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(54) Method for processing silver halide color light-sensitive material

(57) A method for processing a silver halide color light-sensitive material is disclosed, comprising color development, desilvering and water washing and/or processing with a stabilizing solution, wherein the processing solution having fixing ability for use in the desilvering contains a compound represented by formula (A) or (B) and has a pH of from 6.1 to 8.0.

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Description

FIELD OF THE INVENTION

The present invention relates to a processing composition having fixing ability for use in the processing of a silver halide color photographic light-sensitive material (hereinafter sometimes referred to simply as "light-sensitive material") and a processing method using the same, more specifically, the present invention relates to a processing composition capable of achieving good solution stability and good photographic properties, and a processing method using the same.

BACKGROUND OF THE INVENTION

A light-sensitive material is processed, after exposure and development, with a bleaching solution or with a fixing solution. As the fixing agent contained in the fixing solution, a thiosulfate is known from the old and it has been widely used in combination with a sulfite as a preservative therefor, an aminopolycarboxylic acid and/or an organic phosphonic acid as 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.

The processing solution having fixing ability is preferably used at a pH in the vicinity of 7 because the solution is readily deteriorated or coloring property of the dye is adversely affected when the pH is lowered. However, the processing solution may react with calcium or magnesium contained in water used for the adjustment or in eluate from the light-sensitive material, or with metal ion such as iron carried over from the bleaching solution, to cause precipitation, sludge or coloration of the light-sensitive material. Hence, the processing solution is not necessarily satisfied with respect to various problems such as aging change in the photographic property after processing and it is in need of further improvement. In the case of the light-sensitive material having a magnetic recording layer described in International Patent Publication WO90/04205, a problem of remarkable reduction in the reading capability of magnetic information is also caused.

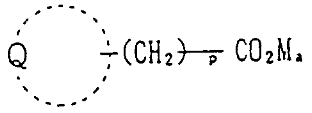
SUMMARY OF THE INVENTION

A first object of the present invention is to provide a method for processing a silver halide color photographic light-sensitive material using a processing solution having fixing ability, which has excellent solution stability and is capable of showing excellent property with respect to stains and aging change of an image after processing.

A second object of the present invention is to provide a method for processing a light-sensitive material having a magnetic recording layer, involving no reduction in the magnetic output even when magnetic reading is effected.

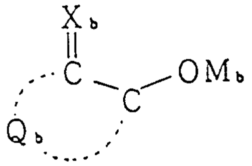
As a result of extensive investigations on the above-described problems, the present inventors have found a processing method described below:

a method for processing a silver halide color photographic light-sensitive material comprising color development, desilvering and water washing and/or processing with a stabilizing solution, wherein the processing solution having fixing ability for use in the desilvering contains a compound represented by the following formula (A) or (B) and has a pH of from 6.1 to 8.0:



(A)

wherein Q represents a nonmetallic atom group necessary for forming a heterocyclic ring, p represents 0 or 1 and M_a represents a hydrogen aton or a cation;



(B)

wherein Q_b represents a nonmetallic atom group necessary for forming a cyclic structure, X_b represents an oxygen atom, a sulfur atom or N-R_b (wherein R_b represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group), and M_b represents a hydrogen atom or a cation.

DETAILED DESCRIPTION OF THE INVENTION

JP-A-51-7930 discloses a processing solution having fixing ability, which contains a pyridine-2,6-dicarboxylic acid as one of the compounds represented by formula (A), however, this technique relates to stains of a light-sensitive material ascribable to an ion chloride bleaching solution and a cyan coupler. Research Disclosure, No. 16768 (March, 1978) discloses a fixing solution containing a kojic acid which is one of the compounds represented by formula (B), however, this technique relates to a hardening fixing solution containing an aluminum complex salt. Thus, these techniques fail to have any recognition on the technical region of the present invention.

In the present invention, the light-sensitive material is processed with a color developer, desilvered and then subjected to water washing and/or processing with a stabilizing solution.

In the desilvering, the light-sensitive material is fundamentally bleached with a solution having bleaching ability and then fixed with a processing solution having fixing ability. The bleaching and the fixing may be performed separately as described above, or they may be performed simultaneously with a bleach-fixing solution having both bleaching ability and fixing ability (bleach-fixing). The bleaching, the fixing and the bleach-fixing each may be performed in a single tank or in two or more tanks.

The term "processing solution having fixing ability" as used in the present invention means a processing solution containing a fixing agent among processing solutions used in the desilvering step, more specifically, it includes a fixing solution and a bleach-fixing solution. The term "processing solution having bleaching ability" as used herein means a processing solution containing a bleaching agent among the processing solutions used in the desilvering step, more specifically, it includes a bleaching solution and a bleach-fixing solution.

Specific examples of the desilvering in the present invention are described below, but the present invention is by no means limited thereto:

1. bleaching - fixing
2. bleach-fixing
3. bleaching - bleach-fixing
4. bleach-fixing - bleach-fixing
5. bleaching - bleach-fixing - fixing
6. bleaching - bleach-fixing - bleach-fixing
7. bleaching - fixing - fixing
8. bleaching - fixing - bleach-fixing
9. bleach-fixing - fixing
10. bleach-fixing - bleaching

Between these processing steps, a water-washing step may be freely interposed.

The compound represented by formula (A) is described in detail below. The term "carbon number" used in the following indicate a carbon number exclusive of carbon atoms in the substituent moiety.

The heterocyclic residue represented by Q is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated or unsaturated heterocyclic residue containing at least one of N, O and S atoms. The heterocyclic residue may be monocyclic or may be condensed to other ring.

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

Specific examples of the heterocyclic residue include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidyl, 3-piperidyl, 4-piperidyl, 2-piperazinyl, 2-morpholinyl, 3-morpholinyl, 2-thienyl, 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-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-phthalazinyl, 5-phthalazinyl, 6-phthalazinyl, 2-naphthylidinyl, 3-naphthylidinyl, 4-naphthylidinyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 5-quinazolinyl, 6-quinazolinyl, 7-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 4-cinnolinyl, 5-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 8-cinnolinyl, 2-pteridinyl, 4-pteridinyl, 6-pteridinyl, 7-pteridinyl, 1-acridinyl, 2-acridinyl, 3-acridinyl, 4-acridinyl, 9-acridinyl, 2-(1,10-phenanthronilyl), 3-(1,10-phenanthronilyl), 4-(1,10-phenanthronilyl), 5-(1,10-phenanthronilyl), 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.

The heterocyclic residue is preferably 2-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 3-

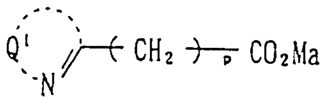
pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl), 3-(1,2,4-triazinyl), 5-(1,2,4-triazinyl), 6-(1,2,4-triazinyl), 2-indolyl, 3-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthalazinyl, 2-quinoxalinyl, 5-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 8-cinnolinyl, 2-(1,10-phenanthrolinyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl or 4-oxazolyl, more preferably 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 or 4-oxazolyl, still more preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl or 8-quinolyl, particularly preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl or 2-quinolyl, and most preferably 2-pyridyl.

The heterocyclic residue may have a substituent in addition to $(CH_2)_pCO_2M_a$. Examples of the substituent include an alkyl group (preferably an alkyl group having from 1 to 12, more preferably from 1 to 6, still more preferably from 1 to 3 carbon atoms, e.g., methyl, ethyl), an aralkyl group (preferably an aralkyl group having from 7 to 20, more preferably from 7 to 15, still more preferably from 7 to 11 carbon atoms, e.g., phenylmethyl, phenylethyl), an alkenyl group (preferably an alkenyl group having from 2 to 12, more preferably from 2 to 6, still more preferably 2 to 4 carbon atoms, e.g., allyl), an alkynyl group (preferably an alkynyl group having from 2 to 12, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., propargyl), an aryl group (preferably an aryl group having from 6 to 20, more preferably from 6 to 15, still more preferably from 6 to 10 carbon atoms, e.g., phenyl, p-methylphenyl), an amino group (preferably an amino group having from 0 to 20, more preferably from 0 to 10, still more preferably from 0 to 6 carbon atoms, e.g., amino, methylamino, dimethylamino, diethylamino), an alkoxy group (preferably an alkoxy group having from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy), an aryloxy group (preferably an aryloxy group having from 6 to 12, more preferably from 6 to 10, still more preferably from 6 to 8 carbon atoms, e.g., phenyloxy), an acyl group (preferably an acyl group having from 1 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., acetyl), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., methoxycarbonyl), an acyloxy group (preferably an acyloxy group having from 1 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., acetoxy), an acylamino group (preferably an acylamino group having from 1 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., acetylamino), a sulfonylamino group (preferably a sulfonylamino group having from 1 to 10, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino), a sulfamoyl group (preferably a sulfamoyl group having from 0 to 10, more preferably from 0 to 6, still more preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl), a carbamoyl group (preferably a carbamoyl group having from 1 to 10, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl), an alkylthio group (preferably an alkylthio group having from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio), an arylthio group (preferably an arylthio group having from 6 to 20, more preferably from 6 to 10, still more preferably from 6 to 8 carbon atoms, e.g., phenylthio), a sulfonyl group (preferably a sulfonyl group having from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl), a sulfinyl group (preferably a sulfinyl group having from 1 to 8, more Preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl), a ureido group, a hydroxy group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group, a hydroxamic acid group, a mercapto group and a heterocyclic group (e.g., imidazolyl, pyridyl). These substituents may be substituted with further substituent(s). Such a substituent is preferably an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group, more preferably an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group or a halogen atom, still more preferably an amino group, a carboxyl group or a hydroxy group, and most preferably a carboxyl group. When two or more substituents are present, they may be the same or different.

p represents 0 or 1 and p is preferably 0.

The cation represented by M_a includes organic and inorganic cations and examples thereof include an alkali metal ion (e.g., Li^+, Na^+, K^+, Cs^+), an alkaline earth metal ion (e.g., Ca^{2+}, Mg^{2+}), an ammonium (e.g., ammonium, tetraethylammonium), pyridinium and phosphonium (e.g., tetrabutylphosphonium, tetraphenylphosphonium).

Among the compounds represented by formula (A), preferred are the compounds represented by the following formula (A-a):



(A-a)

wherein p and M_a have the same meaning as those defined in formula (A), Q^1 represents a nonmetallic atom group necessary for forming a nitrogen-containing heterocyclic ring.

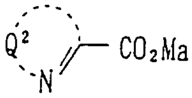
The nitrogen-containing heterocyclic residue formed by Q^1 is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated or unsaturated heterocyclic residue containing at least one nitrogen and the heterocyclic residue may be monocyclic or may be condensed to other ring.

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

Specific examples of the nitrogen-containing heterocyclic residue include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidinyl, 3-piperidyl, 4-piperidyl, 2-piperazinyl, 2-morpholinyl, 3-morpholinyl, 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-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-phthalazinyl, 5-phthalazinyl, 6-phthalazinyl, 2-naphthyridinyl, 3-naphthyridinyl, 4-naphthyridinyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 5-quinazolinyl, 6-quinazolinyl, 7-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 4-cinnolinyl, 5-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 8-cinnolinyl, 2-pteridinyl, 4-pteridinyl, 6-pteridinyl, 7-pteridinyl, 1-acridinyl, 2-acridinyl, 3-acridinyl, 4-acridinyl, 9-acridinyl, 2-(1,10-phenanthrolinyl), 3-(1,10-phenanthrolinyl), 4-(1,10-phenanthronilyl), 5-(1,10-phenanthronilyl), 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. The nitrogen-containing heterocyclic residue is preferably 2-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl), 3-(1,2,4-triazinyl), 5-(1,2,4-triazinyl), 6-(1,2,4-triazinyl), 2-indolyl, 3-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthalazinyl, 2-quinoxalinyl, 5-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 8-cinnolinyl, 2-(1,10-phenanthrolinyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl or 4-oxazolyl, more preferably 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 or 4-oxazolyl, still more preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl or 8-quinolyl, particularly preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl or 2-quinolyl, most preferably 2-pyridyl.

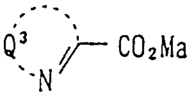
The nitrogen-containing heterocyclic residue may have a substituent in addition to $(CH_2)_pCO_2M_a$ and examples of the substituent include those described above for the heterocyclic group formed by Q in formula (A) and preferred substituents are also the same.

p and M_a have the same meaning as those defined in formula (A) and the preferred ranges thereof are also the same. Among the compounds represented by formula (A-a), preferred are the compounds represented by the following formula (A-b):


(A-b)

wherein M_a has the same meaning as that defined in formula (A), and Q^2 represents a 5- or 6-membered nitrogen-containing heterocyclic group which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group.

Among the compounds represented by formula (A-b), preferred are those represented by the following formula (A-c):

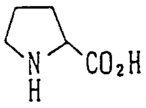

(A-c)

wherein M_a has the same meaning as that defined in formula (A), and Q^3 represents an atomic group necessary for forming a pyridine ring or an imidazole ring which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group.

