₋₄ alkyl group), -PO₃M₂, -CH₂PO₃M₂, -N(CH₂PO₃M₂)₂, -COOM₂, and -N(CH₂COOM₂)); and M represents a hydrogen atom, alkali metal atom or ammonium group.



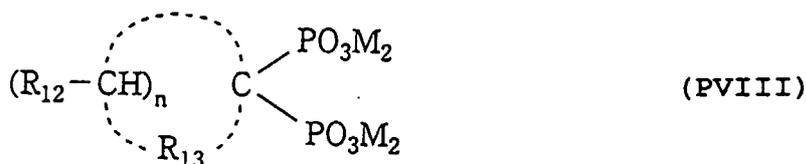
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20 wherein R₆ and R₇ each are a hydrogen atom, C₁₋₄ alkyl group, -COOH, NJ₂ (in which J is H, OH, C₁₋₃ alkyl group or -C₂H₄OH); R₈ represents a hydrogen atom, C₁₋₃ alkyl group, -OH or -NL₂ (in which L is H, OH, -CH₂, -C₂H₅, -C₂H₄OH or -PO₃M₂); X, Y and Z each represent a hydrogen atom, -OH, -COOM or PO₃M₂; M represents a hydrogen atom, alkali metal atom or ammonium group; n represents an integer of 0 or 1; and m represents an integer of 0 or 1.



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30 wherein R₉ and R₁₀ each represent a hydrogen atom, alkali metal atom, ammonium group, C₁₋₁₂ substituted or unsubstituted alkyl group, alkenyl group or cyclic alkyl group.



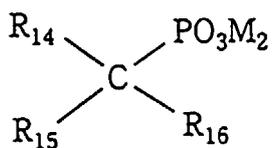
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45 wherein R₁₁ represents a C₁₋₁₂ substituted or unsubstituted alkyl group, C₁₋₁₂ substituted or unsubstituted alkoxy group, C₁₋₁₂ substituted or unsubstituted monoalkylamino group, C₂₋₁₂ substituted or unsubstituted dialkylamino group, amino group, C₆₋₂₄ substituted or unsubstituted aryloxy group, C₆₋₂₄ substituted or unsubstituted arylamino group or amyloxy group; and Q₁ to Q₂ each represent -OH, C₁₋₂₄ substituted or unsubstituted alkoxy group, C₇₋₂₄ substituted or unsubstituted aralkyloxy group or allyloxy group, -OM₂ (in which M₂ is a cationic group), amino group, morpholino group, cyclic amino group, alkylamino group, dialkylamino group, arylamino group or alkyloxy group.



50
55 wherein R₁₂ and R₁₃ each represent a hydrogen atom, C₁₋₆ alkyl group or imine (which may be substituted by a C₁₋₆ alkyl group or CH₂CH₂COONa); M represents a hydrogen atom, alkali metal atom or ammonium group; and n represents

sents an integer of from 2 to 16.

5



(PIX)

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wherein R_{14} to R_{16} each represent a hydrogen atom or alkyl group which may have as a substituent $-OH$, $-OC_nH_{2n+1}$ (in which n is an integer of from 1 to 4), $-PO_3M_2$, $-CH_2PO_3M$ (in which M is a hydrogen atom, alkali metal atom or ammonium group), $-NR_2$ (in which R is a C_{1-6} alkyl group) or $-N(CH_2PO_3M_2)_2$.

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[0093] Preferred among the compounds represented by the foregoing formulae are those represented by formulae (PII) and (PV).

[0094] Specific examples of the compounds represented by formulae (PI) to (PIX) will be given below.

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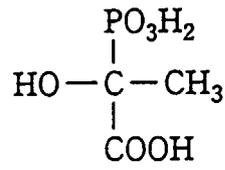
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P-1

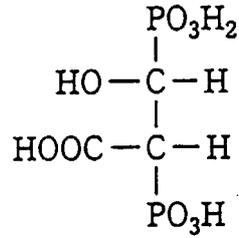
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P-2

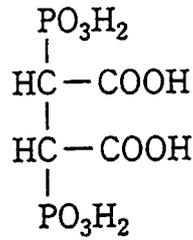
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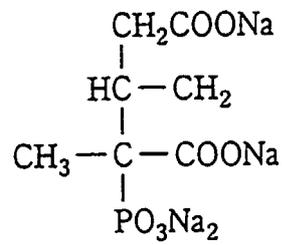
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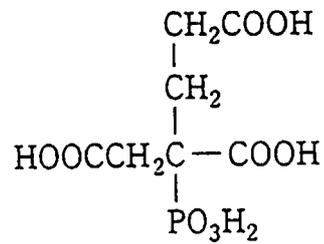
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P-5

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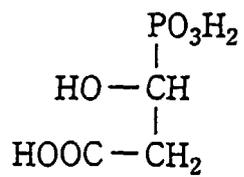


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P-6

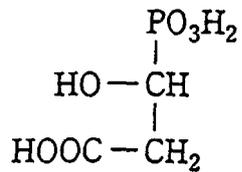
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P-7

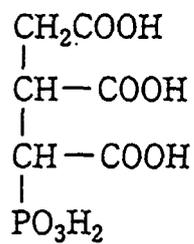
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P-8

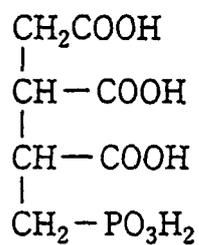
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P-9

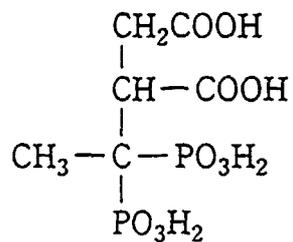
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P-10

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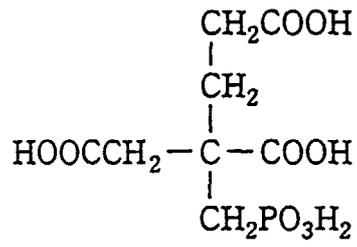


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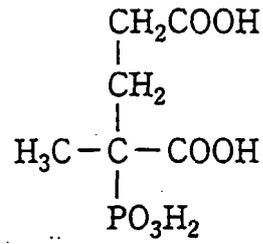
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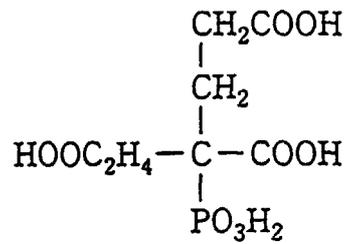
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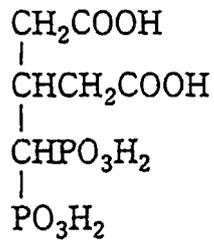
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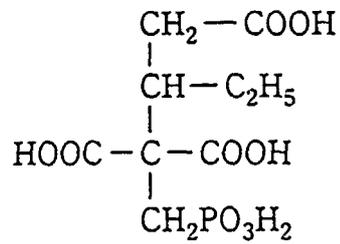
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P-15

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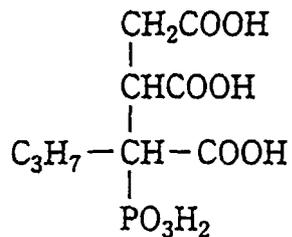


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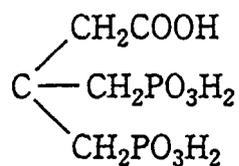
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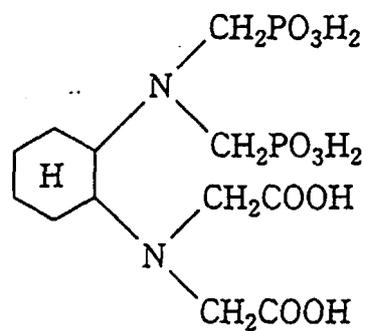
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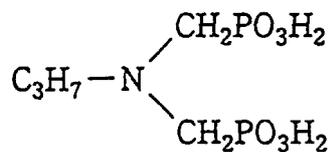
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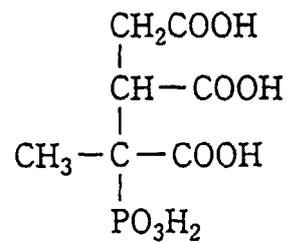
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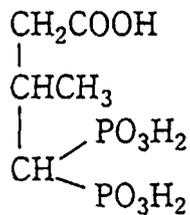
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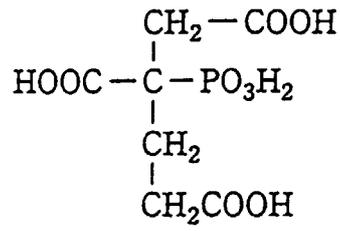
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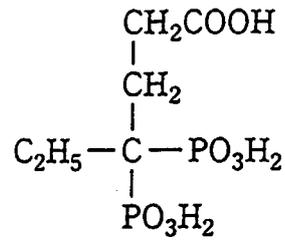


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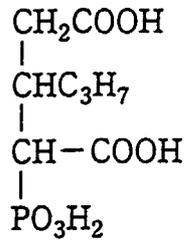
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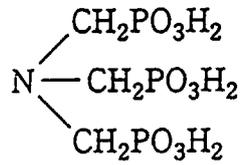
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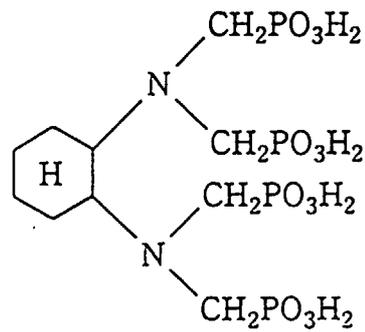
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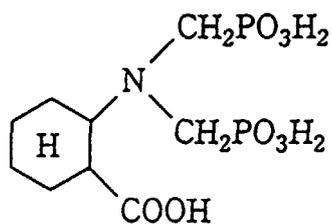


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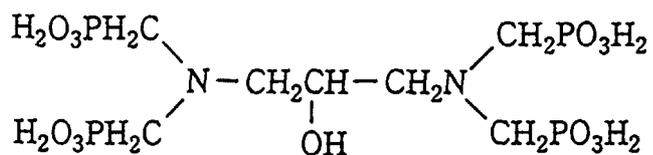
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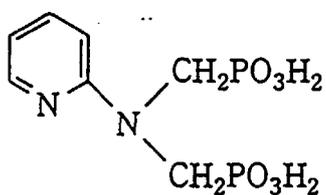
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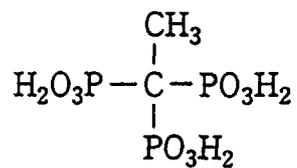
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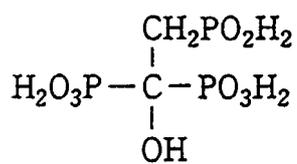
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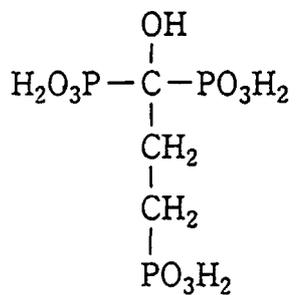
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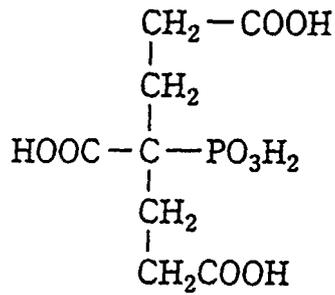
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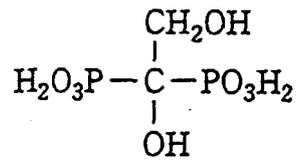
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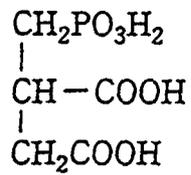
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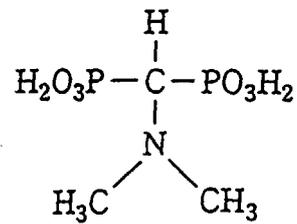
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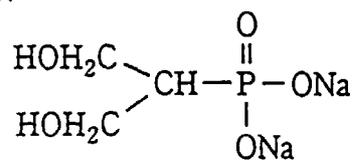
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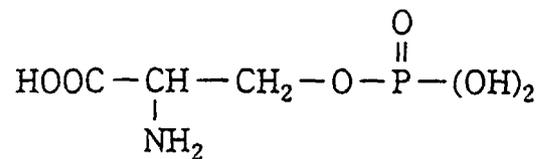
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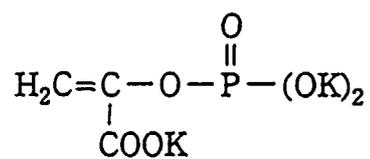


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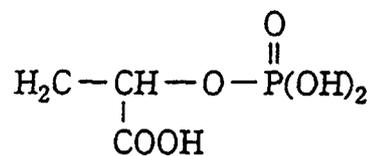
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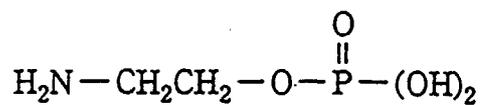
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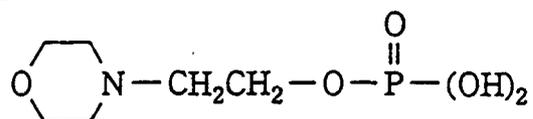
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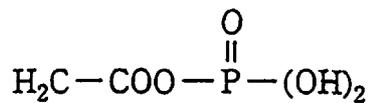
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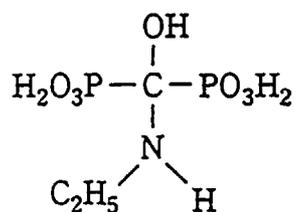
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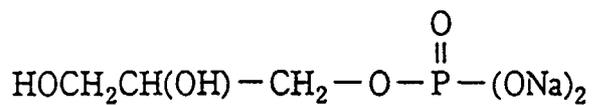
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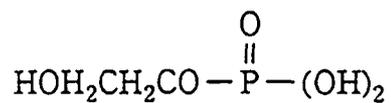
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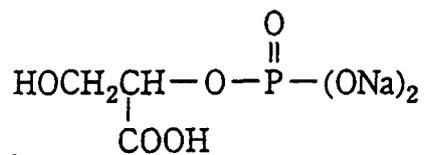
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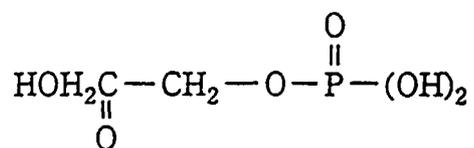
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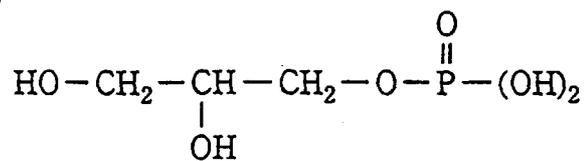
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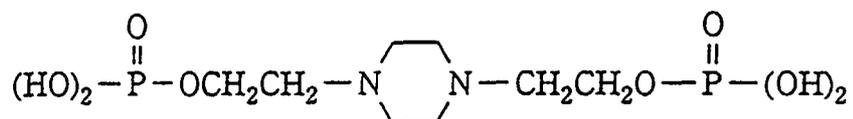
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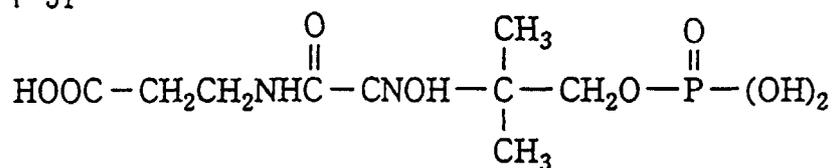
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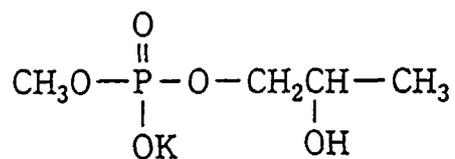
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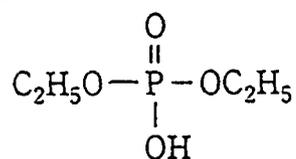
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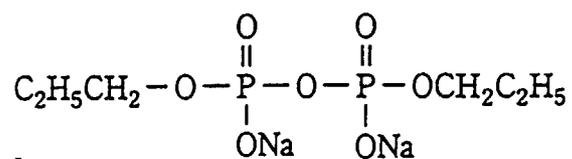


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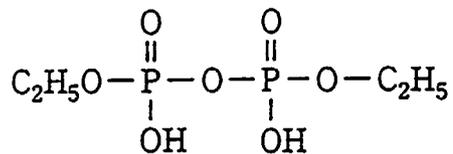
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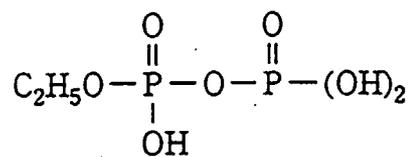
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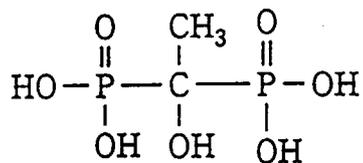
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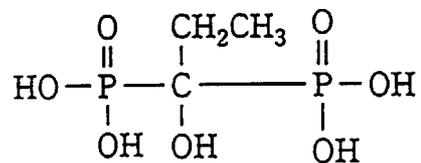
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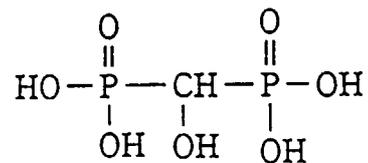
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P-59

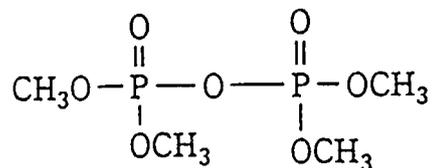
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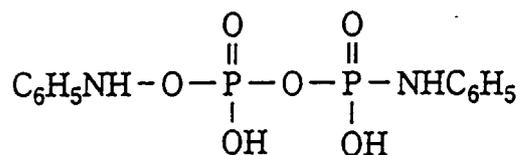
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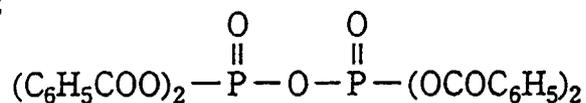


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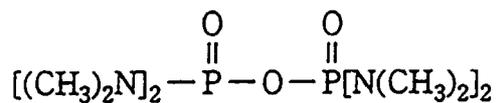
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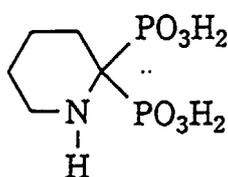
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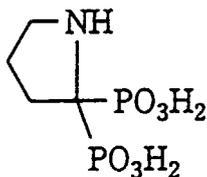
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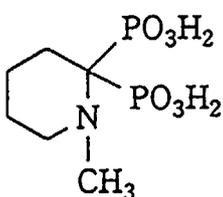
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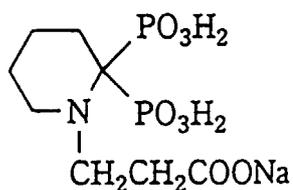
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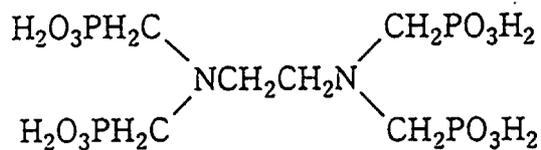
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P-67



P-68



[0095] The foregoing compounds represented by formulae (PI) to (PIX) can be synthesized by any well-known method. Many of these compounds are commercially available.

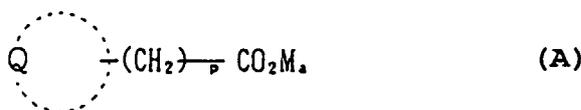
[0096] Preferred among these compounds are P-19, P-25, P-26, P-30, P-31, P-34, P-41, P-44, P-56, P-57, P-59 and P-68. Particularly preferred among these compounds are P-25, P-57 and P-68.

[0097] The compound of the present invention represented by any of formulae (PI) to (PIX) is preferably incorporated in an amount of from 0.001 to 0.5 mols, more preferably from 0.005 to 0.4 mols, most preferably from 0.01 to 0.3 mols per 1 of processing solution having a fixing ability.

[0098] It is also preferred that the compound represented by any of formulae (PI) to (PIX) be incorporated in the processing solution having a bleaching ability in an amount similar to that defined in the processing solution having a fixing ability.

[0099] In the present invention, the compounds represented by formulae (PI) to (PIX) may be used singly or in combination of two or more thereof. The compounds represented by formulae (PI) to (PIX) may be used in combination with the compound represented by formula (II).

[0100] The compound represented by formula (A) which is preferably incorporated in the fixing solution besides the foregoing complex-forming agent in the process of the present invention will be further described hereinafter. The term "number of carbon atoms" as used hereinafter means the number of carbon atoms excluding those in the substituent moiety.



[0101] In formula (A), the heterocyclic residue formed by Q is a 3- to 10-membered saturated or unsaturated heterocyclic residue containing at least one of N, O and S atoms which may be monocyclic or may form a condensed ring with other rings.

[0102] The heterocyclic residue is preferably a 5- or 6-membered aromatic heterocyclic residue, more preferably a 5- or 6-membered aromatic heterocyclic residue containing nitrogen atoms, most preferably a 5- or 6-membered aromatic heterocyclic residue containing one or two nitrogen atoms.

[0103] Specific examples of the heterocyclic residue include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidinyl, 3-piperidyl, 3-piperidyl, 4-piperidyl, 2-piperazinyl, 2-morpholinyl, 3-morpholinyl, 2-chenyl, 2-furyl, 3-furyl, 2-pyrrolyl, 3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 4-pyrazolyl, 2-pyridyl, 3-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-prinyl, 6-prinyl, 8-prinyl, 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-phthaladinyl, 5-phthaladinyl, 6-phthaladinyl, 2-naphthylidinyl, 3-naphthylidinyl, 4-naphthylidinyl, 2-quinoxalyl, 5-quinoxalyl, 6-quinoxalyl, 2-quinazolyl, 4-quinazolyl, 5-quinazolyl, 6-quinazolyl, 7-quinazolyl, 8-quinazolyl, 3-cinnolyl, 4-cinnolyl, 5-cinnolyl, 6-cinnolyl, 7-cinnolyl, 8-cinnolyl, 2-pteridinyl, 4-pteridinyl, 6-pteridinyl, 7-pteridinyl, 1-acrydinyl, 2-acrydinyl, 3-acrydinyl, 4-acrydinyl, 9-acrydinyl, 2-(1,10-phenanthrolyl), 3-(1,10-phenanthrolyl), 4-(1,10-phenanthrolyl), 5-(1,10-phenanthrolyl), 1-phenazinyl, 2-phenazinyl, 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolidyl, 4-thiazolidyl, and 5-thiazolidinyl.