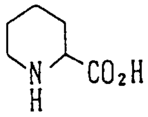
Details of the above-described substituents for the group represented by Q^2 or Q^3 are the same as those for the nitrogen-containing heterocyclic group represented by Q in formula (A).

Specific examples of the compound represented by formula (A) are set forth below, however, the present invention is by no means limited thereto.

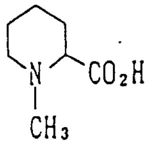
A-1



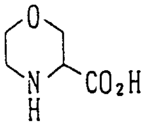
A-2



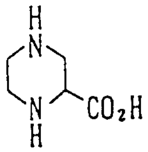
A-3



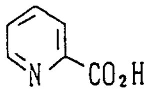
A-4



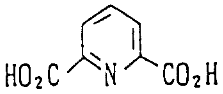
A-5



A-6



A-7



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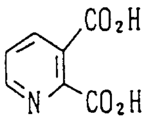

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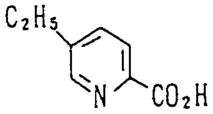

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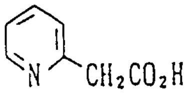

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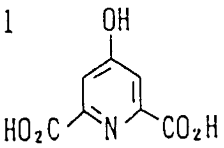
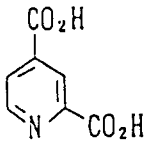


A-12



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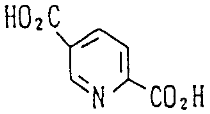
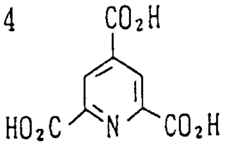
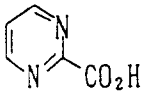


A-14



A-15



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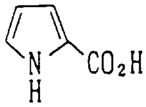

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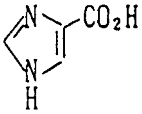

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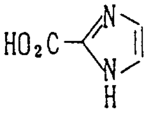

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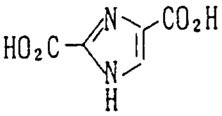

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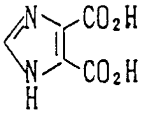

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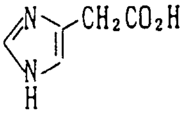

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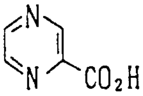

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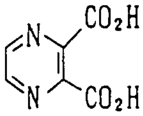

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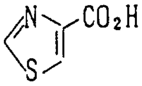

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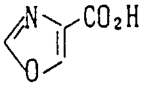

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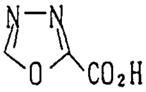

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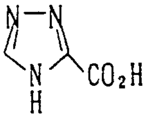

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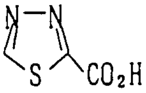

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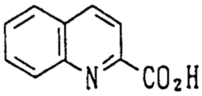

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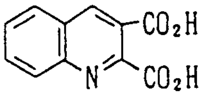

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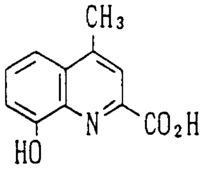

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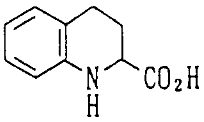

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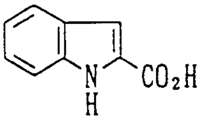

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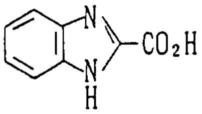

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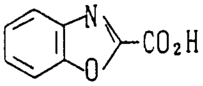

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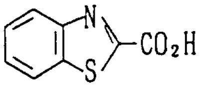

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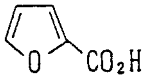

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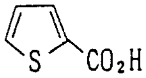

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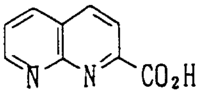

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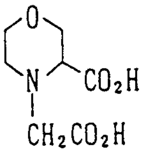

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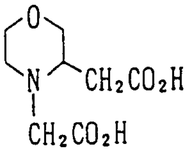

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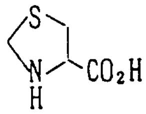

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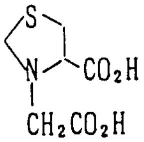

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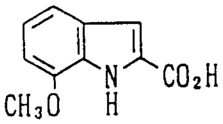

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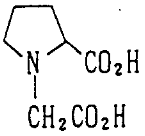

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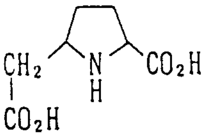

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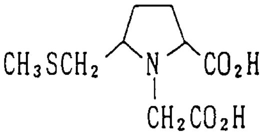

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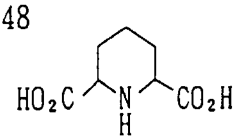

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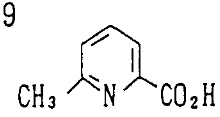

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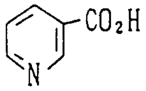

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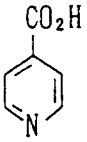

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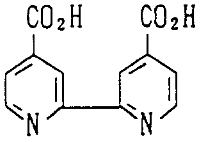

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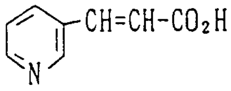

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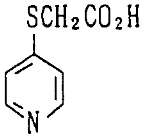

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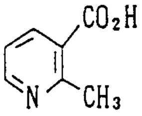

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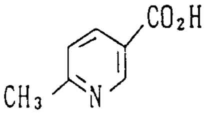

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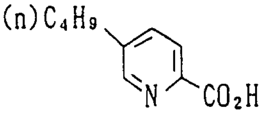

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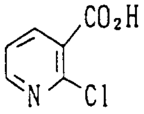

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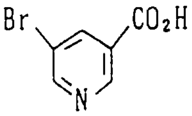

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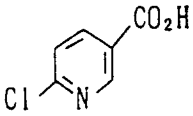

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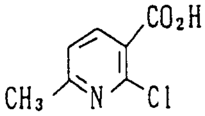

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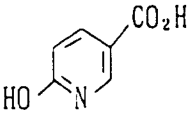

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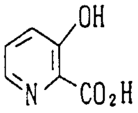

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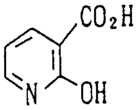

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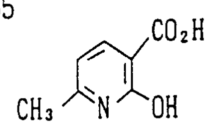

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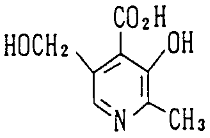

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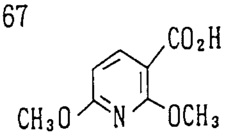

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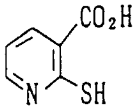

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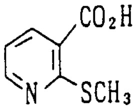

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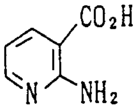

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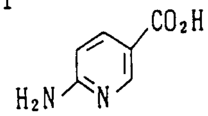

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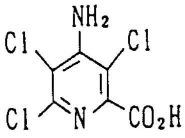

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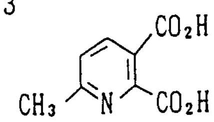

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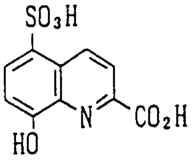

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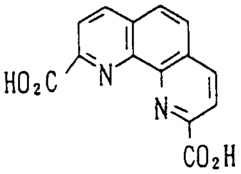

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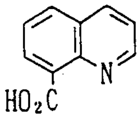

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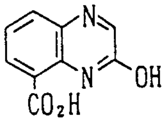

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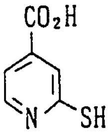

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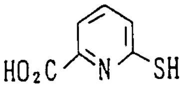

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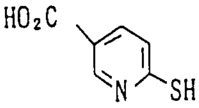

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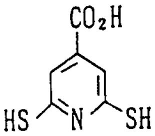


The above-described compounds each may be used in the form of an ammonium salt or an alkali metal salt.

The compound represented by formula (A) can be synthesized according to the method described in Organic Syntheses Collective, Volume 3, page 740 or commercially available products may be used.

Among the above-described compounds, preferred are Compounds (A-6), (A-7), (A-8), (A-13), (A-14), (A-20), (A-

22), (A-29) and (A-49), and more preferred is Compound (A-7).

The compound represented by formula (B) is described in detail below.

The ring structure formed by Q_b is a 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated or unsaturated ring containing at least one of C, N, O and S atoms. The ring may be monocyclic or may be condensed to other ring. The ring structure formed by Q_b is preferably a 5-, 6- or 7-membered unsaturated ring, more preferably a 5- or 6-membered unsaturated ring.

Specific examples of the ring structure formed by Q_b include cyclobutane, cyclobutene, cyclopentane, cyclopentene, cyclohexane, cyclohexene, cycloheptane, cycloheptene, cyclopentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cycloheptadiene, 1,3,5-cycloheptatriene, 2H-pyran, 4H-pyran, 2H-chromene, 4H-chromene, 2H-pyrrole, 3H-pyrrole, 2-pyrroline, 3-pyrazoline, 3H-indole, 4H-quinolidine, 2H-furo[3,2-b]pyran, 2,3-dihydrofuran, 2,5-dihydrofuran, 3,4-dihydro-2H-pyran, 5,6-dihydro-2H-pyran, 5H-thiophene, 1,2-dihydropyridine, 1,4-dihydropyridine, 2H-thiopyran, 4H-thiopyran, 3,4-dihydro-2H-thiopyran and 5,6-dihydro-2H-thiopyran. The ring structure is preferably cyclopentene, cyclohexene, 2H-pyran, 4H-pyran, 2H-chromene, 4H-chromene, 1,2-dihydropyridine or 1,4-dihydropyridine, more preferably 2H-pyran, 4H-pyran, 1,2-dihydropyridine or 1,4-dihydropyridine, more preferably 2H-pyran or 4H-pyran, particularly preferably 4H-pyran.

The ring formed by Q_b may have a substituent and examples of the substituent include an alkyl group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methyl, ethyl), an alkenyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, ally]), an alkynyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., propargyl), an aryl group (having preferably from 6 to 12, more preferably from 6 to 10, still more preferably from 6 to 8 carbon atoms, e.g., phenyl, p-methylphenyl), an alkoxy group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy), an aryloxy group (having preferably from 6 to 12, more preferably from 6 to 10, still more preferably from 6 to 8 carbon atoms, e.g., phenyloxy), an acyl group (having preferably from 1 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., acetyl), an alkoxycarbonyl group (having preferably from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., methoxycarbonyl), an acyloxy group (having preferably from 1 to 12, more preferably from 2 to 10, still more preferably from 2 to 8 carbon atoms, e.g., acetoxy), an acylamino group (having preferably from 1 to 10, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., acetylamino), a sulfonylamino group (having preferably from 1 to 10, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino), a sulfamoyl group (having preferably from 0 to 10, more preferably from 0 to 6, still more preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl), a carbamoyl group (having preferably from 1 to 10, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl), an alkylthio group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio), a sulfonyl group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl), a sulfinyl group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl), a hydroxy group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), a cyano group, a sulfo group, a carboxy group, a nitro group and a heterocyclic group (e.g., imidazolyl, pyridyl). These substituents each may be substituted with further substituent(s), which is preferably a substituted or unsubstituted alkyl group, a hydroxy group or a carboxy group, more preferably a methyl group, an ethyl group, a hydroxymethyl group, a hydroxyethyl group or a carboxy group. When two or more substituents are present, they may be the same or different.

X_b represents an oxygen atom, a sulfur atom or an N-R_b (wherein R_b represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group).

The aliphatic hydrocarbon group represented by R_b is a linear, branched or cyclic alkyl group (having preferably from 1 to 12, more preferably from 1 to 10, still more preferably from 1 to 8 carbon atoms), an alkenyl group (having preferably from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 7 carbon atoms) or an alkynyl group (having preferably from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 7 carbon atoms), and the aliphatic hydrocarbon group may have a substituent.

Examples of the substituent include those described above as the substituent for the ring formed by Q_b. The substituent for the aliphatic hydrocarbon group represented by R_b is preferably an alkoxy group, a carboxy group, a hydroxy group or a sulfo group, more preferably a carboxy group or a hydroxy group.

The aliphatic hydrocarbon group represented by R_b is preferably an alkyl group, more preferably a chained alkyl group, still more preferably methyl, ethyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, hydroxymethyl, 2-hydroxyethyl, methoxymethyl or sulfomethyl, particularly preferably methyl, ethyl or hydroxymethyl.

The aryl group represented by R_b is preferably a monocyclic or bicyclic aryl group having from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), more preferably a phenyl group having from 6 to 15 carbon atoms, still more preferably a phenyl group having from 6 to 10 carbon atoms.

The aryl group represented by R_b may have a substituent and examples of the substituent include those described above as the substituent of the ring formed by Q_b. The substituent for the aryl group represented by R_b is preferably an alkyl group, an alkoxy group, a carboxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, an alkoxy group, a carboxy group or a hydroxy group.