[0104] Preferred among these 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-prinyl, 6-prinyl, 8-prinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthaladinyl, 2-quinoxalyl, 5-quinoxalyl, 2-quinazolyl, 4-quinazolyl, 8-quinazolyl, 3-cinnolyl, 8-cinnolyl, 2-(1,10-phenanthrolyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl, and 4-oxazolyl. More desirable among these heterocyclic residues 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. Most preferably among these heterocyclic residues are 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl, and 8-quinolyl. Particularly preferred among these heterocyclic residues are 2-imidazolyl, 4-imidazolyl, 2-pyridyl, and 2-quinolyl. Further, particularly most preferred among these heterocyclic residues is 2-pyridyl.

[0105] The foregoing heterocyclic residue may have substituents besides $(\text{CH}_2)_p\text{CO}_2\text{M}_a$. Examples of these substituents include alkyl group preferably having from 1 to 12 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 3 carbon atoms such as methyl and ethyl, aralkyl group preferably having from 7 to 20 carbon atoms, more preferably from 7 to 15 carbon atoms, particularly preferably from 7 to 11 carbon atoms such as phenylmethyl and phenylethyl, alkenyl group preferably having from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as allyl, alkynyl group preferably having from 2 to

12 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as propargyl, aryl group preferably having from 6 to 20 carbon atoms, more preferably from 6 to 15 carbon atoms, particularly preferably from 6 to 10 carbon atoms such as phenyl and p-methylphenyl, amino group preferably having from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms, particularly preferably from 0 to 6 carbon atoms such as amino, methylamino, dimethylamino and diethylamino, alkoxy group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methoxy and ethoxy, aryloxy group preferably having from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, particularly preferably from 6 to 8 carbon atoms such as phenoxy, acyl group preferably having from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as acetyl group, alkoxycarbonyl group preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as methoxycarbonyl, acyloxy group preferably having from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, particularly preferably from 2 to 8 carbon atoms such as acetoxyl, acylamino group preferably having from 1 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, particularly preferably from 2 to 4 carbon atoms such as acetylamino, sulfonyl amino group preferably having from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfonylamino, sulfamoyl group preferably having from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, particularly preferably from 0 to 4 carbon atoms such as sulfamoyl and methylsulfamoyl, carbamoyl group preferably having from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as carbamoyl and methylcarbamoyl, alkylthio group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methylthio and ethylthio, arylthio group preferably having from 6 to 20 carbon atoms, more preferably from 6 to 10 carbon atoms, particularly preferably from 6 to 8 carbon atoms such as phenylthio, sulfonyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfonyl, sulfinyl group preferably having from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, particularly preferably from 1 to 4 carbon atoms such as methanesulfinyl, ureide group, hydroxyl group, halogen atom such as fluorine, chlorine, bromine and iodine, cyano group, sulfo group, carboxyl group, nitro group, hydroxamic acid group, mercapto group, and heterocyclic group such as imidazolyl and pyridyl.

[0106] These substituents may be further substituted. When there are two or more of these substituents, they may be the same or different. Preferred among the foregoing substituents are alkyl group, amino group, alkoxy group, carboxyl group, hydroxyl group, halogen atom, cyano group, nitro group, and mercapto group. More preferable among these substituents are alkyl group, amino group, alkoxy group, carboxyl group, hydroxyl group, and halogen atom. Most preferable among these substituents are amino group, carboxyl group, and hydroxyl group. Further, particularly preferable among these substituents is carboxyl group.

[0107] The suffix p represents an integer of 0 or 1, preferably 0.

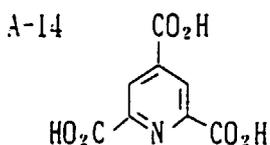
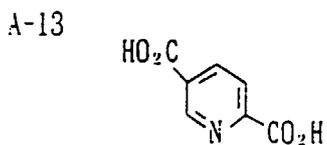
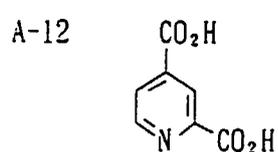
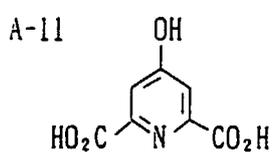
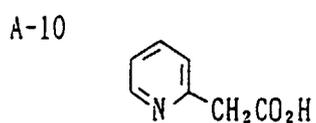
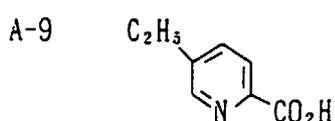
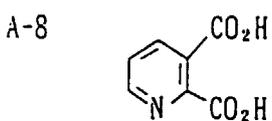
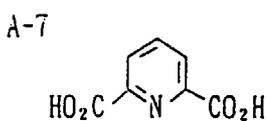
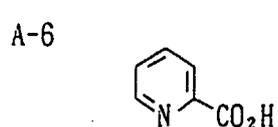
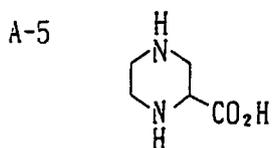
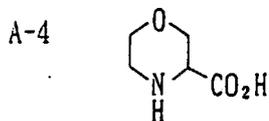
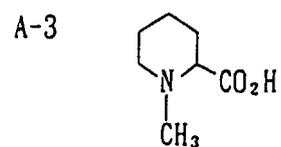
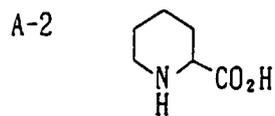
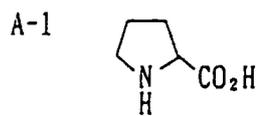
[0108] The cation represented by Ma is an organic or inorganic cation. Examples of the organic or inorganic cation include alkali metal ion such as Li⁺, Na⁺, K⁺ and Cs⁺, alkaline earth metal ion such as Ca²⁺ and Mg²⁺, ammonium ion such as ammonium ion and tetraethylammonium ion, pyridinium ion, and phosphonium ion such as tetrabutylphosphonium ion and tetraphenylphosphonium ion.

[0109] Specific examples of the compound represented by formula (A) will be given below, but the present invention should not be construed as being limited thereto.

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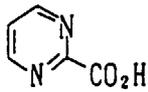
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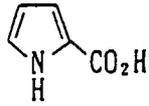
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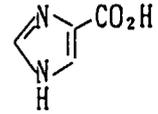
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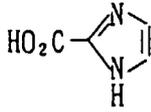
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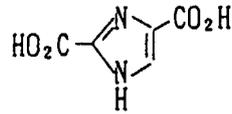
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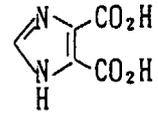
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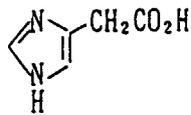
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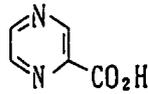
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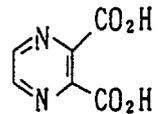
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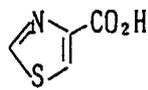
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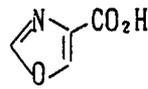
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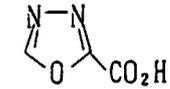
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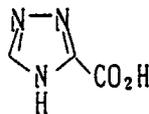
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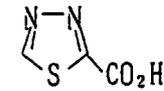
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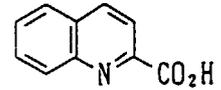
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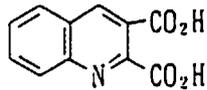
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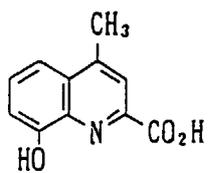
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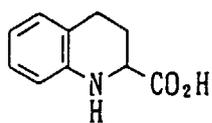
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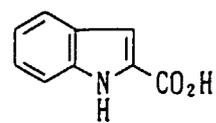
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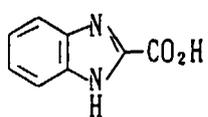
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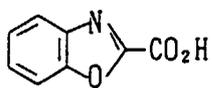
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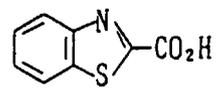
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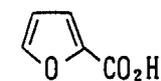
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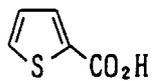
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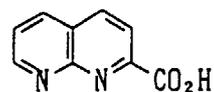
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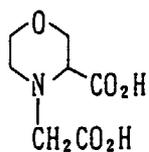
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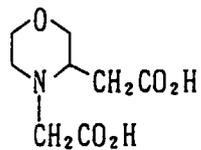
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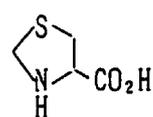
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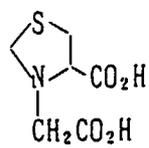
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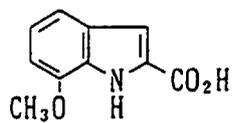
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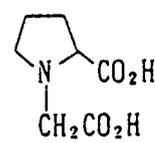
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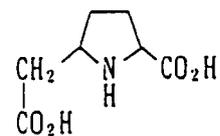
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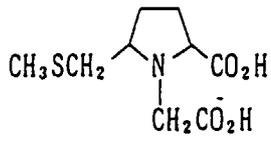


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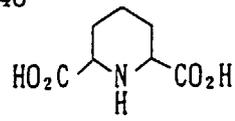
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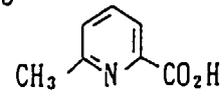
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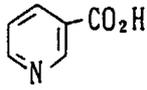
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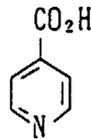
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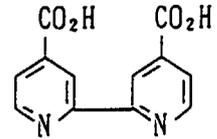
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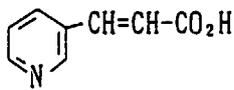
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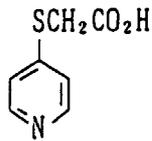
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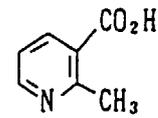
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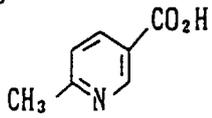
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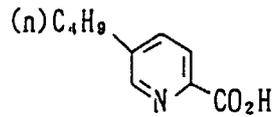
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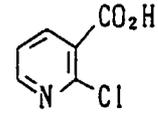
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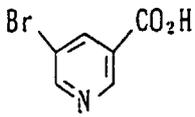
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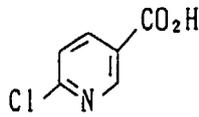
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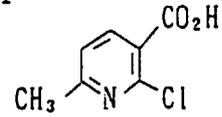
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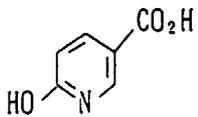
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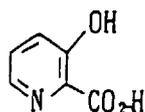
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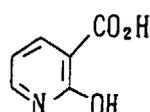
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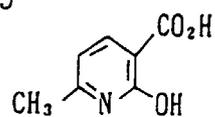
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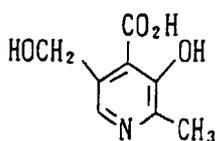
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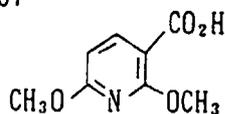
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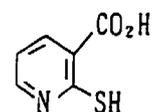
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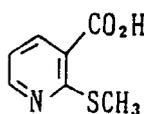
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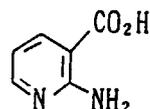
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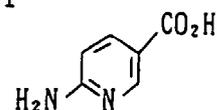
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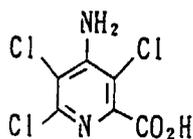
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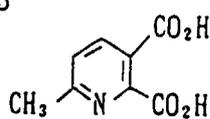
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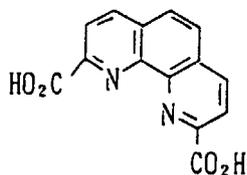
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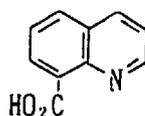
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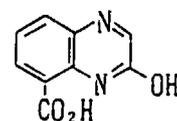
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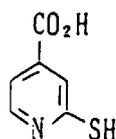
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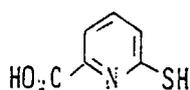
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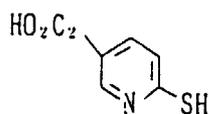
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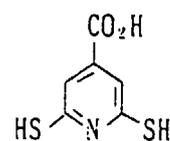
A-79



A-80



A-81



[0110] The foregoing compounds may be used in the form of ammonium salt or alkali metal salt.

[0111] The foregoing compound represented by formula (A) can be synthesized by the method described in "Organic Syntheses Collective", Vol. 3, page 740. Alternatively, commercially available products can be used.

[0112] Preferred among these exemplified compounds are (A-6), (A-7), (A-8), (A-13), (A-14), (A-20), (A-22), (A-29), and (A-49). Particularly preferred among these compounds is (A-7).

[0113] The compound of the present invention represented by formula (A) is preferably incorporated in an amount of from 0.001 to 0.3 mols, more preferably from 0.005 to 0.2 mols, particularly preferably from 0.01 to 0.15 mols per l of processing solution having a fixing ability.

[0114] In the present invention, the compound represented by formula (A) is preferably incorporated also in the processing solution having a bleaching ability in an amount similar to that defined in the processing solution having a fixing ability.

[0115] In the present invention, the compounds represented by formula (A) may be used singly or in combination of two or more thereof.

[0116] The processing solution having a fixing ability may comprise as a preservative a sulfite (e.g., sodium sulfite, potassium sulfite, ammonium sulfite), hydroxylamine, hydrazine, bisulfite adduct of aldehyde compound (e.g., sodium acetaldehydebisulfite, particularly preferably compound described in JP-A-3-158848) or sulfinic acid compound described in JP-A-1-231051. The processing solution having a fixing ability may comprise various fluorescent brightening agents, antifoaming agents, surface active agents and organic solvents such as polyvinylpyrrolidone and methanol incorporated therein.

[0117] The processing solution having a fixing ability may comprise various chelating agents such as aminopoly-carboxylic acid and organic phosphonic acid incorporated therein besides the compound of the present invention for the purpose of stabilizing the processing solution. Preferred examples of the chelating agent to be incorporated include 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid), nitrilotri-methylenephosphonic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid, and 1,2-propylenediaminetetraacetic acid.

[0118] The present invention can exert its effect when the processing solution having a fixing ability has a pH value of from 6.1 to 8.0. When the pH value of the processing solution having a fixing ability falls outside the above defined range, the stability of the processing solution is deteriorated, giving generation of turbidity. In particular, the pH value of the processing solution having a fixing ability is preferably from 6.4 to 7.7.

[0119] For the processing solution having a fixing ability, the compound and processing conditions described in JP-A-4-125558, line 10, lower left column, page 7 - line 19, lower right column, page 8, can be applied.

[0120] In particular, the compounds represented by formulae (I) and (II) described in JP-A-6-301169 are preferably incorporated in the processing solution having a fixing ability singly or in combination to enhance the fixing rate and preservability. It is also preferred from the standpoint of enhancement of preservability that p-toluenesulfonic acid salt or sulfinic acid described in JP-A-1-224762 be incorporated in the processing solution having a fixing ability.

[0121] The processing solution having a fixing ability preferably comprises a buffer incorporated therein to keep the pH value of the solution constant. Examples of the buffer include monobasic acids such as acetic acid and glycolic acid, polybasic acids such as succinic acid, malonic acid, maleic acid and citric acid, phosphate, imidazoles such as imidazole, 1-methyl-imidazole, 2-methyl-imidazole and 1-ethyl-imidazole, triethanolamine, N-allylmorpholine, and N-benzoyl-piperadine.

[0122] The replenishment rate of the processing solution having a fixing ability of the present invention is from 50 to 1,000 ml, preferably from 100 to 600 ml per m² of light-sensitive material.

[0123] The processing time with the processing solution having a fixing ability is 7 minutes or less, more preferably from 10 seconds to 6 minutes, most preferably from 15 seconds to 5 minutes.

[0124] In the present invention, the replenisher for the processing solution having a bleaching ability and the processing solution having a fixing ability may be in the form of liquid or solid (powder, granule, pellet). When the replenisher is in the form of granule or pellet, a polyethyleneglycol-based surface active agent is preferably used to act as a binder as well.

[0125] The solidification of the photographic processing agent can be accomplished by any proper method such as method which comprises mixing a concentrated solution or finely divided or powdery photographic processing agent with a water-soluble binder, and then molding the mixture and method which comprises spraying a water-soluble binder onto the surface of a temporarily molded photographic processing agent to form a coat layer as disclosed in JP-A-4-29136, JP-A-4-85535, JP-A-4-85536, JP-A-4-88533, JP-A-4-85534, and JP-A-4-172341.

[0126] The production of the pelletized processing agent can be accomplished by any conventional method as disclosed in JP-A-51-61837, JP-A-54-155038, JP-A-52-88025, and British Patent 1,213,808. The production of the granular processing agent can be accomplished by any conventional method as disclosed in JP-A-2-109042, JP-A-2-109043, JP-A-3-39735, and JP-A-3-39739. The production of the powdery processing agent can be accomplished by any conventional method as disclosed in JP-A-54-133332, British Patents 725,892 and 729,862, and German Patent 3,733,861.

[0127] When the replenisher for the processing solution having a bleaching ability and the processing solution having a fixing ability is in liquid form, it is preferably used as a one-pack or two-pack solution, particularly preferably one-

pack solution. In this case, the specific gravity of the replenisher agent is preferably from 1.0 to 5 times, particularly preferably from 1.5 to 3 times that of the replenisher.

[0128] The total desilvering time is preferably as short as possible so far no failure of desilvering can occur. In practice, it is preferably from 1 to 12 minutes, more preferably from 1 to 8 minutes. The processing temperature is from 25°C to 50°C, preferably from 35°C to 45°C. In this preferred temperature range, the desilvering rate can be enhanced, and the occurrence of stain after processing can be effectively inhibited.

[0129] It is particularly preferred that the processing solution having a bleaching ability of the present invention be subjected to aeration during processing to keep the photographic properties extremely stable. The aeration can be accomplished by any method well-known in the art such as air blowing method, air absorption method using an ejector and method described in Eastman Kodak's bulletin Z-121 (Using Process C-41), 3rd edition, 1982, pp. BL-1 to BL-2.

[0130] In the present invention, the prebath for the processing solution having a bleaching ability may comprise various bleaching accelerators incorporated therein. Examples of these bleaching accelerators to be incorporated in the prebath include compounds having mercapto or disulfide group described in US Patent 3,893,858, German Patent 1,290,821, British Patent 1,138,842, JP-A-53-95630, and Research Disclosure No. 17,129 (July 1978), thiazoline derivatives described in JP-A-50-140129, thiourea derivatives described in US Patent 3,706,561, iodides described in JP-A-58-16235, polyethylene oxides described in German Patent 2,748,430, and polyamine compounds described in JP-B-45-8836 (The term "JP-B" as used herein means an "examined Japanese patent publication"). Further, compounds described in US Patent 4,552,834 are desirable. These bleaching accelerators may be incorporated in the light-sensitive material.

[0131] The processing solution having a bleaching ability or fixing ability preferably comprises as a cation an ammonium ion incorporated therein to enhance the desilvering properties. In practice, however, ammonium ion is preferably minimized or eliminated for the purpose of lessening environmental pollution.

[0132] The bleaching or fixing step is preferably provided with various silver recovering apparatus on an in-line or off-line basis to recover silver. The provision of such a silver recovering apparatus on an in-line basis makes it possible to effect processing with a lowered silver concentration in the processing solution, resulting in the reduction of replenishment rate. Alternatively, silver is preferably recovered on an off-line basis so that the residue can be re-used as a replenisher.

[0133] The blixing step or fixing step can be composed of a plurality of processing tanks. The various tanks are preferably cascade-connected to form a multi-stage countercurrent system. Taking into account the balance with the size of the developing machine, a two-tank cascade structure is normally efficient. The ratio of processing time at the pre-stage tank to that at the subsequent tank is preferably from 0.5 : 1 to 1 : 0.5, particularly preferably from 0.8 : 1 to 1 : 0.8.

[0134] At the desilvering step, agitation is preferably intensified as much as possible. Specific examples of method for intensifying agitation include a method which comprises allowing a jet of processing solution to impact with the emulsion surface of the light-sensitive material as described in JP-A-62-183460 and JP-A-3-33847, line 6, upper right column - line 2, lower left column, page 8, a method which comprises enhancing the agitating effect using a rotary means as described in JP-A-62-183461, a method which comprises effecting jet agitation as described in JP-A-1-309059, a method which comprises allowing the light-sensitive material to move in contact with a wiper blade provided in the processing solution on the emulsion surface thereof so that turbulence can occur on the emulsion surface to enhance the agitation effect, and a method which comprises raising the total circulation of the processing solution. Such an agitation intensifying method is useful all for the bleaching solution, blixing solution and fixing solution.

[0135] The automatic developing machine to be used for the light-sensitive material of the present invention preferably has a light-sensitive material conveying means as described in JP-A-60-191257, JP-A-60-191258, and JP-A-60-191259. As described in the above described JP-A-60-191257, the use of such a conveying means makes it possible to remarkably reduce the amount of processing solution to be carried over from one bath to a subsequent bath and hence exert a high effect of inhibiting the deterioration of the properties of the processing solution. Such an effect is particularly useful for the reduction of the processing time and the amount of the replenisher to be supplied at the various steps.

[0136] The overflow of the processing solution having a bleaching ability of the present invention after processing can be recovered, and then provided with necessary components to modify the composition thereof for re-use. Such a use is normally called regeneration. In the present invention, regeneration is preferably effected. For the details of regeneration, reference can be made to "Fuji Film Processing Manual: Fuji Color Negative Film; CN-16 processing (revised in August 1,999)", published by Fuji Photo Film Co., Ltd., pp. 39 - 40.