Specific examples of the aryl group represented by R_b include phenyl, 4-methylphenyl, 2-carboxyphenyl, 4-carboxyphenyl and 4-methoxyphenyl.

The heterocyclic group represented by R_b is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 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 be condensed to other ring.

The heterocyclic group is preferably a 5- or 6-membered heterocyclic group, more preferably a 5- or 6-membered heterocyclic group containing a nitrogen atom, still more preferably a 5- or 6-membered heterocyclic group having one or two nitrogen atom.

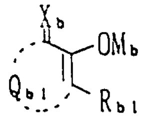
Specific examples of the heterocyclic group include thienyl, furyl, pyranyl, pyrrolyl, imidazolyl, pyrazolyl, isothiazolyl, isooxazolyl, thiazolyl, oxazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1,3,4-oxadiazolyl, 1,3,4-thiadiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, 3H-indolyl, indolyl, 1H-indazolyl, purinyl, 4H-quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthylidinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, isochromanyl, chromanyl, pyrrolinyl, imidazolidinyl, imidazolinyl, pyrazolidinyl, pyrazolinyl, piperidinyl, piperazinyl, indolinyl, isoindolinyl, quinacridinyl, morpholinyl, tetrazolyl, benzimidazolyl, benzoxazolyl, benzthiazolyl and benztriazolyl, with morpholyl, pyrrolidinyl, piperidyl, imidazolyl and pyridyl being preferred.

The heterocyclic group represented by R_b may have a substituent and examples of the substituent include those described above as the substituent for the ring formed by Q_b. The substituent of the heterocyclic group represented by R_b is preferably an alkyl group, an alkoxy group, a carboxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, an alkoxy group, a carboxy group or a hydroxy group.

X_b is preferably an oxygen atom or a sulfur atom, more preferably an oxygen atom.

The cation represented by M_b includes organic and inorganic cations and examples thereof include alkali metals (e.g., Li^+, Na^+, K^+, Cs^+), alkaline earth metals (e.g., Mg^{2+}, Ca^{2+}), ammonium (e.g., ammonium, trimethylammonium, triethylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, 1,2-ethanediammonium), pyrdinium, imidazolium and phosphonium (e.g., tetrabutylphosphonium). M_b is preferably a hydrogen atom, an alkali metal or ammonium, more preferably a hydrogen atom.

Among the compounds represented by formula (B), preferred are the compounds represented by the following formula (B-a):



(B-a)

wherein X_b and M_b have the same meaning as those defined in formula (B) and the preferred ranges thereof are also the same, Q_{b1} represents a nonmetallic atom group necessary for forming a ring structure, and R_{b1} represents a hydrogen atom, a carboxy group, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group.

The ring structure formed by Q_{b1} is a 4-, 5-, 6-, 7-, 8-, 9- or 10-membered unsaturated ring containing at least one of C, N, O and S atoms and the ring may be monocyclic or may be condensed to other ring. The ring structure formed by Q_{b1} is preferably a 5-, 6- or 7-membered unsaturated ring, more preferably a 5- or 6-membered unsaturated ring.

Specific examples of the ring structure formed by Q_{b1} include cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclopentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cycloheptadiene, 1,3,5-cycloheptatriene, 2H-pyran, 4H-pyran, 2H-chromene, 4H-chromene, 2H-pyrrole, 3H-pyrrole, 2-pyrroline, 3-pyrazoline, 3H-indole, 4H-quinolizine, 2H-furo[3,2-b]pyran, 2,3-dihydrofuran, 2,5-dihydrofuran, 3,4-dihydro-2H-pyran, 5,6-dihydro-2H-pyran, 5H-thiophene, 1,2-dihydropyridine, 1,4-dihydropyridine, 2H-thiopyran, 4H-thiopyran, 3,4-dihydro-2H-thiopyran and 5,6-dihydro-2H-thiopyran. The ring structure is preferably cyclopentene, cyclohexene, 2H-pyran, 4H-pyran, 2H-chromene, 4H-chromene, 1,2-dihydropyridine or 1,4-dihydropyridine, more preferably 2H-pyran, 4H-pyran, 1,2-dihydropyridine or 1,4-dihydropyridine, still more preferably 2H-pyran or 4H-pyran, particularly preferably 4H-pyran.

The ring formed by Q_{b1} may have a substituent and examples of the substituent include those described above as the substituent for the ring formed by Q_b.

The aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R_{b1} have the same meaning as those defined in formula (B) and the preferred ranges thereof are also the same.

R_{b1} is preferably a hydrogen atom or an alkyl group having from 1 to 8 carbon atoms, more preferably a hydrogen atom, methyl, ethyl, 1-carboxyethyl, 2-carboxyethyl, hydroxymethyl or 2-hydroxyethyl, particularly preferably a hydrogen atom, methyl, ethyl or hydroxymethyl.

Among the compounds represented by formula (B-a), preferred are the compounds represented by the following

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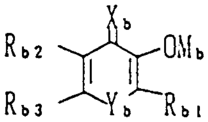
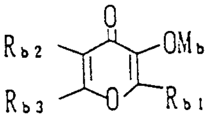
formula (B-b):


(B-b)

wherein X_b, M_b and R_{b1} have the same meaning as those defined in formula (B-a) and the preferred ranges thereof are also the same, R_{b2} and R_{b3} have the same meaning as those defined in formula (B-a) and the preferred ranges thereof are also the same, R_{b2} and R_{b3} may be combined to form a ring, and Y_b represents an oxygen atom, a sulfur atom, SO, SO_2 or N-R_y (wherein R_y has the same meaning as R_b defined in formula (B) and the preferred range thereof is also the same), preferably an oxygen atom, a sulfur atom or N-R_y, more preferably an oxygen atom.

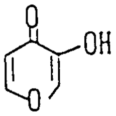
Among the compounds represented by formula (B-b), preferred are the compounds represented by formula (B-c):


(B-c)

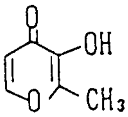
wherein M_b, R_{b1}, R_{b2} and R_{b3} have the same meaning as those defined in formula (B-b) and the preferred ranges thereof are also the same.

Among the compounds represented by formula (B), preferred are those having a total carbon number of from 4 to 20, more preferably from 5 to 14.

B－1



B－2



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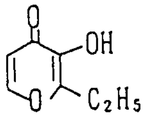
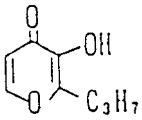
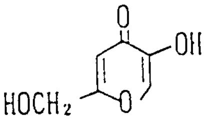


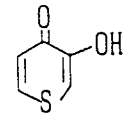
B－4



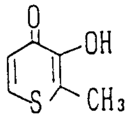
B－5



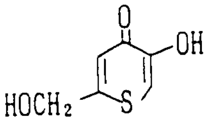
B－6



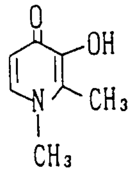
B－7



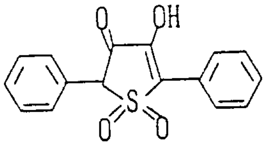
B－8



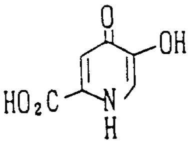
B－9



B－10



B－11



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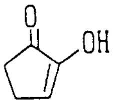

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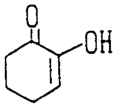

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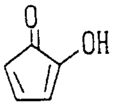

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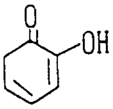

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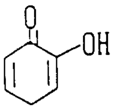

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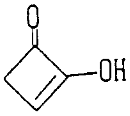

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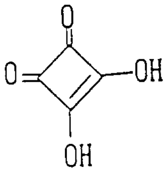

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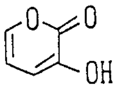

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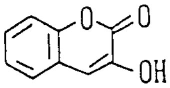

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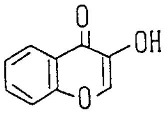

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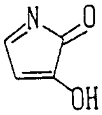

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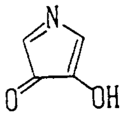

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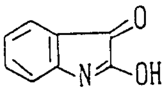

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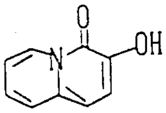

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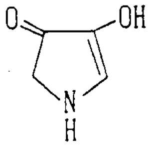

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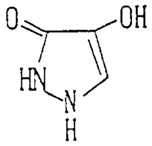

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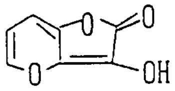

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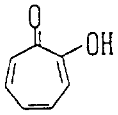

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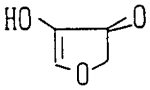

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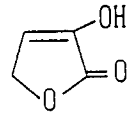

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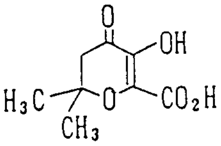

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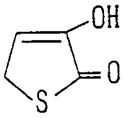

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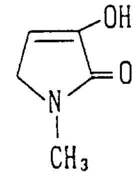

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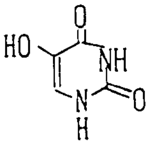
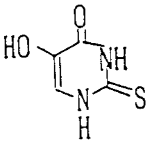


B −36



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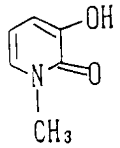

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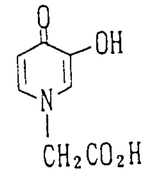
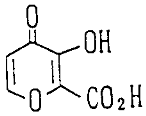


B −39



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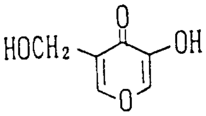

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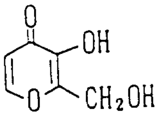

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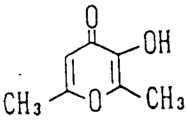

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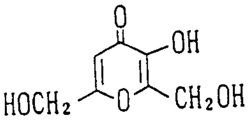

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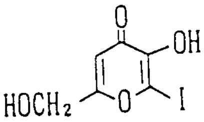
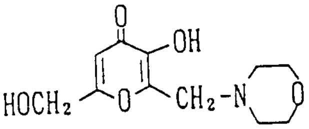


B −45



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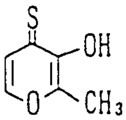

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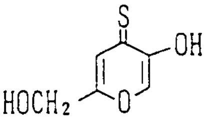
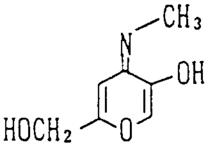
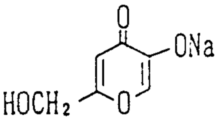


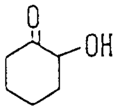
B −48



B −49



B −50



The above-described compounds each includes, if possible, a conjugated isomer thereof.

The compound represented by formula (B) may be a commercially available product or may be synthesized according to the methods described, for example, in Journal of the American chemical Society, Vol. 67, page 2276 (1945), ibid., Vol. 68, page 2744 (1946) and ibid., Vol. 69, page 2908 (1947).

Among the above-described compounds, Compounds (B-1), (B-2), (B-3), (B-5), (B-21), (B-39), (B-40), (B-41), (B-42) and (B-43) are preferred, and Compounds (B-2), (B-3) and (B-5) are more preferred.

In the present invention, the compound represented by formula (A) or (B) is incorporated into the processing solution having fixing ability in a total amount of preferably from 0.001 to 0.3 mol/ℓ, more preferably from 0.005 to 0.2 mol/ℓ, still more preferably from 0.01 to 0.15 mol/ℓ.

The effect of the present invention can be provided when the processing solution having fixing ability has a pH of from 6.1 to 8.0, more preferably from 6.4 to 7.7.

In the present invention, the compound represented by formula (A) or (B) is preferably added also to a processing solution having bleaching ability and the addition amount is preferably the same as that in the case of a processing solution having fixing ability.

In the present invention, the compound represented by formula (A) or (B) may be used individually or in combination of two or more thereof.

The replenishing amount of the processing solution having fixing ability of the present invention is from 100 to 1,000 ml, preferably from 150 to 700 ml, more preferably from 200 to 600 ml per one square meter of the light-sensitive material.

The processing solution having fixing ability may contain a sulfite (e.g., sodium sulfite, potassium sulfite, ammonium sulfite), a hydroxylamine, a hydrazine, a bisulfite adduct of aldehyde compounds (e.g., sodium acetaldehyde bisulfite, preferably the compound described in JP-A-3-158848) or a sulfinic acid compound described in JP-A-1-231051, as a preservative. Further, the processing solution having fixing ability may contain a fluorescent brightening agent, a defoaming agent, a surface active agent or an organic solvent such as polyvinyl pyrrolidone and methanol.

Furthermore, in order to stabilize the processing solution having fixing ability, the solution may contain an aminopolycarboxylic acid or an organic phosphonic acids as a chelating agent in addition to the compound of the present invention. Preferred examples of the chelating agent include 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid), nitrilotrimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetraacetic aid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid, 1,2-propylenediaminetetraacetic acid and the compounds represented by formulae (I) and (II) of the present invention.