[0137] For the regeneration of the processing solution having a bleaching ability, a method described in "Shashin Kogaku no Kiso-Ginen Shashin hen (Elementary Photographic Engineering-Silver Salt Photograph)", compiled by Society of Photographic Science and Technology of Japan, published by Corona Co., Ltd., 1979 can be used. In some detail, electrolytic regeneration can be used. Further, a method involving the regeneration of the bleaching solution with bromic acid, chlorous acid, bromine, bromine precursor, persulfate, hydrogen peroxide, hydrogen peroxide in the presence of a catalyst, bromous acid, ozone, etc. can be used.

[0138] The electrolytic regeneration can be carried out with a cathode and an anode put in the same bleaching bath or with an anode bath and a cathode bath separately provided with a separating membrane interposed therebetween. Alternatively, the bleaching solution and developer and/or fixing solution can be simultaneously regenerated using a separating membrane.

5 **[0139]** The regeneration of the fixing solution and blixing solution can be accomplished by the electrolytic reduction of accumulated silver ions. Further, the removal of accumulated halogen ions through an anion exchange resin is desirable from the standpoint of maintenance of fixing properties.

[0140] The processing solution having a bleaching ability of the present invention is preferably received in a sealed vessel having an oxygen permeability of 1 cc/m².day.atm or more during storage.

10 **[0141]** The bleaching solution of the present invention preferably comprises at least one of isothiazolones such as 1,2-benzisothiazoline-3-one and 2-methyl-1,2-benzisothiazoline-3-one or derivatives thereof incorporated therein.

[0142] The amount of such a compound to be incorporated is preferably from 0.001 to 1 g, more preferably from 0.01 to 0.5 g, particularly preferably from 0.02 to 0.2 g per l of bleaching solution. Such a compound may be incorporated in the form of salt. Two or more of these compounds may be used in combination.

15 **[0143]** The replenisher for the processing solution having a bleaching ability comprises various components incorporated therein in an amount basically calculated by the following equation. Thus, the concentration in the mother liquor can be kept constant.

$$C_R = C_T \times (V_1 + V_2)/V_1 + C_p$$

20 where

C_R : Concentration of component in replenisher

C_T : Concentration of component in mother liquor (processing tank solution)

25 C_p : Concentration of component consumed during processing

V_1 : Supplying rate (ml) of replenisher having a bleaching ability per m² of light-sensitive material

V_2 : Amount (ml) of processing solution carried over from prebath by light-sensitive material per m²

30

[0144] The color developer will be further described hereinafter.

[0145] The color developer may comprise a compound described in JP-A-4-121739, line 1, upper right column, page 9 - line 4, lower left column, page 11, incorporated therein. In particular, as the color developing agent to be used in quick processing there may be preferably used 2-methyl-4-[N-ethyl-N-(2-hydroxyethyl) amino]aniline, 2-methyl-4-[N-ethyl-N-(3-hydroxypropyl) amino]aniline, 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl) amino] aniline or 2-methyl-4-[N-ethyl-N-(β-methylsulfoamideethyl) amino]aniline. These compounds may be used in the form of salt such as sulfate, hydrochloride and p-toluenesulfonate.

[0146] The color developer preferably comprises such a color developing agent incorporated therein in an amount of from 0.01 to 0.20 mols/l, particularly preferably from 0.012 to 0.12 mols/l, most preferably from 0.15 to 0.08 mols/l. The color developer replenisher preferably comprises such a color developing agent incorporated therein in an amount of from 1.1 to 1.4 times the above defined value.

[0147] The color developer normally comprises a pH buffer such as carbonate, borate and phosphate of alkali metal and a development inhibitor or fog inhibitor such as chloride, bromide, iodide, benzimidazole, benzothiazole and mercapto compound incorporated therein. As necessary, the color developer may comprise various preservatives such as hydroxylamine, diethylhydroxylamine, hydroxylamine represented by formula (I) described in JP-A-3-144446, including N,N-bis(2-sulfonateethyl)hydroxylamine, sulfite and hydrazine (e.g., N,N-biscarboxylmethylhydrazine), phenyl semicarbazide, triethanolamine and catecholsulfonic acid, 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 development agents such as 1-phenyl-3-pyrazolidone, tackifiers, various chelating agents such as aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid and phosphonocarboxylic acid, e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid), salt thereof.

55 **[0148]** The processing temperature of the color developer in the present invention is from 20°C to 55°C, preferably from 30°C to 55°C. The processing time of the color developer in the present invention is from 20 seconds to 10 minutes, preferably from 30 seconds to 8 minutes, more preferably from 1 to 6 minutes, particularly preferably from 1 minutes and 10 seconds to 3 minutes and 30 seconds, if a light-sensitive material for photography is processed. The

processing time of the color developer in the present invention is from 10 seconds to 1 minute and 20 seconds, preferably from 10 seconds to 60 seconds, more preferably from 10 seconds to 40 seconds, if a light-sensitive material for printing is processed.

5 **[0149]** In the case where reversal development is effected, color development is normally preceded by black-and-white development. The black-and-white developer to be used herein may comprise well-known black-and-white developing agents such as dihydroxybenzene (e.g., hydroquinone, hydroquinone monosulfonate), 3-pyrazolidone (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone) and aminophenol (e.g., N-methyl-p-aminophenol) incorporated therein, singly or in combination.

10 **[0150]** The foregoing color developer normally has a pH value of from 9 to 12.7. The foregoing black-and-white developer has a pH value-of from 9 to 11.5. The replenishment rate of these developers is 3 l or less per m² of the light-sensitive material, though depending on the kind of the color light-sensitive material to be processed. By reducing the bromide ion concentration in the replenisher, the replenishment rate can be reduced to 500 ml or less. In order to reduce the replenishment rate, the contact area of the processing bath with air is preferably reduced to inhibit the evaporation and air oxidation of the processing solution.

15 **[0151]** For the rinsing and stabilizing steps, the contents described in JP-A-4-125558, line 6, lower right column, page 12 - line 16, lower right column, page 13, can be preferably applied. In particular, it is preferred from the standpoint of protection of working atmosphere that the stabilizing solution comprise an azolylmethylamine as described in European Patent Publication Nos. 504609 and 519190 or N-methylolazole as described in JP-A-4-362943 incorporated therein instead of formaldehyde, the magenta coupler be rendered two-equivalent and a surface active agent solution
20 free of image stabilizer such as formaldehyde be used.

[0152] In the present invention, it is particularly preferred from the standpoint of enhancement of readability of magnetically recorded data that the final step bath be free of image stabilizer.

25 **[0153]** The processing solution has various ionic components such as calcium ion, magnesium ion, sodium ion and potassium ion coming from water used to prepare the replenisher or eluted from the light-sensitive material. In the present invention, the sodium ion concentration in the final bath at the rinsing step or stabilizing step is preferably from 0 to 50 mg/l, particularly preferably from 0 to 20 mg/l.

30 **[0154]** The replenishment rate at the rinsing step and stabilizing step is preferably from 80 to 1,000 ml, more preferably from 100 to 500 ml, most preferably from 150 to 300 ml per m² of light-sensitive material from the standpoint of both assurance of rinsing and stabilizing functions and reduction of waste water for environmental protection. In the processing with the above defined replenishment rate, a well-known antifungal agent such as thiabendazole, 1,2-benzisothiazoline-3-one and 5-chloro-2-methylisothiazoline- 3-one, an antibiotic such as gentamicin or water deionized with an ion-exchange resin is preferably used to prevent the proliferation of bacteria or fungi. It is more effective to use deionized water, antibacterial agent and antibiotic in combination.

35 **[0155]** The processing solution in the rinsing solution or stabilizer tank is preferably subjected to reverse osmosis membrane treatment as described in JP-A-3-46652, JP-A-3-53246, JP-A-3-121448 and JP-A-3-126030 to reduce the replenishment rate. The reverse osmosis membrane to be used herein is preferably a low pressure reverse osmosis membrane.

40 **[0156]** In the processing of the present invention, it is particularly preferred that the evaporation loss of processing solution be made up for as disclosed in Hatsumei Kyokai Kokai Giho (Japan Institute of Invention and Innovation's Kokai Giho) No. 94-4992. In particular, the evaporation loss of processing solution is preferably corrected using the data of temperature and humidity around the developing machine according to Equation-1 on page 2. Water to be used to correct the evaporation loss of processing solution is preferably taken from the rinsing water replenisher tank. In this case, as the rinsing water replenisher there is preferably used deionized water.

45 **[0157]** As the automatic developing machine to be used herein there is preferably used a film processor described in the above described Kokai Giho, line 22 - line 28, right column, page 3.

[0158] Specific examples of processing agents, automatic developing machine and method for correcting evaporation loss which can be preferably used to implicate the present invention are described in the above described Kokai Giho, line 11, right column, page 5 - final line, right column, page 7.

50 **[0159]** The silver halide color photographic material which can be preferably subjected to processing according to the invention will be further described hereinafter.

[0160] The silver halide color photographic material to which the present invention can be preferably applied may be in the form of color negative film or color reversal film comprising a silver bromiodide emulsion coat layer, more preferably color negative film, particularly preferably one having a magnetic recording layer provided on a support.

55 **[0161]** The magnetic recording layer which can be preferably processed according to the present invention will be further described hereinafter.

[0162] The magnetic recording layer is formed by applying an aqueous or organic solvent-based coating solution having magnetic particles dispersed in a binder to a support. As the magnetic particle there may be used ferromagnetic iron oxide such as γ -Fe₂O₃, Co-coated γ -Fe₂O₃, Co-coated magnetite, Co-containing magnetite, ferromagnetic chro-

mium dioxide, ferromagnetic metal, ferromagnetic alloy or hexagonal Ba ferrite, Sr ferrite, Pb ferrite or Ca ferrite. Particularly preferred among these magnetic materials is Co-coated ferromagnetic iron oxide such as Co-coated γ -Fe₂O₃.

[0163] The shape of the magnetic material particles may be any of acicular, ellipsoidal, spherical, cubic and tabular form. The specific surface area of the magnetic particles is preferably 20 m²/g or more, particularly preferably 30 m²/g or more as determined by S_{BET}. The saturated magnetization (σ_s) of the ferromagnetic particle is preferably from 3.0 x 10⁴ to 3.0 x 10⁵ A/m, particularly preferably from 4.0 x 10⁴ to 2.5 x 10⁵ A/m. The ferromagnetic particles may be subjected to surface treatment with silica and/or alumina or an organic material. Further, the magnetic material particles may be treated with a silane coupling agent or titanium coupling agent on the surface thereof as described in JP-A-6-161032. Alternatively, magnetic particles coated with an inorganic or organic material on the surface thereof as described in JP-A-4-259911 and JP-A-5-81652 may be used.

[0164] Examples of the binder for magnetic particles include thermoplastic resin, thermosetting resin, radiation-curing resin, reactive resin, acid-decomposable, alkali-decomposable or biodegradable polymer, natural polymer (cellulose derivative, saccharide derivative, etc.), and mixture thereof as disclosed in JP-A-4-219569. The foregoing resins exhibit a glass transition temperature T_g of from - 40°C to 300°C and a weight-average molecular weight of from 2,000 to 1,000,000. Examples of such resins include vinyl copolymers, cellulose derivatives such as cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate and cellulose tripropionate, acrylic resin, and polyvinyl acetal resin. Gelatin is also desirable. Cellulose di(tri)acetate is particularly preferred. The binder may be cured with an epoxy-based, aziridine-based or isocyanate-based crosslinking agent. Examples of the isocyanate-based crosslinking include isocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate and xylylene diisocyanate, products of the reaction of these diisocyanates with polyalcohols (e.g., product of reaction of 3 mols of tolylene diisocyanate with 1 mol of trimethylol propane), and polyisocyanates produced by the condensation of these isocyanates. These examples are described in, e.g., JP-A-6-59357.

[0165] The thickness of the magnetic recording layer is from 0.1 μ m to 10 μ m, preferably 0.2 μ m to 5 μ m, more preferably from 0.3 μ m to 3 μ m. The weight ratio of magnetic particles to binder is preferably from 0.5 : 100 to 60 : 100, more preferably from 1 : 100 to 30 : 100. The applied amount of magnetic particles is from 0.005 to 3 g/m², preferably from 0.01 to 2 g/m², more preferably from 0.02 to 0.5 g/m².

[0166] The magnetic recording layer may be provided all over the back surface of the photographic support or in stripe by coating or printing. The coating of the magnetic recording layer can be accomplished by means of air doctor, blade, air knife, squeeze rollers, immersion bath, reverse rolls, transfer rolls, gravure coater, kiss-roll coater, cast coater, spray coater, dip coater, bar coater, extruder or the like. The coating solution described in JP-A-5-341436 is preferably used.

[0167] The magnetic recording layer may be capable of improving lubricity, adjusting curling, inhibiting electrification and adhesion and abrading head in combination. Alternatively, the magnetic recording layer may be provided with other functional layers so that these functions can be added to the magnetic recording layer. The magnetic particle preferably acts as an abrasive comprising nonspherical inorganic particles at least one of which has a Mohs' hardness of 5 or more. The composition of the nonspherical inorganic particles comprises a fine powder of oxide such as aluminum oxide, chromium oxide, silicon dioxide and titanium dioxide, carbide such as silicon carbide and titanium carbide or diamond. Such an abrasive may be treated with a silane coupling agent or titanium coupling agent on the surface thereof. These particles may be incorporated in the magnetic recording layer or may be applied to the magnetic recording layer as an overcoat (e.g., protective layer, lubricant layer). As the binder to be used herein there may be used one previously mentioned, preferably the same binder as used for the magnetic recording layer. For the details of light-sensitive material comprising such a magnetic recording layer, reference can be made to US Patents 5,336,589, 5,250,404, 5,229,259 and 5,215,874, and EP 466,130.

[0168] When the magnetic recording layer is contaminated by precipitates during development, it is disadvantageous in that the precision in reading magnetically recorded data from the light-sensitive material which has been developed is deteriorated. However, the processing method according to the present invention using a fixing solution containing a compound represented by formula (P) or formula (A) is further advantageous in that the deterioration of precision in reading magnetically recorded data is minimized.

[0169] The light-sensitive material to be processed according to the present invention is preferably a light-sensitive material for photography. The support for the light-sensitive material is preferably a polyester. For the details of such a light-sensitive material for photography, reference can be made to Kokai Giho No. 94-6023 (Japan Institute of Invention and Innovation; March 15, 1994).

[0170] The polyester to be used herein can be formed by a diol and an aromatic dicarboxylic acid as essential components. Examples of the aromatic dicarboxylic acid employable herein include 2,6-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid, and phthalic acid. Examples of the diol employable herein include diethylene glycol, triethylene glycol, cyclohexane dimethanol, bisphenol A, and bisphenol. Examples of the polymer thus prepared include homopolymers such as polyethylene terephthalate, polyethylene naphthalate and polycyclohexane dimethanol terephthalate. A partic-

ularly preferred polymer is a polyester containing 2,6-naphthalenedicarboxylic acid in an amount of from 50 mol-% to 100 mol-%. Particularly preferred among these polyesters are polyethylene, and 2,6-naphthalate. The average molecular weight of the polyester is from about 5,000 to 200,000. The polyester of the invention has Tg of 50°C or higher, preferably 90°C or higher.

5 **[0171]** The polyester support is preferably subjected to heat treatment at a temperature of from not lower than 40°C to lower than Tg, more preferably from Tg - 20°C to lower than Tg to render itself little curlable. The heat treatment may be effected at a constant temperature or lowering temperature within the above defined range. The heat treatment time is from 0.1 to 1,500 hours, preferably from 0.5 to 200 hours. The support may be subjected to heat treatment in the form of roll or while being conveyed in the form of web. The surface of the support may be roughened (e.g., by applying a
10 conductive inorganic fine particle such as SnO₂ and Sb₂O₅) to improve the surface conditions thereof. The support is preferably knurled at the end thereof so that it is slightly thicker at the end thereof than at other areas to prevent the cut edge of the core from affecting the other areas. The heat treatment may be effected at any steps after the preparation of support, after surface treatment, after the coating of back layer (e.g., antistatic agent, sliding agent) or after the application of undercoating, preferably after the application of antistatic agent.

15 **[0172]** The foregoing polyester may comprise an ultraviolet absorber incorporated therein. In order to prevent light-piping, the foregoing polyester may comprise a dye or pigment commercially available for polyester such as Diaresin (produced by Mitsubishi Chemical Corporation) and Kayaset (produced by NIPPON KAYAKU CO.,LTD.) incorporated therein.

[0173] Referring to the undercoating method, the undercoating layer may consist of a single layer or two or more
20 layers. Examples of the binder for undercoating layer include copolymers obtained by polymerizing monomers selected from the group consisting of vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid and maleic anhydride as starting materials, polyethyleneimine, epoxy resin, grafted gelatin, nitrocellulose, and gelatin.

[0174] The light-sensitive material to be used in the present invention preferably comprises an antistatic agent such as carboxylic acid, carboxylate, high molecular compound containing sulfonic acid, cationic high molecular compound
25 and ionic surface active agent incorporated therein. The most desirable antistatic agent is a particulate crystalline metal oxide comprising at least one selected from the group consisting of ZnO, TiO₂, SnO₂, Al₂O₃, In₂O₃, SiO₂, MgO, BaO, MoO₃ and V₂O₅ having a volume resistivity of 10⁷ Ω·cm or less, preferably 10⁵ Ω·cm or less, and a particle size of from 0.001 to 1.0 μm or a particulate composite oxide thereof (e.g., Sb, P, B, In, S, Si, C). Further, a sol metal oxide or particulate composite oxide thereof is mostly preferred. The content of such an antistatic agent in the light-sensitive
30 material is preferably from 5 to 500 mg/m², particularly preferably from 10 to 350 mg/m². The ratio of amount of electrically-conductive crystalline oxide or composite oxide thereof to binder is preferably from 1/300 to 100/1, more preferably from 1/100 to 100/5.

[0175] The light-sensitive material has preferably sliding property. The sliding agent-containing layer is preferably provided on both of the light-sensitive layer surface and the back surface thereof.

35 **[0176]** Examples of the sliding agent employable herein include polyorganosiloxane, higher aliphatic acid amide, higher aliphatic acid metal salt, and ester of higher aliphatic acid with higher alcohol. Examples of the polyorganosiloxane employable herein include polydimethyl siloxane, polydiethyl siloxane, polystyryl methyl siloxane, and polymethyl phenyl siloxane. The layer in which the sliding agent is incorporated is preferably the outermost layer of the emulsion layer or the back layer. Particularly preferred among these sliding agents are polydimethyl siloxane and ester
40 having long-chain alkyl group.

[0177] Further, the light-sensitive material of the invention preferably comprises a matting agent incorporated therein. The matting agent may be incorporated in either the emulsion surface or the back surface. In practice, however, the matting agent is preferably incorporated in the outermost layer on the emulsion layer side. The matting agent may be either soluble or insoluble in the processing solution. Preferably, the two types of matting agents are used in combi-
45 nation. Preferred examples of the matting agent employable herein include polymethyl methacrylate, poly(methyl methacrylate/methacrylic acid = 9/1 or 5/5 (molar ratio)) and polystyrene in particulate form. The particle diameter of the matting agent is preferably from 0.8 to 10 μm. The distribution of particle diameters is preferably narrow. It is preferred that 90% or more of all the particles fall within the range of from 0.9 to 1.1 times the average particle diameter.

[0178] In order to enhance matting property, a fine particle having a size of not more than 0.8 μm is preferably
50 added at the same time. Examples of such a fine particle include particulate polymethyl methacrylate having a size of 0.2 μm, particulate poly(methyl methacrylate/methacrylic acid = 9/1 (molar ratio)) having a size of 0.3 μm, particulate polystyrene having a size of 0.25 μm, and colloidal silica having a size of 0.03 μm.

[0179] As the light-sensitive material to be used herein there is preferably used one described in JP-A-4-125558,
55 line 1, upper left column, page 14 - line 11, lower left column, page 18. In particular, as the silver halide emulsion there is preferably used a silver bromoiodide emulsion having an average silver iodide content of from 3 to 20 mol-%. The silver halide grains are preferably in the form of tabular grain having an aspect ratio of 5 or more or double structure grain having halogen composition differing between inside and outside. The silver halide grains are also preferably in a layered structure which is distinct between inside and outside. The aspect ratio of the silver halide grains is preferably

from 5 to 20, more preferably from 6 to 12.

[0180] The monodisperse emulsion described in US Patents 3,574,628 and 3,655,394 is desirable as well.

[0181] The light-sensitive material to be used in the present invention preferably has a layer containing light-insensitive silver halide grains having an average grain diameter of from 0.02 to 0.2 μm. The particulate silver halide is preferably silver bromide having an iodide content of from 0.5 to 10 mol-%.

[0182] For the details of the additives to be incorporated in the light-sensitive material of the present invention, reference can be made to the following citations:

Kind of Additives	RD17643	RD18716	RD307105
1. Chemical sensitizer	Page 23	R.C., page 648	Page 866
2. Sensitivity improver		R.C., page 648	
3. Spectral sensitizer, supersensitizer	Pp.23-24	R.C., page 648 - R.C., page 649	pp. 866 - 868
4. Brightening agent	Page 24	R.C., page 647	Page 868
5. Light absorber, filter dye, ultraviolet absorber	Pp.25-26	R.C., page 649 - L.C., page 650	Page 873
6. Binder	Page 26	L.C., page 651	pp. 873 - 874
7. Plasticizer, lubricant	Page 27	R.C., page 650	Page 876
8. Coating aid, surface active agent	pp.26 - 27	R.C., page 650	pp. 875 - 876
9. Antistatic agent	Page 27	R.C., page 650	pp. 876 - 877
10. Matting agent			pp. 878 - 879

[0183] The light-sensitive material of the present invention may comprise various dye-forming couplers incorporated therein. The following couplers are particularly preferred.

Yellow coupler: couplers represented by formulae (I) and (II) in EP 502,424A; couplers represented by formulae (1) and (2) in EP 513,496A (particularly Y-28 on page 18); couplers represented by formula (I) in Claim 1 of EP 568,037A; couplers represented by formula (I) in lines 45 to 55 on Column 1 of US Patent 5,066,576; couplers represented by formula (I) on Paragraph 0008 of JP-A-4-274425; couplers described in Claim 1 on page 40 of EP 498,381A1 (particularly D-35 on page 18); couplers represented by formula (Y) on page 4 of EP 447,969A1 (particularly Y-1 (page 17) and Y-54 (page 41)); couplers represented by formulae (II) to (IV) in lines 36 to 58 on Column 7 of US Patent 4,476,219 (particularly II-17, 19 (Column 17), II-24 (Column 19)).