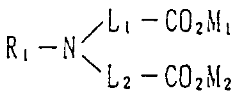
With respect to the processing solution having fixing ability, the compounds and the processing conditions described in JP-A-4-125558, from page 7, left lower column, line 10 to page 8, right lower column, line 19 may be applied. The processing solution having fixing ability which can be used in the present invention preferably contains a fixing agent such as thiosulfate in a concentration of 0.8 to 3 mol/liter.

In particular, in order to improve the fixing rate and the preservability, the compounds represented by formulae (I) and (II) of JP-A-6-301169 are preferably used individually or in combination, in the processing solution having fixing ability. It is also preferred in view of improvement in the preservability to use sulfinic acids described in JP-A-1-114762 including p-toluenesulfinate.

Further, in order to maintain the pH of the processing solution having bleaching ability constant, a buffer agent is preferably added to the solution. Examples of the buffer agent include monobasic acids such as acetic acid and glycolic acid, polybasic acids such as succinic acid, malonic acid, maleic acid and citric acid, phosphoric acid salts, imidazoles such as imidazole, 1-methylimidazole, 2-methylimidazole and 1-ethylimidazole, triethanolamine, N-allylmorpholine and N-benzoylpiperazine.

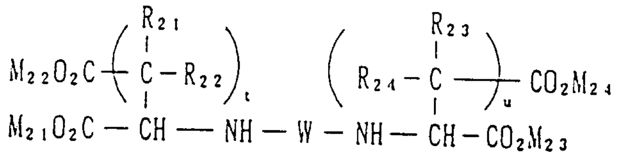
As the bleaching solution contained in the processing solution having bleaching ability, inorganic oxidizing agents such as red prussiate of potash, ferric chloride, bichromate, persulfate, bromate and hydrogen peroxide, and organic acid iron(III) complex salts are known, however, in the present invention, in view of environmental conservation, safety in handling and corrosion of metals, organic acid iron(III) complex salts are preferred.

Preferred examples of the organic acid iron(III) complex salt which can be contained in the processing solution having bleaching ability for use in the present invention include iron(III) complex salts of an 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 glycol ether diaminetetraacetic acid, bleaching agents described in JP-A-4-121739, from page 4, right lower column, page 5, left upper column including 1,3-propanediamine-N,N,N',N'-tetraacetic iron(III) salts, carbamoyl-based bleaching agents described in Unexamined European Patent Publication No. 461413, bleaching agents having a heterocyclic ring described in JP-A-4-174432, bleaching agents including N-(2-carboxyphenyl)iminodiacetic acid iron(III) complex salt described in Unexamined European Patent Publication No. 520457, bleaching agents including ethylenediamine-N-(2-carboxyphenyl)-N,N',N'-triacetic acid iron(III) complex salt described in Unexamined European Patent Publication No. 530828, bleaching agents including N,N'-bis(1,2-dicarboxyethyl)ethylenediamine iron(III) complex salt described in Unexamined European Patent Publication No. 567,126, bleaching agents including N-(1-carboxy-2-phenylethyl)aspartic acid iron(III) complex salt described in Unexamined European Patent Publication No. 588289, bleaching agents including N-(1-carboxyethyl)iminodiacetic acid iron(III) complex salt described in Unexamined European Patent Publication No. 591934, bleaching agents described in Unexamined European Patent Publication No. 501479, bleaching agents described in Unexamined European Patent Publication No. 461670, bleaching agents described in Unexamined European Patent Publication No. 430000 and aminopolycarboxylic acid iron(III) complex salts described in JP-A-3-144446. However, iron(III) complex salts of the compounds represented by the following formulae (I) and (II) are particularly preferred:



$$R_1-N\begin{cases}L_1-CO_2M_1\\L_2-CO_2M_2\end{cases}\qquad (I)$$

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



$$\begin{array}{l}M_{22}O_2C\left(\overset{R_{21}}{\underset{|}{\overset{|}{C}}}-R_{22}\right)_t\qquad\left(R_{24}-\overset{R_{23}}{\underset{|}{\overset{|}{C}}}\right)_u CO_2M_{24}\\M_{21}O_2C-CH-NH-W-NH-CH-CO_2M_{23}\end{array}\qquad (II)$$

wherein R_{21}, R_{22}, R_{23} and R_{24} each represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, a hydroxy group or a carboxy group, t and u each represents 0 or 1, W represents a divalent linking group including a carbon atom, and M_{21}, M_{22}, M_{23} and M_{24} each represents a hydrogen atom or a cation.

The compound represented by formula (I) is described in detail below. The number of carbon atoms used in the following indicates the number of carbon atoms excluding carbon atoms in the substituent moiety.

The aliphatic hydrocarbon group represented by R_1 includes linear, branched and cyclic alkyl groups (having preferably from 1 to 12, more preferably from 1 to 10, still more preferably from 1 to 8 carbon atoms), an alkenyl group (having preferably from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 7 carbon atoms) and an alkynyl group (having from 2 to 12, more preferably from 2 to 10, still more preferably from 2 to 7 carbon atoms), which groups each may have a substituent.

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

The substituent for the aliphatic hydrocarbon group represented by R_1 is preferably an alkoxy group, a carboxy group, a hydroxy group or a sulfo group, more preferably a carboxy group or a hydroxy group.

The aliphatic hydrocarbon group represented by R_1 is preferably an alkyl group, more preferably a chain alkyl group, still more 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-2-methylthiopropyl.

The aryl group represented by R_1 is preferably a monocyclic or bicyclic aryl group having from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), more preferably a phenyl group having from 6 to 15 carbon atoms, still more preferably a phenyl group having from 6 to 10 carbon atoms.

The aryl group represented by R_1 may have a substituent and examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, include an alkyl group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methyl, ethyl), an alkenyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, allyl) and an alkynyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., propargyl).

The substituent for the aryl group represented by R_1 is preferably an alkyl group, an alkoxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, a carboxy group or a hydroxy group.

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

The heterocyclic group represented by R_1 includes 3- to 10-membered saturated or unsaturated heterocyclic rings having at least one of N, O and S atoms. The heterocyclic ring may be monocyclic or may be condensed to other ring.

The heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic group, more preferably a 5- or 6-membered aromatic heterocyclic group containing a nitrogen atom, still more preferably a 5- or 6-membered aromatic heterocyclic group containing one or two nitrogen atom.

Specific examples of the heterocyclic group include pyrrolidinyl, piperidinyl, piperazinyl, imidazolyl, pyrazolyl, pyridyl and quinolyl, and among these, imidazolyl and pyridyl are preferred.

The heterocyclic group represented by R_1 may have a substituent and examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, include an alkyl group (having preferably from 1 to 8, more preferably from 1 to 6, still more preferably from 1 to 4 carbon atoms, e.g., methyl, ethyl), an alkenyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, allyl) and an alkynyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g, propargyl).

The substituent for the heterocyclic group represented by R_1 is preferably an alkyl group, an alkoxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, a carboxy group or a hydroxy group.

R_1 is preferably a hydrogen atom or an alkyl group having from 1 to 8 carbon atoms, more preferably a hydrogen atom, methyl, ethyl, 1-carboxyethyl, 2-carboxyethyl, hydroxyethyl or 2-carboxy-2-hydroxyethyl, still more preferably a hydrogen atom.

The alkylene groups represented by L_1 and L_2 may be the same or different and each may be linear, branched or cyclic. The alkylene group may have a substituent and examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, include an alkenyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, ally]) and an alkynyl group (having preferably from 2 to 8, more preferably from 2 to 6, still more preferably from 2 to 4 carbon atoms, e.g., propargyl).

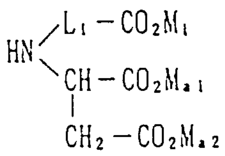
The substituent for the alkylene group represented by L_1 or L_2 is preferably an aryl group, an alkoxy group, a hydroxy group, a carboxy group or a sulfo group, more preferably an aryl group, a carboxy group or a hydroxy group.

The alkylene group represented by L_1 or L_2 is preferably an alkylene group with the alkylene group moiety having from 1 to 6, more preferably an alkylene group with the alkylene group moiety having from 1 to 4 carbon atoms, and still more preferably substituted or unsubstituted methylene or ethylene.

Preferred specific examples of the alkylene group include methylene, ethylene, trimethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1,2-cyclohexylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, 2-hydroxyethylmethylene, carbamoylmethylmethylene, phenylmethylene, benzylmethylene, 3-imidazolylmethylmethylene and 2-methylthioethylmethylene. Among these, more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, benzylmethylene, 4-imidazolylmethylene and 2-methylthioethylmethylene, still more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, hydroxymethylmethylene and benzyl methylene.

The cation represented by M_1 or M_2 includes organic and inorganic cations and examples thereof include an alkali metal (e.g., Li^+, Na^+, K^+, Cs^+), an alkaline earth metal (e.g., Mg^{2+}, Ca^{2+}), ammonium (e.g., ammonium, trimethylammonium, triethylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, 1,2-ethanediammonium), pyridinium, imidazolium and phosphonium (e.g., tetrabutyl phosphonium). M_1 and M_2 each is preferably an alkali metal or an ammonium, more preferably Na^+, K^+ or NH_4^+.

Among the compounds represented by formula (I), preferred are the compounds represented by the following formula (I-a):



$$\mathrm{HN}\begin{matrix}\diagup L_1-CO_2M_1\\ \diagdown CH-CO_2M_{a1}\\ \quad |\\ \quad CH_2-CO_2M_{a2}\end{matrix}\qquad (I\text{-}a)$$

wherein L_1 and M_1 have the same meaning as those defined in formula (I) and the preferred ranges thereof are also the same, M_{a1} and M_{a2} each has the same meaning as M_2 defined in formula (I).

In formula (I-a), preferably, L_1 is substituted or unsubstituted methylene or ethylene, and M_1, M_{a1} and M_{a2} each is a hydrogen atom, an alkali metal or an ammonium, more preferably, L_1 is substituted or unsubstituted methylene, and M_1, M_{a1} and M_{a2} each is a hydrogen atom, an alkali metal or an ammonium, still more preferably, L_1 is substituted or unsubstituted methylene having a total carbon number inclusive of carbon atoms in the substituent, of from 1 to 10, and M_1, M_{a1} and M_{a2} each is a hydrogen atom, Na^+, K^+ or NH_4^+.

The compound represented by formula (II) is described in detail below.

The aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R_{21}, R_{22}, R_{23} or R_{24} have the same meaning as the aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R_1, respectively, and the preferred ranges thereof are also the same.

R_{21}, R_{22}, R_{23} and R_{24} each is preferably a hydrogen atom or a hydroxy group, more preferably a hydrogen atom.

t and u each represents 0 or 1, preferably 1.

The divalent linking group represented by W can be represented by the following formula (W):

$$-(W^1\text{-}D)_v\text{-}(W^2)_w\text{-} \quad (W)$$

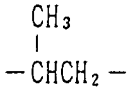
wherein W^1 and W^2, which may be the same or different, each represents a linear or branched alkylene group having from 2 to 8 carbon atoms (e.g., ethylene, propylene, trimethylene), a cycloalkylene group having from 5 to 10 carbon atoms (e.g., 1,2-cyclohexylene), an arylene group having from 6 to 10 carbon atoms (e.g., o-phenylene), an aralkylene group having from 7 to 10 carbon atoms (e.g., o-xylylenyl), a divalent nitrogen-containing heterocyclic group or a carbonyl group. The divalent nitrogen-containing heterocyclic group is preferably a 5- or 6-membered heterocyclic group having nitrogen as a hetero atom and the bonding to W^1 and W^2 is preferably made through the carbon atoms adjacent to each other as in an imidazolyl group. D represents -O-, -S- or $-N(R_w)-$. R_w represents a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms (e.g., methyl) which may be substituted by a carboxyl group, a phosphono group, a hydroxy group or a sulfo group, or an aryl group having from 6 to 10 carbon atoms (e.g., phenyl) which may be substituted by a carboxyl group, a phosphono group, a hydroxy group or a sulfo group.

W_1 and W_2 each is preferably an alkylene group having from 2 to 4 carbon atoms.

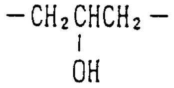
v represents an integer of from 0 to 3 and when v is 2 or 3, the W^1-D groups may be the same or different. v is preferably 0, 1 or 2, more preferably 0 or 1, still more preferably 0. w represents an integer of from 1 to 3 and when w is 2 or 3, the W^2 groups may be the same or different. w is preferably 1 or 2.

Specific examples of the divalent linking group represented by W are set forth below.

$-(CH_2)_2-$ 、 $-(CH_2)_3-$ 、 $-(CH_2)_4-$ 、



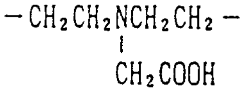
$-CH(CH_3)CH_2-$ 、



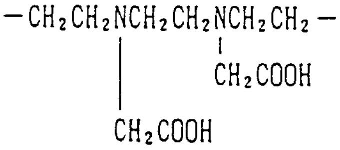
$-CH_2CH(OH)CH_2-$ 、 $-CH_2CH_2CH_2OCH_2CH_2-$ 、

$-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ 、 $-CH_2CH_2SCH_2CH_2-$ 、

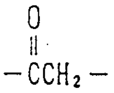
$-CH_2CH_2SCH_2CH_2SCH_2CH_2-$ 、



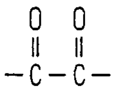
$-CH_2CH_2N(CH_2COOH)CH_2CH_2-$ 、



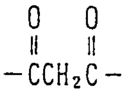
$-CH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)CH_2CH_2-$ 、



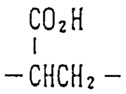
$-C(=O)CH_2-$ 、



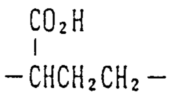
$-C(=O)-C(=O)-$ 、



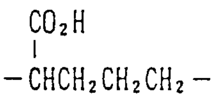
$-C(=O)CH_2C(=O)-$ 、



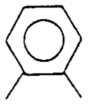
$-CH(CO_2H)CH_2-$ 、



$-CH(CO_2H)CH_2CH_2-$ 、



$-CH(CO_2H)CH_2CH_2CH_2-$.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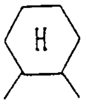
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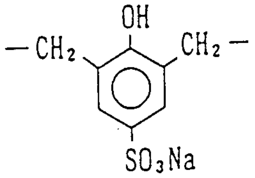
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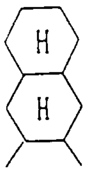
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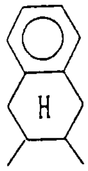
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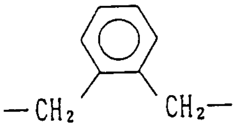
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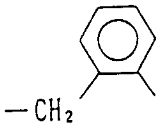
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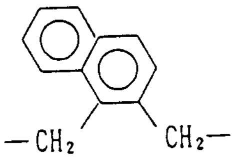
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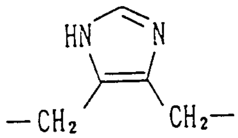
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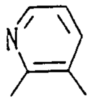
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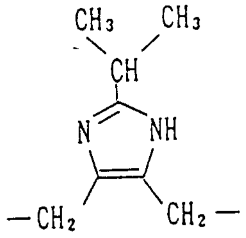
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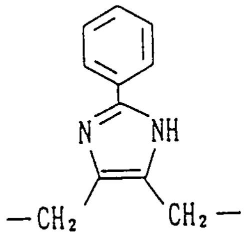

、

$-CH_2-CH=CH-CH_2-$.

W is more preferably ethylene, propylene, trimethylene or 2,2-dimethyltrimethylene, most preferably ethylene or trimethylene.

M_{21}, M_{22}, M_{23} and M_{24} each represents a hydrogen atom or a cation and they have the same meaning as M_1 and M_2 defined in formula (I).

Among the compounds represented by formula (II), those where R_{22} and R_{24} each is a hydrogen atom, and t and u each is 1 are preferred, and those where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, and t an u each is 1 are more preferred.

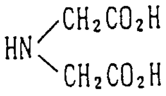
Among the compounds represented by formula (II), still more preferred are those where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, t and u each is 1, W is ethylene, and M_{21}, M_{22}, M_{23} and M_{24} each is selected from a hydrogen atom, Na^+, K^+ and NH_4^+, and those where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, t and u each is 1, W is trimethylene, and M_{21}, M_{22}, M_{23} and M_{24} each is selected from a hydrogen atom, Na^+, K^+ and NH_4^+.

When the compound represented by formula (I) or (II) has an asymmetric carbon in the molecule, at least one asymmetric carbon is preferably an L-form. When two or more asymmetric carbons are present, the number of L-form structures in the asymmetric carbon moiety is preferably larger.

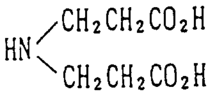
Specific examples of the compounds represented by formulae (I) and (II) are set forth below, however, the present invention is by no means limited thereto.

The mark L in the following compounds indicates that the asymmetric carbon moiety marked is an L-form. When not marked, the moiety is a mixture of D-form and L-form.

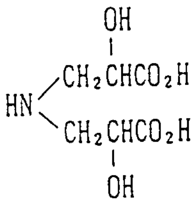
I − 1



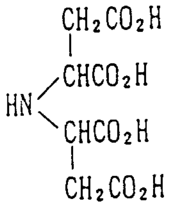
I − 2



I − 3



I − 4



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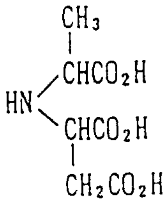

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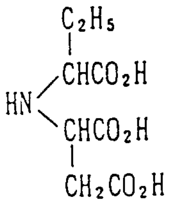
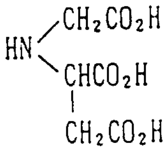
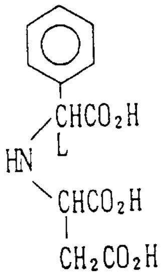


I − 7



I-8



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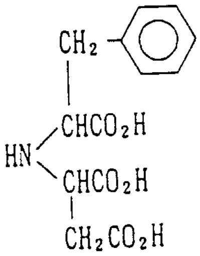

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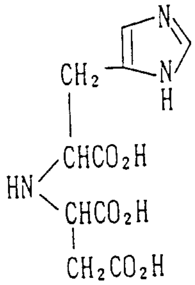

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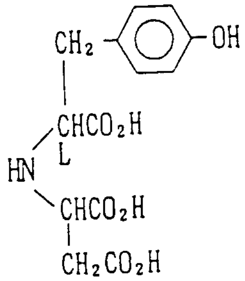

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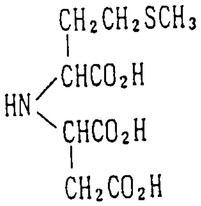

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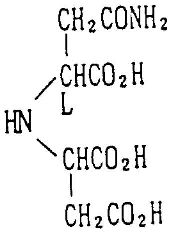

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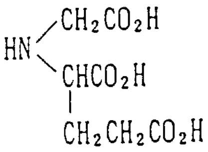

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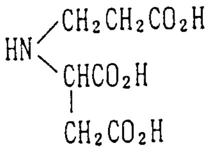

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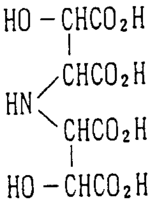

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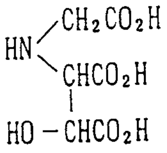

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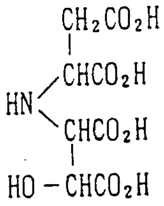

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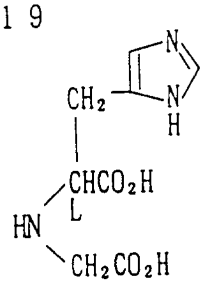

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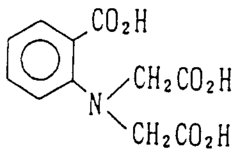

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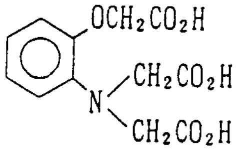

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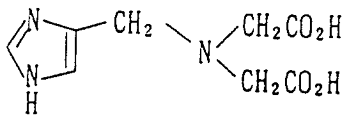

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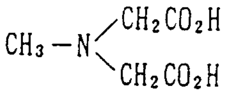

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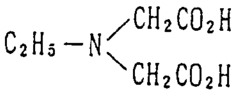

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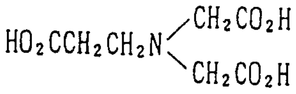

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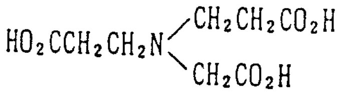

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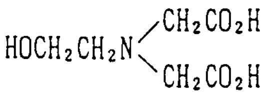

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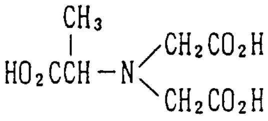

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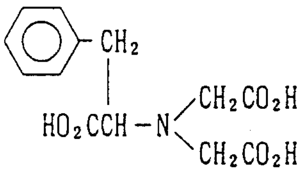

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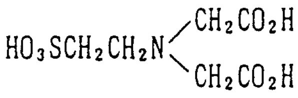

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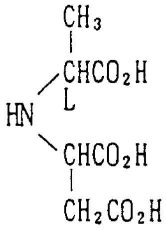

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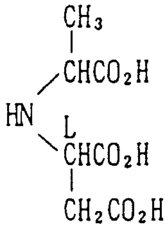

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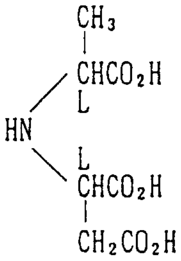

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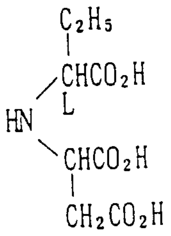

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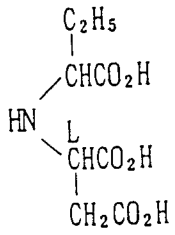

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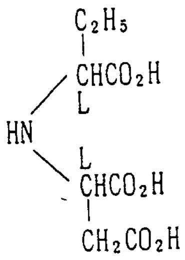

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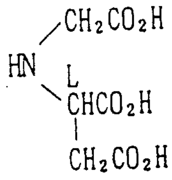

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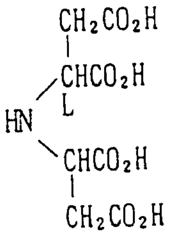

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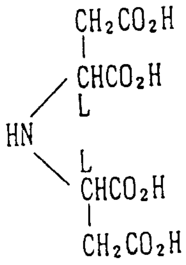

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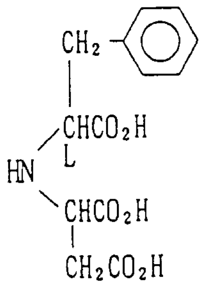

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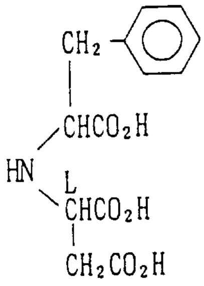

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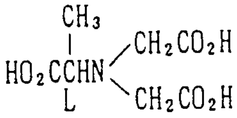

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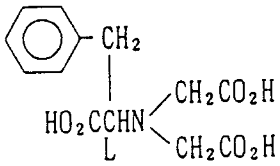

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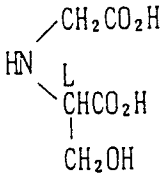

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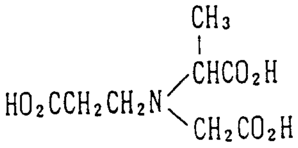

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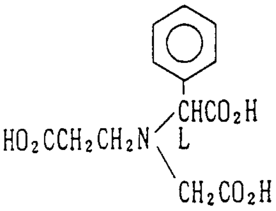

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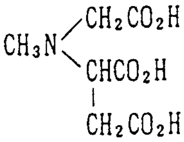

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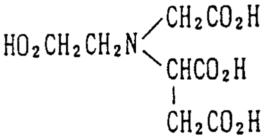

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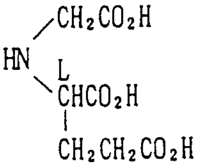

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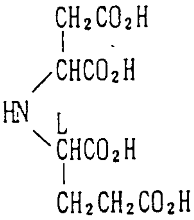

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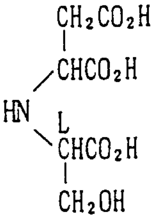
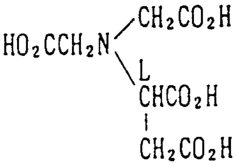
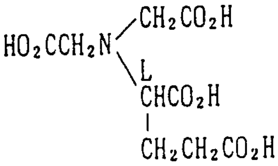


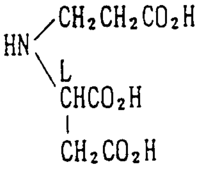
I－52



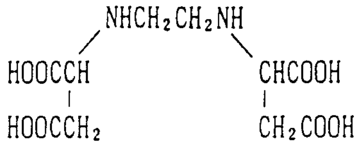
I－53



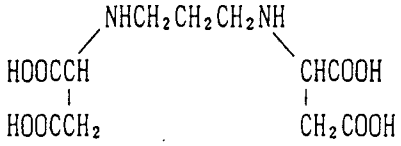
I－54



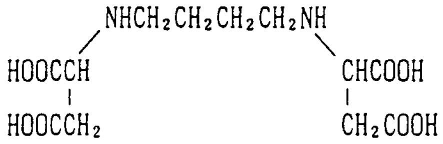
II－1



II－2



II－3



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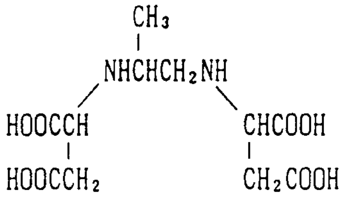