Magenta coupler: L-57 (lower right column, page 11), L-68 (lower right column, page 12), L-77 (lower right column, page 13) in JP-A-3-39737; A-4-63 (page 134), A-4-73, A-4-75 (page 139) in EP 456,257; M-4, M-6 (page 26), M-7 (page 27) in EP 486,965; M-45 (page 19) in EP 571,959A; (M-1) (page 6) in JP-A-5-204106; M-22 on Paragraph 0237 of JP-A-4-362631

Cyan coupler: CX-1,3,4,5,11,12,14,15 (pp. 14 - 16) in JP-A-4-204843; C-7, 10 (page 35), 34, 35 (page 37), (I-1), (I-17) (pp. 42 - 43) in JP-A-4-43345; couplers represented by formulae (Ia) and (Ib) in Claim 1 of JP-A-6-67385

Polymer coupler: P-1, P-5 (page 11) in JP-A-2-44345

[0184] Preferred examples of couplers in which a color-forming dye has a proper diffusibility include those described in US Patent 4,366,237, GB Patent 2,125,570, EP 96,873B, and DE 3,234,533.

EXAMPLE

[0185] 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

[0186] A commercially available 135 type film format (corresponding international Standard: ISO 1007) color negative film was subjected to exposure, development and evaluation of properties of processing solution and light-sensitive material according to the present invention as mentioned below.

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(Specimen of light-sensitive material)

[0187] As light-sensitive materials there were used three commercially available films, i.e., Fuji Color Negative Film "SUPER G ACE400", Fuji Color Negative Film "SUPER G ACE100" and Fuji Color Negative Film "REAREA400" in 35 mm size (135-24 ex format) in a mixing proportion of 40 : 40 : 20. (Test)

[0188] These film specimens were each subjected to wedge (optical wedge) exposure according to the international Standard (ISO5800) defining the sensitometry of color negative film.

[0189] These film specimens thus exposed were each developed per 6 m² a day under the following conditions for 2 months. As the automatic developing machine there was used a Type FNCP-300II automatic developing machine produced by Fuji Photo Film Co., Ltd. The temperature of the processing solutions were continuously kept at the predetermined value during the test period.

Processing steps and conditions

[0190]

Processing Step	Processing time	Temperature	Replenishment rate	Tank ability
Color development	3min. and 15sec.	38.0°C	550 ml/m ²	82 l
Bleaching	3min. and 00sec.	38.0°C	150 ml/m ²	118 l
Rinsing (1)	15 sec.	24.0°C	Countercurrent from (2) to (1)	20 l
Rinsing (2)	15 sec.	24.0°C	200 ml/m ²	20 l
Fixing	3min. and 00sec.	38.0°C	400 ml/m ²	77 l
Rinsing (3)	30 sec.	24.0°C	Countercurrent from (4) to (3)	40 l
Rinsing (4)	30 sec.	24.0°C	1,000 ml/m ²	40 l
Stabilization	30 sec.	38.0°C	300 ml/m ²	40 l
Drying	4min. and 20sec.	55°C		

[0191] The composition of the processing solutions will be described hereinafter.

Color developer	Running (g)	solution 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	2.4	3.3
Disodium-N,N-bis(sulfonateethyl) hydroxylamine	2.0	2.8
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	6.0
Water to make	1,000 ml	1,000 ml
PH	10.05	10.15

5	Bleaching solution	Running solution	Replenisher
	Compound I-54	0.17 mols	0.25 mols
	Ferric nitrate (III) nonahydrate	65.0 g	100.0 g
	Ammonium bromide	80.0 g	120.0 g
10	90% Acetic acid	50.0 g	75.0 g
	Water to make	1,000 ml	1,000 ml
	pH (adjusted with aqueous ammonia and nitric acid)	4.3	3.8
15			
	Fixing solution	Running solution	Replenisher
	Ammonium thiosulfate	0.7 mols	1.0 mol
20	Ammonium sulfite	0.2 mols	0.3 mols
	Compound of the invention (shown in Table 1)	0.04 mols	0.05 mols
	90% Acetic acid	3.0 g	4.0 g
	Water to make	1,000 ml	1,000 ml
25	pH (shown in Table 1) (adjusted with aqueous ammonia and acetic acid)		
	Stabilizing solution	Running solution/(same as replenisher) (g)	
30	p-Nonylphenoxypolyglycidol(Average polymerization degree of glycidol: 10)	0.2	
	Ethylenediamine-N,N,N',N'-tetraacetic acid	0.05	
	1,2,4-Triazole	1.3	
35	1,4-Bis(1,2,4-triazole-1-yl-methyl) piperazine	0.75	
	Glycolic acid	0.02	
	Gentamicin	0.01	
40	Hydroxyethyl cellulose (HEC SP-2000, produced by DAICEL CHEMICAL INDUSTRIES, LTD.)	0.1	
	1,2-Benzisothiazoline-3-one	0.05	
	Water to make	1 l	
45	pH (adjusted with aqueous ammonia and nitric acid)		8.5

Measurement

50 **[0192]** The light-sensitive materials thus processed were each then evaluated for stain, image preservability, color density and liquid stability in accordance with the following methods.

Stain:

55 **[0193]** The light-sensitive material specimens thus developed were each then measured for density by an apparatus and method according to the international standard ISO5 group. From the characteristic curve thus obtained was read Dmin (density at unexposed area) measured with red light (R light), i.e., Dmin (R).

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Image change with time:

[0194] From the characteristic curve determined by the measurement of density on the specimens developed was read Dmax (density at the highest density area) measured with green light (G light), i.e., Dmax(G). Subsequently, the light-sensitive material specimens thus measured were each aged under the following severe conditions, and then similarly measured for Dmax(G). From both the measurements was determined the change of density of magenta dye at the highest density area (Dmax(G)) with time.

[0195] Storage conditions: 70°C, relative humidity: 70%; 4 weeks

Change of Dmax with time $[\Delta D_{max}(G)] = [D_{max}(G) \text{ after storage}] - [D_{max}(G) \text{ before storage}]$

Color density:

[0196] From the characteristic curve was read Dmax [density at the highest density area] measured with red light (R light), i.e., Dmax(R).

Liquid stability:

A liquid specimen was prepared by adding ferric (III) ion, calcium ion and magnesium ion to the same processing solution as the running fixing solution used in the foregoing development process in an amount of 2,000 ppm, 400 ppm and 150 ppm, respectively. The liquid specimen was then allowed to stand at a temperature of 40°C for 4 weeks. The liquid specimen was then observed for occurrence of precipitation.

(Results)

[0198] The results are shown in Table 1 below.

TABLE 1

Test No.	Additive for fixing solution (molar ratio)	PH of fixing solution	Condition of Aged Liquid	Dmin (R)	ΔD_{max} (G)	Dmax (R)	Remarks
1	EDTA	5.4	Turbid	0.29	0.37	2.27	Comparison
2	"	6.0	"	0.29	0.39	2.23	"
3	"	6.1	Slightly turbid	0.28	0.39	2.17	Invention
4	"	6.4	Not turbid	0.28	0.40	2.17	"
5	"	7.7	"	0.27	0.41	2.11	"
6	"	8.0	"	0.27	0.41	2.09	"
7	"	8.1	"	0.28	0.42	2.04	Comparison
8	"	8.4	"	0.28	0.42	1.97	"
9	1,3-PDTA	6.4	Slightly turbid	0.33	0.44	2.27	"
10	NTA	6.4	Turbid	0.30	0.53	2.27	"
11	II-15	6.4	Not turbid	0.26	0.36	2.24	Invention
12	II-16	6.4	"	0.26	0.36	2.21	"
13	P-19	6.4	"	0.27	0.35	2.19	"
14	P-25	5.4	Precipitated	0.28	0.47	2.28	Comparison
15	"	6.0	Slightly turbid	0.28	0.40	2.27	"
16	"	6.1	Not turbid	0.24	0.35	2.23	Invention
17	"	6.4	"	0.23	0.33	2.21	"

TABLE 1 (continued)

Test No.	Additive for fixing solution (molar ratio)	PH of fixing solution	Condition of Aged Liquid	Dmin (R)	Δ Dmax (G)	Dmax (R)	Remarks
18	"	7.7	"	0.24	0.33	2.21	"
19	"	8.0	"	0.26	0.33	2.19	"
20	"	8.1	Slightly turbid	0.31	0.40	1.96	Comparison
21	"	8.4	"	0.34	0.40	1.89	"
22	P-34	6.4	Not turbid	0.24	0.30	2.24	Invention
23	P-56	6.4	"	0.25	0.35	2.24	"
24	P-57	6.4	Slightly turbid	0.28	0.32	2.21	"
25	P-68	6.4	Not turbid	0.28	0.36	2.21	Invention
26	P-25+A-6 (1 : 1)	6.4	"	0.25	0.30	2.29	"
27	P-25+A-6 (7 : 3)	6.4	"	0.26	0.29	2.30	"
28	P-25+A-7 (1 : 1)	6.4	"	0.27	0.29	2.29	"
29	P-57+A-7 (1 : 1)	6.4	"	0.26	0.29	2.31	"
30	II-15+A-7 (1 : 1)	6.4	"	0.27	0.29	2.29	"
31	II-16+A-7 (1 : 1)	6.4	"	0.23	0.29	2.31	"
32	P-25+II-15 (1 : 1)	6.4	"	0.25	0.31	2.28	"
33	P-25+II-15+A-6 (1 : 1 : 1)	6.4	"	0.25	0.32	2.27	"
EDTA: Ethylenediamine-N,N,N',N'-tetraacetic acid 1,3-PDTA: 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid NTA: Nitritotriacetic acid							

[0199] As is apparent from the result of Table 1, Test Nos. 3 to 6, 11 to 13, 16 to 19 and 22 to 33, which are processing processes according to the present invention, gave results that the fixing solution is excellent all in stability, occurrence of cyan stain and stability of magenta dye with time.

[0200] In some detail, the examples of the invention (Test Nos. 4, 11 to 13, 17 and 22 to 25) using a bleaching solution comprising a ferric complex salt (III) of compound represented by formula (I) incorporated therein and a fixing solution with a pH value of 6.4 comprising a complex-forming agent selected from the group consisting of compound represented by formula (II), EDTA and phosphonic acid incorporated therein are superior to the comparative examples (Test Nos. 9 and 10) using a fixing solution with the same pH value comprising a complex-forming agent other than compound represented by formula (II), EDTA and phosphonic acid incorporated therein in all the evaluations. In particular, the examples of the invention exhibit an improved stability of magenta dye with time and show minimized cyan stain.

[0201] Referring to the pH value of fixing solution, Test Nos. 14 to 21 show that even if a phosphonic acid compound is used, when the pH value of the fixing solution is higher than the range of the present invention, the red light density is insufficiently color-formed, the stability of magenta dye image is deteriorated and the fixing solution is slightly instabilized. On the other hand, even if the pH value of the fixing solution is lower than the range of the present invention, the magenta dye becomes unstable, and the fixing solution is observed turbid. On the contrary, when the pH value of the fixing solution falls within the range of the present invention, the results are excellent all in the various properties. Also, the specimens comprising a phosphonic acid compound of the present invention incorporated therein exhibit a high cyan density over various pH ranges.