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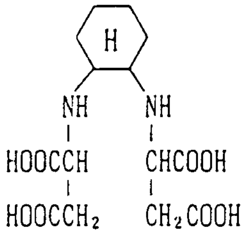
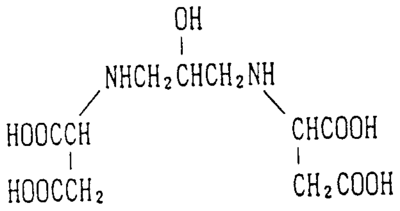
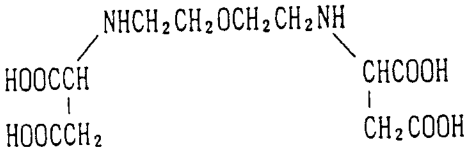


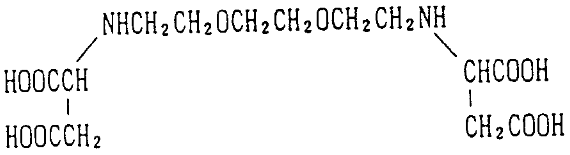
II－6



II－7



II－8



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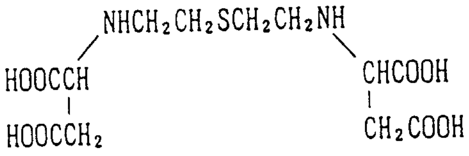

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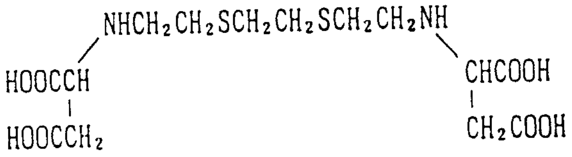
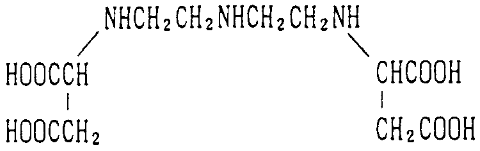
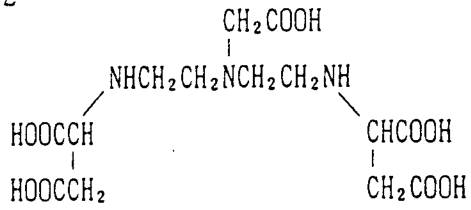


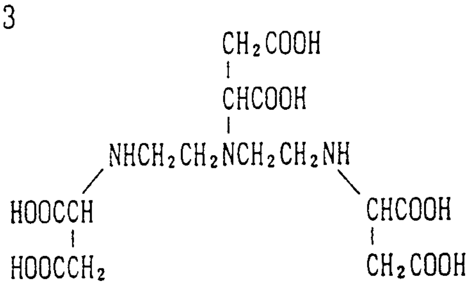
II－１１



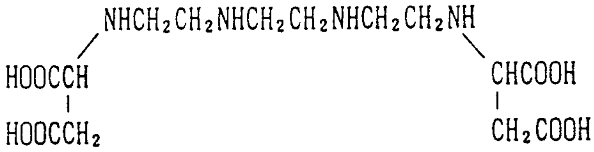
II－１２



II－１３



II－１４



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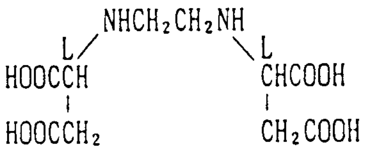

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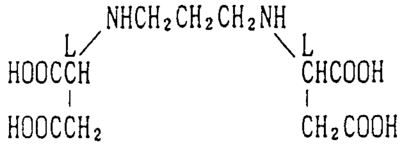

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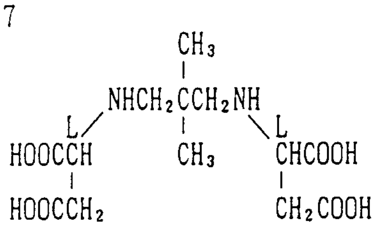

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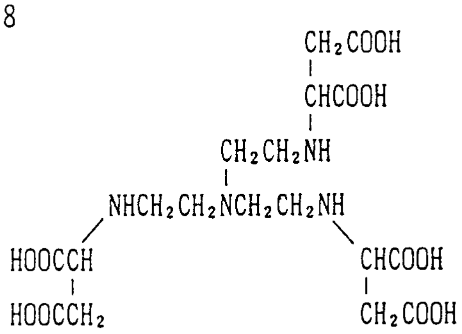

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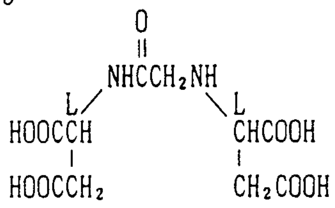

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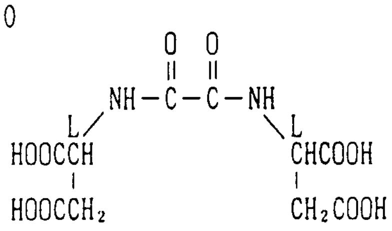
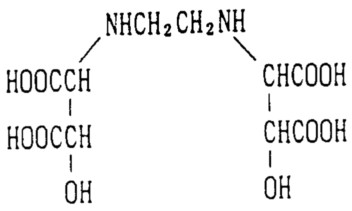


II－2 1



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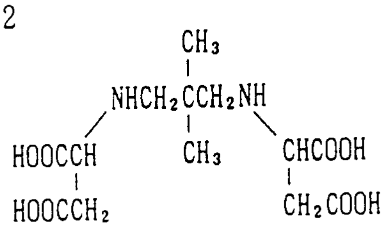
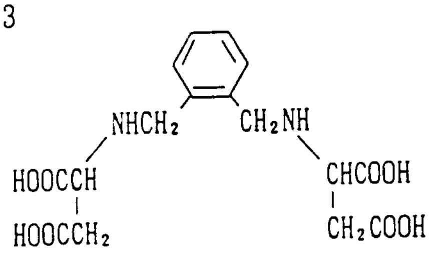
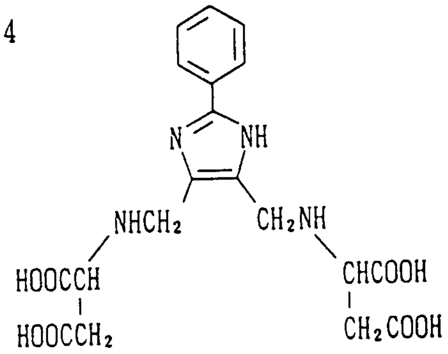


II－2 3



II－2 4



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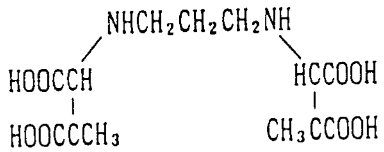

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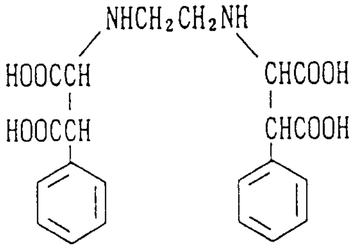

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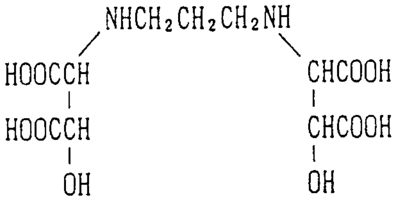
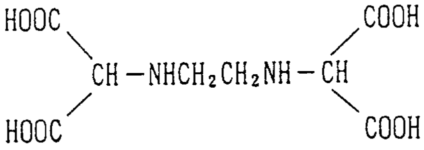


II－２８



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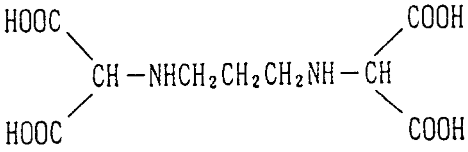
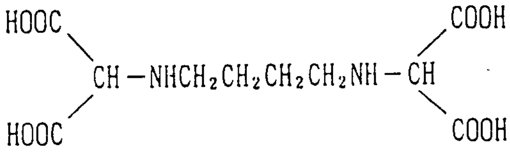


II－３０



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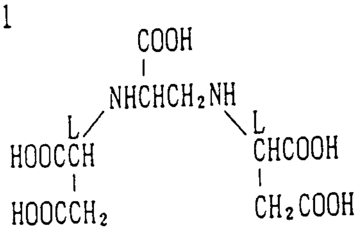

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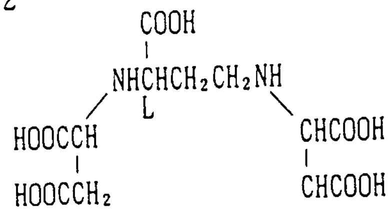

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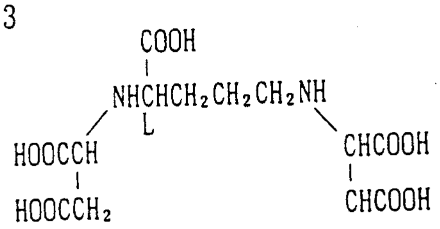

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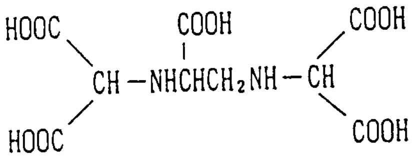

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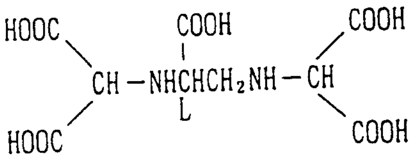
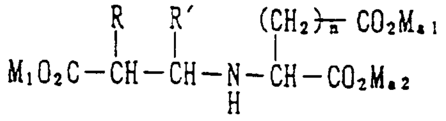


In the above-described compounds, the hydrogen atom in the carboxy group may be replaced by a cation and in this case, the cation has the same meaning as the cation represented by M_1 or M_2 in formula (I).

The compound represented by formula (I) of the present invention can be synthesized by the method described, for example, in Journal of Inorganic and Nuclear Chemistry, Vol. 35, page 523 (1973), Swiss Patent 561504, German Patent Publication Nos. 3,912,551A1, 3,939,755A1 and 3,939,756A1, JP-A-5-265159, JP-A-6-59422 (describing synthesis methods of L-forms of Compounds I-42, I-43, I-46, I-52 and I-53 as Synthesis Methods 1, 2, 3, 4 and 6), JP-A-6-

95319 (describing synthesis method of L-forms of Compounds I-8, I-11, I-37, I-38 and I-40 as Synthesis Examples 2 to 6), JP-A-6-161054, JP-A-6-161065, Helvetica Chimica Acta, Vol. 38, p. 2038 (1955) (describing a synthesis method of L-form of Compound I-54), and Journal of American Chemical Society, Vol. 74, p. 1942 (1952) (describing a synthesis method of D,L-mixed form of Compound I-15).

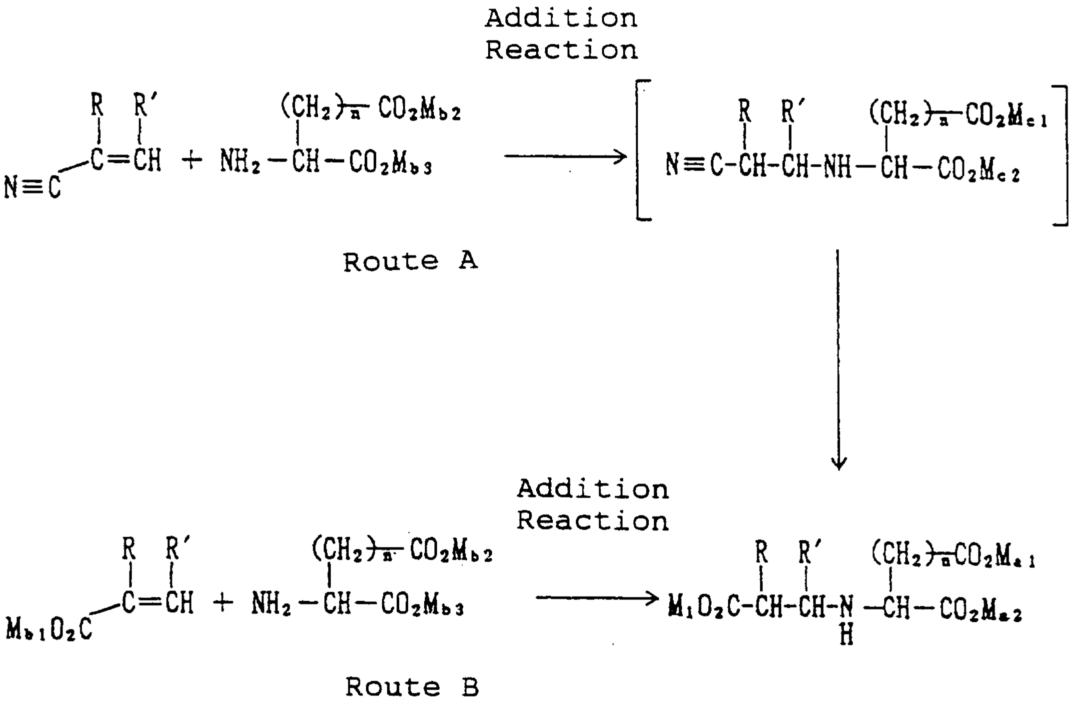
The compound group represented by the following formula (I-b) including Compounds I-15 and I-54 can be synthesized, for example, by an addition reaction method of an aspartic acid or a glutamic acid to an acrylic acid derivative or an acrylonitrile derivative (when an acrylonitrile derivative is used, an N-(2-cyanoalkyl)-amino acid produced by the addition reaction must be hydrolyzed);



$$M_1O_2C-\overset{R}{CH}-\overset{R'}{CH}-\underset{H}{N}-\overset{(CH_2)_n-CO_2M_{a1}}{CH}-CO_2M_{a2}$$

(I-b)

wherein R and R' each represents an aliphatic hydrocarbon group, an aryl group, a heterocyclic group or a hydrogen atom, n represents 1 or 2, and M_1, M_{a1} and M_{a2} each represents a hydrogen atom or a cation;



wherein R and R' each represents an aliphatic hydrocarbon group, an aryl group, a heterocyclic group or a hydrogen atom, n represents 1 or 2, M_1, M_{a1}, M_{a2}, M_{b1}, M_{b2}, M_{b3}, M_{c1} and M_2 have the same meaning and each represents a hydrogen atom or a cation (provided that M_{b1}, M_{b2}, M_{b3}, M_{c1} and M_{c2} are not a primary or secondary ammonium).

The aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R or R' have the same meaning as those represented by R_1 in formula (I). R and R' each is preferably an aliphatic hydrocarbon group or a hydrogen atom, more preferably a hydrogen atom.

M_1, M_{a1} and M_{a2} have the same meaning as those in formula (I-a) and their preferred ranges are also the same.

Aspartic acids and glutamic acids used as a raw material are not particularly limited and an industrially available one can be used. These acids may be used in the form of a metal salt (for example, an alkali metal salt (e.g., Li salt, Na salt, K salt, Rb salt, Cs salt), an alkaline earth metal salt (e.g., Ca salt, Mg salt, Ba salt), a transition metal salt (e.g., Zn salt)), a tertiary ammonium salt (e.g., triethylammonium salt), a quaternary ammonium salt (e.g. tetrabutylammonium salt) or a pyridinium salt, or of course in the form of a free acid. The shape thereof may be any of a solid, a slurry and an aqueous solution.

The asymmetric moiety thereof may be either a D-form or a L-form or may be a mixture thereof, however, the L-form is preferred.

The acrylic acid derivative and the acrylonitrile derivative as a raw material are not particularly limited and an industrially available one can be used. The amount of the acrylic acid derivative or the acrylonitrile derivative for use in the reaction is from 0.5 to 5 mols, preferably from 0.7 to 3 mols, more preferably from 0.9 to 1.5 mols, per mol of the amino acid.

The addition reaction of an aspartic acid or a glutamic acid to an acrylic acid derivative or an acrylonitrile derivative is preferably performed under an alkaline condition.

Examples of the base for use in the reaction include alkali metal hydroxides (e.g., lithium hydroxide, sodium hydroxide, potassium hydroxide, bidium hydroxide), alkaline earth metal hydroxides (e.g., calcium hydroxide, barium hydroxide), alkali metal salts (e.g., sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, trisodium phosphate, disodium hydrogenphosphate, tripotassium phosphate, dipotassium hydrogenphosphate, sodium pyrophosphate, sodium borate, sodium aluminate, sodium silicate), tertiary amines (e.g., trimethylamine, triethylamine, tripropylamine, tributylamine, diisopropylethylamine), pyridines (e.g., pyridine, 4-picoline, 2,6-lutidine), quaternary ammonium hydroxide compounds (e.g., tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylbenzylammonium hydroxide, cetyltrimethylammonium hydroxide, cetylpyridinium hydroxide) and metal alkoxides (e.g., sodium methoxide, sodium ethoxide, potassium ethoxide, potassium t-butoxide). These bases may be used individually or may be combined at any ratio.

The base is preferably an alkali metal hydroxide, an alkali metal salt or a metal alkoxide, more preferably an alkali metal hydroxide.

The solvent for use in the reaction in the method of the present invention is not limited as long as it does not participate in the reaction, and water or an organic solvent may be used. Examples of the organic solvent include alcohols (e.g., methanol, ethanol, 2-propanol, n-butanol), ketones (e.g., acetone, methyl ethyl ketone), eaters (e.g., methyl acetate, ethyl acetate, butyl acetate), aliphatic hydrocarbons (e.g., n-pentane, n-hexane, cylohexane), aromatic hydrocarbons (e.g., benzene, toluene, xylene), ethers (e.g., diethyl ether, tetrahydrofuran, dioxane) and acetonitrile. The solvent is preferably water, methanol, ethanol, 2-propanol, acetonitrile, tetrahydrofuran or dioxane, more preferably water, methanol, ethanol or 2-propanol, still more preferably water. These solvents may be used in combination and in this case, the mixing ratio may be freely selected.

The reaction temperature in the addition reaction varies depending upon the raw materials for reaction, the reaction concentration or the reaction scale, however, when an acrylic acid derivative is used, it is usually preferably from 0 to 140°C, more preferably from 20 to 120°C, still more preferably from 30 to 110°C. When an acrylonitrile derivative is used, it is usually preferably from 0 to 120°C, more preferably from 10 to 100°C, still more preferably from 20 to 80°C.

The reaction time in the addition reaction varies depending upon the raw materials for reaction, the reaction temperature, the reaction concentration or the reaction scale, however, when an acrylic acid derivative is used, it is usually within 10 hours, preferably within 6 hours, more preferably within 4 hours. When an acrylonitrile derivative is used, it is usually within 5 hours, preferably within 3 hours, more preferably within 1 hour.

The mixing order of raw materials is not particularly limited, however, a representative procedure is such that a solvent is added to an amino acid, a base is added, and to the resulting solution, an acrylic acid derivative or an acrylonitrile derivative is added.

The amount of the solvent in the addition reaction varies depending upon the raw materials for reaction, the reaction temperature or the reaction scale, however, it is from 1 to 15 times, preferably from 0.9 to 10 times, more preferably from 1 to 5 times, still more preferably from 1 to 3 times, the weight of the amino acids.

Hydrolysis of a nitrile form as an addition reaction product produced when an acrylonitrile derivative is used, may be performed either in an acidic condition or in a basic condition and, for example, a general method described in Shin Jikken Kagaku Koza 14 (II), pp. 947-950, Maruzen, and Jikken Kagaku Koza (4th Ed.), 22, pp. 12-13, Maruzen, can be used. In this case, N-(2-cyanoalkyl)-amino acids as an addition reaction product may be isolated before use or may be not be isolated but hydrolyzed as they are.

Examples of the acid for use in the acid hydrolysis include a mineral acid (e.g., hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid) and an organic acid (e.g., acetic acid, oxalic acid, glycolic acid, succinic acid, tartaric acid, and among these, a mineral acid, particularly, a hydrochloric acid and a sulfuric acid are preferred.

Examples of the base for use in the alkali hydrolysis include, in addition to those described above as the base for use in the addition reaction, ammonia. Among these, an alkali metal hydroxide, an alkali metal salt and a metal alkoxide are preferred, and an alkali metal hydroxide is more preferred.

The acid and the base for use in the hydrolysis of nitrile may be a commercially available product and the shape thereof may be any of a solid, a slurry and an aqueous solution. The amount of the acid or the base is usually from 0.5 to 10 equivalents, preferably from 1 to 5 equivalents, more preferably from 1 to 3 equivalents, to the cyano group. Examples of the solvent include those described above with respect to the addition reaction conditions and the preferred range is also the same.

The reaction temperature in the hydrolysis of nirile varies depending upon the raw materials for reaction, the reaction temperature, the reaction concentration or the reaction scale, however, it is usually from 20 to 120°C, preferably from 20 to 100°C, more preferably from 30 to 100°C. The reaction time varies depending upon the raw materials for reaction, the reaction temperature, the reaction concentration or the reaction scale, however, it is usually within 5 hours, preferably within 3 hours, more preferably within 2 hours.

The hydrolysis reaction of nitrile is preferably performed using a hydrochloric acid, a sulfuric acid or an alkali metal hydroxide in an amount of from 1 to 3 equivalent to the cyano group, in a water solvent at a temperature of from 30 to 100°C within 2 hours.

The addition reaction is preferably performed, when an acrylic acid derivative is used, using a metal hydroxide as the base and water in an amount of from 1 to 3 equivalents to the amino acids as a solvent at a temperature of from 30 to 110°C within 4 hours.

When an acrylonitrile derivative is used, the addition reaction is preferably performed using an alkali metal hydroxide as the base and water in an amount of from 1 to 3 times the amino acids as a solvent at a temperature of from 20 to 80°C within 1 hour.

After completion of the reaction, the compound represented by formula (I-b) as a reaction product is present in the solution in the form of a salt and this can be isolated as a glass solid or crystal by cooling or concentrating the reaction solution. Further, the reaction solution may be used directly or after adjusting the concentration by concentrating the solution, in the preparation of, for example, a photographic processing solution. Furthermore, by adjusting the pH of the reaction solution, the compound represented by formula (I-b) can be isolated as a free acid.

Examples of the acid for use in adjusting the pH include a mineral acid (e.g., hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid) and an organic acid (e.g., acetic acid, oxalic acid, glycolic acid, succinic acid, tartaric acid), and among these, a mineral acid, particularly, a hydrochloric acid and a sulfuric acid are preferred.

Examples of the base for use in adjusting the pH include, in addition to those described above as the base for use in the addition reaction, ammonia. Among these, an alkali metal hydroxide, an alkali metal salt, a metal alkoxide and ammonia are preferred, and an alkali metal hydroxide and ammonia are more preferred.

Specific synthesis examples are described below.

Production Process of Compound I-54 (Acrylic Acid Process)

To 450 g of water, 528.4 g (3.97 mol) of L-aspartic acid was added, and thereto 1,025.6 g (12.31 mol) of a 48 wt% sodium hydroxide aqueous solution was gradually added while cooling and stirring. Further, 315.0 g (4.37 mol) of an acrylic acid was added thereto while cooling and stirring with care so that the temperature did not exceed 70°C (in this system, water as a solvent was present in an amount of 1.71 times the L-aspartic acid disodium salt). The system was refluxed under heating for 3 hours while stirring and thereto a 36 wt% hydrochloric acid was added while cooling to 60°C or less until the pH reached 2. The mixture was cooled to room temperature while stirring and after 2 hours, white crystals produced was washed by splashing water and acetone thereon and dried under reduced pressure to obtain 560.0 g (2.73 mol) of Compound I-54 (yield: 68.8%).

Production Process of Compound I-54 (Acrylonitrile Process)

To 700 g (5.26 mol) of L-aspartic acid, 520 g of water was added, and thereto 956.4 g (10.52 mol) of a 44 wt% sodium hydroxide aqueous solution was gradually added while cooling and stirring (in this system, water as a solvent was present in an amount of 1.34 times the L-aspartic acid disodium salt). After cooling to 30°C, 310 g (5.84 mol) of acrylonitrile was added while stirring. The reaction solution which was initially non-uniform, gradually turned to be uniform as the reaction proceeded and the solution temperature elevated to about 45°C. After 30 minutes, the addition reaction was quantitatively completed (confirmed by ^{1}H NMR). To the resulting reaction solution, 616.7 g (5.55 mol) of a 36 wt% sodium hydroxide aqueous solution was added and after stirring the mixture under heating at from 75 to 85°C or 30 minutes, it was confirmed by ^{1}H NMR that the objective sodium salt was produced almost quantitatively.

To the resulting reaction solution, a 36 wt% hydrochloric acid was added while cooling to 60°C under stirring until the pH reached 2. The mixture was cooled to room temperature while stirring and after 2 hours, white crystals produced was washed by splashing water and acetone thereon and dried under reduced pressure to obtain 887.0 g (4.32 mol) (yield: 82.2%).

The compound represented by formula (II) can be synthesized according to the method described, for example, 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 2405 (1968) (describing synthesis method of L,L-form of Compound II-15).