[0202] Referring to cyan density, the specimens comprising a compound represented by formula (A) incorporated therein in addition to the compound of the present invention represented by formula (II), EDTA or phosphonic acid (Test Nos. 26 - 33) show excellent results.

EXAMPLE 2

[0203] The same procedure as in Example 1 was carried out except that the composition of the bleaching solution, fixing solution and stabilizing solution were changed to the following ones. Cyan stain, change of magenta dye with time, color density and stability of fixing solution were then determined in the same manner as in Example 1. The results are shown in Table 2.

10	Bleaching solution	Running solution	Replenisher
	Chelating agent for bleaching solution (shown in Table 2)	0.17 mols	0.25 mols
15	Ferric nitrate (III) nonahydrate	65.0 g	100.0 g
	Sodium bromide	80.0 g	120.0 g
	Glycolic acid	40.0 g	65.0 g
	Succinic acid	20.0 g	30.0 g
20	Water to make	1,000 ml	1,000 ml
	pH (adjusted with NaOH and nitric acid as shown in Table 2)		
	Fixing solution	Running solution	Replenisher
25	Sodium thiosulfate	0.7 mols	1.0 mol
	Sodium sulfite	0.2 mols	0.3 mols
	Compound of the invention (shown in Table 2)	0.05 mols	0.08 mols
30	90% Acetic acid	3.0 g	4.0 g
	Water to make	1,000 ml	1,000 ml
	pH (adjusted with NaOH and acetic acid)	6.4	6.6
35	Stabilizing solution	Running solution (same to replenisher)(g)	
	Polyoxyethylene-p-monononylphenyl ether(Average polymerization degree: 10)	0.2	
40	1,2,4-Triazole	1.3	
	1-Hydroxymethyl-1,2,4-triazole	0.75	
	Gentamicin	0.01	
	1,2-Benzisothiazoline-3-one	0.05	
45	Water to make	1 l	
	pH (adjusted with aqueous ammonia and nitric acid)	8.5	

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TABLE 2

5	Test No.	Bleaching solution		Additive for fixing solution	Condition of aged solution	Dmin (R)	Δ Dmax (G)	Dmax (R)	Remarks
		Bleaching agent	pH						
10	101	1,3-PDТА	5.0	-	Slightly turbid	0.35	0.47	2.27	Comparison
	102	I-15	5.0	P-25	Not turbid	0.27	0.36	2.27	Invention
	103	"	2.0	P-57	"	0.31	0.41	2.28	Comparison
15	104	"	3.0	"	"	0.27	0.36	2.27	Indention
	105	"	3.5	"	"	0.27	0.35	2.27	"
	106	"	5.0	"	"	0.27	0.34	2.28	"
20	107	"	7.0	"	"	0.29	0.37	2.29	"
	108	"	8.0	"	"	0.33	0.40	2.26	Comparison
25	109	"	5.0	P-68	"	0.29	0.38	2.27	Invention
	110	I-45	4.0	-	Turbid	0.34	0.58	2.09	Comparison
	111	"	4.0	P-25	Not turbid	0.24	0.31	2.29	Invention
30	112	"	4.0	P-57	"	0.23	0.38	2.19	"
	113	"	4.0	P-57 + A-6	"	0.24	0.37	2.26	"
	114	"	4.0	P-57 + A-7	"	0.24	0.31	2.26	"
35	115	"	4.0	P-25+P-57+A-7	"	0.23	0.31	2.30	"
	116	I-25	4.5	P-25	"	0.24	0.36	2.29	"
	117	"	4.5	P-57 + A-6	"	0.26	0.40	2.30	"
40	(Note 1: 1,3-PDТА: 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid 2: When a compound P and a compound A were incorporated in the fixing solution in combination, they were used in equimolecular amount, totaling 0.05 mols.								

45 **[0204]** Table 2 shows that as compared with the comparative example using ferric complex salt (III) of 1,3-PDТА as a general-purpose bleaching agent (Test No. 1), the examples of the present invention using a bleaching solution and a fixing solution each comprising a compound represented by formula (I) or a compound represented by formula (II) or a phosphonic acid incorporated therein (Test Nos. 102, 104 to 107, 109) show less cyan stain, an improved stability of magenta dye and an enhanced stability of fixing solution. The comparison of Test Nos. 111 to 117, which are according to the present invention, with Test No. 110 shows that cyan stain, particularly instability of magenta dye, developed when the bleaching solution comprises a compound of formula (I) incorporated therein can be eliminated by incorporating a compound of the present invention in the fixing solution. Further, failure of cyan color restoration can be eliminated. Thus, the effect of the present invention can be obtained by the combination of additives for bleaching solution and fixing solution.

50 **[0205]** Test Nos. 111 to 117 provide comparison of examples of the present invention. As can be seen in the results of these tests, when a compound of formula (I) or phosphonic acid and a compound of formula (A) are incorporated in the fixing solution in combination, there can be recognized a further enhancement in color density.

55 **[0206]** To sum up, the incorporation of a compound of formula (I) of the present invention in a processing solution

having a bleaching ability and a compound of formula (II), EDTA or phosphonic acid in a processing solution having a fixing ability makes it possible to improve the occurrence to cyan stain, the stability of magenta dye and the stability of processing solution. When the processing solution having a fixing ability comprises a compound of formula (II), EDTA or phosphonic acid and a compound represented by formula (A) incorporated therein in combination, failure of cyan color restoration can be minimized, and color density can be enhanced. Further, the sulfurization of fixing solution can be prevented, enhancing stability with time.

[0207] In accordance with the processing method of the present invention involving desilvering with a processing solution having a bleaching ability comprising a compound of formula (I) incorporated therein and a processing solution having a fixing ability comprising a complex-forming agent selected from the group consisting of compound represented by formula (II), EDTA and phosphonic acid, preferably further a compound of formula (A), incorporated therein, the stability of the processing solution having a fixing ability can be improved, and the image thus obtained can be remarkably rendered unsusceptible to stain such as cyan stain. In particular, the use of the fixing solution comprising a compound of formula (A) incorporated therein makes it possible to minimize failure of cyan color restoration and hence enhance color density.

[0208] Further, failure of color restoration characteristic to bleaching agent containing a compound of formula (I) cannot take place. Further, there occurs little stain and no dye discoloration with time over various evaluations. Moreover, high color forming property can be obtained.

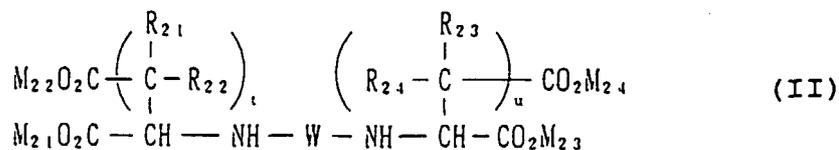
[0209] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A method for processing a silver halide color photographic material comprising color development, desilvering, rinsing and/or processing with a stabilizer, wherein said desilvering is effected with (a) a processing solution with a bleaching ability containing at least one ferric complex salt (III) of a compound represented by formula (I) and having a pH value of from 3 to 7 and (b) a processing solution with a fixing ability containing at least complex-forming agent selected from the group consisting of a compound represented by formula (II), EDTA and an organic phosphonic acid and having a pH value of from 6.1 to 8.0.

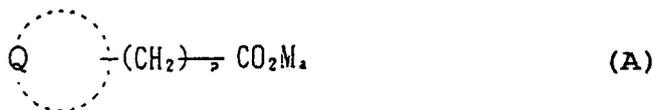


wherein R_1 represents a hydrogen atom, aliphatic hydrocarbon group, aryl group or heterocyclic group; L_1 and L_2 each represent an alkylene group; and M_1 and M_2 each represent a hydrogen atom or cation;



wherein R_{21} , R_{22} , R_{23} and R_{24} each represent a hydrogen atom, aliphatic hydrocarbon group, aryl group, heterocyclic group, hydroxyl group or carboxyl group; t and u each represent an integer of 0 or 1; W represents a divalent connecting group containing carbon atoms; and M_{21} , M_{22} , M_{23} and M_{24} each represent a hydrogen atom or cation.

2. The method for processing a silver halide color photographic material as in Claim 1, wherein said processing solution with a fixing ability to be used in desilvering contains at least one complex-forming agent selected from the group consisting of the compound represented by formula (II), EDTA and an organic phosphonic acid and a compound represented by formula (A):



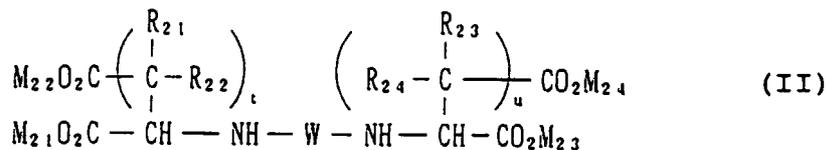
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wherein Q represents a nonmetallic atom group required to form a heterocyclic group; p represents an integer of 0 or 1; and M_a represents a hydrogen atom or cation.

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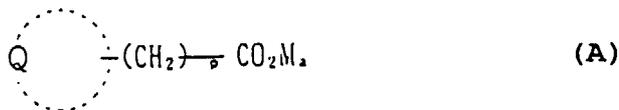
3. A processing solution for a silver halide photographic material with a fixing ability containing at least one complex-forming agent selected from the group consisting of a compound represented by formula (II), EDTA and an organic phosphonic acid and a compound represented by formula (A) and having a pH value of from 6.1 to 8.0:



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wherein R₂₁, R₂₂, R₂₃ and R₂₄ each represent a hydrogen atom, aliphatic hydrocarbon group, aryl group, heterocyclic group, hydroxyl group or carboxyl group; t and u each represent an integer of 0 or 1; W represents a divalent connecting group containing carbon atoms; and M₂₁, M₂₂, M₂₃ and M₂₄ each represent a hydrogen atom or cation;



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wherein Q represents a nonmetallic atom group required to form a heterocyclic group; p represents an integer of 0 or 1; and M_a represents a hydrogen atom or cation.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 6702

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.7)
X	EP 0 663 613 A (EASTMAN KODAK CO) 19 July 1995 (1995-07-19) * Examples 1 and 2 , Bleach and Fixer Formulas *	1	G03C7/42 G03C5/38
X	EP 0 412 532 A (FUJI PHOTO FILM CO LTD) 13 February 1991 (1991-02-13) * Page 38, Bleaching and Fixing solutions * * Table 2 *	1	
X	EP 0 657 777 A (FUJI PHOTO FILM CO LTD) 14 June 1995 (1995-06-14) * tables 2-5 * * table 5, No. 202 *	1-3	
P,X	DE 199 57 346 A (EASTMAN KODAK CO) 21 June 2000 (2000-06-21) * example 1 *	1	
X	EP 0 789 275 A (FUJI PHOTO FILM CO LTD) 13 August 1997 (1997-08-13) * Page 78, Table 2, EDTA/A-7 * * claims 1,4; example 1; tables 2,3 *	3	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G03C
A	US 5 856 074 A (KLAUNZER NORMAN ET AL) 5 January 1999 (1999-01-05) * column 1, line 1 - line 17 * * column 1, line 42 - column 2, line 30 * * column 2, line 40 - line 42 *	1	
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