The iron(III) complex salt of the compound represented by formula (I) or (II) of the present invention may be previously taken out as an iron(III) complex salt before the addition or the compound represented by formula (I) or (II) and an iron(III) salt (e.g., ferric nitrate and ferric chloride) may be placed together in a solution to cause complex formation in the processing solution.

The compounds represented by formulae (I) and (II) of the present invention may be used individually or in combination of two or more thereof.

The compound represented by formula (I) or (II) of the present invention may be used in a slightly excessive amount to the amount necessary for the complex formation of iron(III) ions (for example, an amount of 0.5 mol, an equimolar amount or a two times molar amount, of iron(III) ions). In using the compound in excess, the excess is usually preferably from 0.01 to 15 mol%.

The organic acid iron(III) complex salt which can be contained in the processing solution having bleaching ability of the present invention may be used in the form of an alkali metal salt or an ammonium salt. Examples of the alkali metal salt include lithium salt, sodium salt and potassium salt and examples of the ammonium salt include ammonium salt and tetraethylammonium salt. In the present invention, the ammonium concentration in the processing solution having bleaching ability is preferably from 0 to 0.04 mol/ℓ, more preferably from 0 to 0.2 mol/ℓ.

In addition to the iron(III) complex salt of the compound represented by formula (I) or (II), iron(III) complex salts of known compounds such as ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediaminetetraacetic acid, glycol ether diaminetetraacetic acid and 1,3-propanediamine-N,N,N',N'-tetraacetic acid, and inorganic oxidizing agents such as red prussiate, persulfate, hydrogen peroxide and bromate, may be used in the present invention as the bleaching agent. However, in the present invention, in view of environmental conservation and safety in handling, the compound represented by formula (I) or (II) is preferably used at a proportion of from 70 to 100 mol%, more preferably from 80 to 100 mol%, still more preferably 100 mol% based on the total amount of the bleaching agent.

In the present invention, the compound represented by formula (I) or (II) is used in a concentration of suitably from 0.003 to 3.00 mol/ℓ, preferably from 0.02 to 2.00 mol/ℓ, more preferably from 0.05 to 1.00 mol/ℓ, still more preferably from 0.08 to 0.5 mol/ℓ. However, in the case where the above-described inorganic oxidizing agent is used in combination, the total concentration of iron(III) complex salt is preferably from 0.005 to 0.030 mol/ℓ.

In the present invention, the bleaching solution preferably contains a pH buffer agent and the pH buffer agent is preferably a less odorous organic acid such as glycolic acid, succinic acid, maleic acid, malonic acid or glutaric acid, more preferably glycolic acid, malonic acid or succinic acid. The concentration of the buffer agent is preferably from 0 to 3 mol/ℓ, more preferably from 0.2 to 1.5 mol/ℓ.

The pH of the processing solution having bleaching ability of the present invention is suitably from 3.0 to 7.0. In the case of a bleaching solution, the pH is particularly preferably from 3.5 to 5.0, and in the case of a bleach-fixing solution, the pH is particularly preferably from 4.0 to 6.5. In order to have such a pH, the above-described organic acid is preferably added as a buffer agent in the present invention. The alkali agent for use in adjusting the pH is preferably aqueous ammonia, potassium hydroxide, sodium hydroxide, potassium carbonate or sodium carbonate.

In order to adjust the processing solution having bleaching ability of the present invention to have a pH in the above-described range, an alkali agent described above and a known acid (inorganic acid or organic acid) may be used.

The processing with a solution having bleaching ability of the present invention is preferably performed immediately after color development, but in the case of a reversal processing, it is usually performed through a regulating bath (a bleaching acceleration bath may serve as this). The regulating bath may contain an image stabilizer which will be described later.

In the present invention, the solution having bleaching ability may use, in addition to the bleaching agent, a rehalogenating agent described in JP-A-3-144446, page (12), a pH buffer agent and known additives such as aminopolycarboxylic acids and organic phosphonic acids. The rehalogenating agent is preferably sodium bromide, potassium bromide, ammonium bromide or potassium chloride and the content thereof is preferably from 0.1 to 1.5 mol, more preferably from 0.1 to 1.0 mol, still more preferably from 0.1 to 0.8 mol, per ℓ of the solution having bleaching ability.

In the present invention, the solution having bleaching ability preferably contains a nitric acid compound such as ammonium nitrate and sodium nitrate. In the present invention, the concentration of the nitric acid compound in the solution having bleaching ability is preferably from 0 to 0.3 mol/ℓ, more preferably from 0 to 0.2 mol/ℓ.

The nitric acid compound such as ammonium nitrate and sodium nitrate is usually added to prevent corrosion of stainless steel, however, in the present invention, even if the nitric acid compound is used in a small amount, generation of corrosion is prevented and also good desilvering is achieved.

The replenishing amount of the solution having bleaching ability is preferably from 30 to 600 ml, more preferably from 50 to 400 ml, per m^2 of the light-sensitive material.

When the processing is performed with a bleaching solution, the processing time is preferably 7 minutes or less, more preferably from 10 seconds to 5 minutes, most preferably from 15 seconds to 3 minutes.

In the present invention, the replenishing agent for the processing solution having bleaching ability or for the processing solution having fixing ability may be either a liquid or a solid (e.g., powder, granule, tablet). In the case of granule or tablet, a polyethylene glycol-based surface active agent, which functions as a binder, is preferably used.

The photographic processing agent may be formed into a solid by using any optional means, for example, as described in JP-A-4-29136, 4-85535, JP-A-4-85536, JP-A-4-88533, JP-A-4-85534 and JP-A-4-172341, a thick solution or a fine powder or granular photographic processing agent and a water-soluble binder are mixed, kneaded and shaped, or a water-soluble binder is sprayed over the surface of a temporarily shaped photographic processing agent to form a coating layer.

The tablet processing agent may be produced by a general method described, for example, in JP-A-51-61837, JP-A-54-155038, JP-A-52-88015 and British Patent 1,213,808. The granular processing agent may be produced by a general method described, for example, in JP-A-2-109042, JP-A-2-109043, JP-A-3-39735 and JP-A-3-39739. The powder processing agent may be produced by a general method described, for example, in JP-A-54-133332, British Patents 725,892 and 729,862 and German Patent 3,733,861.

When the replenishing agent for the processing solution having bleaching ability or for the processing solution having fixing ability is constituted by a liquid, either one-part solution or multiple part solution comprising different components may be used, however, in view of the space for storage or operability at the preparation, one-part solution and two-part solution are preferred, and one-part solution is more preferred. In this case, the specific gravity of the replenishing agent is preferably from 1.0 to 5 times, more preferably from 1.5 to 3 times, the specific gravity of the replenisher.

The total processing time in the desilvering step is preferably as short as possible within the range of causing no desilvering failure and it is preferably from 1 to 12 minutes, more preferably from 1 to 8 minutes. The processing temperature is from 25 to 50°C, preferably from 35 to 45°C. In the preferred temperature range, the desilvering rate increases and generation of stains after the processing is effectively prevented.

The processing solution having bleaching ability of the present invention is preferably aerated at the time of processing because the photographic capability can be very stably maintained. The aeration may be performed using a means known in the art and for example, blowing of air into the processing solution having bleaching ability or absorption of air using an ejector may be performed.

In blowing air, the air is preferably released into the solution through a diffusion tube having micropores. The tube diffuser is widely used, for example, in the aeration tank for processing activated sludge. With respect to the aeration, the matters described in Z-121, Using Process • C-41, 3rd ed., pages BL-1 to BL-2, issued by Eastman Kodak Co. (1982) may be used. In the processing using a processing solution having bleaching ability of the present invention, the stirring is preferably intensified and the disclosure in JP-A-3-33847, page 8, from right upper column, line 6 to left lower column, line 2 can be applied to the intensification of stirring.

In the present invention, various bleaching accelerators may be added to the pre-bath of the processing solution having bleaching ability. Examples of the bleaching accelerator include compounds having a mercapto group or a disulfide group described in U.S. Patent 3,893,858, German Patent No. 1,290,821, British Patent 1,138,842, JP-A-53-95630 and Research Disclosure No. 17129 (July, 1978), thiazolidine derivatives described in JP-A-50-140129, thiourea derivatives described in U.S. Patent 3,706,561, iodides described in JP-A-58-16235, polyethylene oxides described in German Patent No. 2,748,430, and polyamine compounds described in JP-B-45-8836. Further, the compounds described in U.S. Patent 4,552,834 are preferred. The bleaching accelerator may be incorporated into the light-sensitive material.

The solution having bleaching ability or the solution having fixing ability preferably uses an ammonium as a cation in view of improvement in the desilvering property, however, for the purpose of reducing the environmental contamination, the ammonium is preferably reduced or not used.

In the bleaching, bleach-fixing or fixing step, jet stirring described in JP-A-1-309059 is particularly preferably performed.

In the bleach-fixing or fixing step, a silver recovery device of various types is preferably provided as an in-line or off-line system to recover silver. By providing the device as an in-line system, the silver concentration in the solution can be reduced during the processing and as a result, the replenishing amount can be reduced. It is also preferred to recover the silver in an off-line system and re-use the residual solution as the replenisher.

The bleach-fixing step or the fixing step may be constituted by a plurality of processing tanks and respective tanks are preferably piped in a cascade manner to provide a multi-stage countercurrent system. In view of balance with the size of the automatic processor, two-tank cascade constitution is generally efficient and the ratio of the processing time in the pre-stage tank to the processing time in the post-stage tank is preferably from 0.5:1 to 1:0.5, more preferably from 0.8:1 to 1:0.8.

In the desilverization, the stirring is preferably intensified as highly as possible. Specific examples of the method for intensifying stirring include a method of colliding a jet stream of a processing solution against the emulsion surface of the light-sensitive material described in JP-A-62-183460 and JP-A-3-33847, page 8, from right upper column, line 6 to left lower column, line 2, a method of increasing the stirring effect using a rotary means described in JP-A-62-183461, a method of increasing the stirring effect by moving the light-sensitive material while bringing the emulsion surface into contact with a wire blade provided in the solution to cause turbulence on the emulsion surface, and a method of increasing the circulative flow rate of the entire processing solutions. Such techniques for intensifying the stirring are effective in any of the bleaching solution, the bleach-fixing solution and the fixing solution. The intensification of stirring is considered to increase the supply rate of the bleaching agent or the fixing agent into the emulsion layer and as a result, to elevate the desilverization rate. The above-described techniques for intensifying stirring are more effective when a bleaching accelerator is used and in this case, the acceleration effect can be outstandingly increased or the fixing inhibitory action of the bleaching accelerator can be eliminated.

The automatic processor used for the light-sensitive material of the present invention preferably has a transportation means of a light-sensitive material described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. As described in JP-A-60-191257, by using the transportation means, the amount of a processing solution carried over from a previous bath to a post bath can be remarkably reduced and a great effect can be achieved on the prevention of deterioration in the capability of the processing solution. This effect is particularly useful for the reduction in the processing time or for the decrease in the replenishing amount of the processing solution, in each processing step.

The solution having bleaching ability of the present invention can be re-used by recovering the overflow solution after use in the processing and adding thereto components to correct the composition. This use method is usually called regeneration and the regeneration is preferred also in the present invention. With respect to the details of the regeneration, matters described in Fuji Film Processing Manual, Fuji Color Negative Film, CN-16 Processing, issued by Fuji Photo Film Co., Ltd., pp. 39-40 (revised in August, 1990) may be applied.

For regenerating the solution having bleaching ability, in addition to the above-described aeration, the methods described in Shashin Kogaku no Kiso-Gin'en Shashin Hen- (Basis of Photographic Engineering-silver salt photograph version-) , Nippon Shashin Gakkai (compiler), Corona Sha (1979) may be used. More specifically, electrolytic regeneration and other regeneration methods of the bleaching solution by hydrogen peroxide, bromous acid or ozone, using bromic acid, chlorous acid, bromine, bromine precursor, persulfate, hydrogen peroxide or a catalyst, may be used.

In the regeneration by electrolysis, a cathode and an anode are placed in the same bleaching bath, an anode tank and a cathode tank are provided as separate baths using a diaphragm to regenerate the solution, or the bleaching solution and the developer and/or the fixing solution may be simultaneously regenerated also using a diaphragm.

The fixing solution and the bleach-fixing solution each is regenerated by electrolytic reduction of silver ions accumulated. Also, it is preferred in order to maintain the fixing capability to remove halogen ions accumulated using an anion exchange resin.

The solution having bleaching ability of the present invention is preferably stored by housing it in a closed container having an oxygen permeation rate of 1 $cc/m^1 \cdot day \cdot atm$ or more.

The bleaching solution of the present invention preferably contains at least one of 1,2-benzoisothiazolin-3-one and derivatives thereof. Specific examples of the compound are described below, but the present invention is by no means limited thereto.

1,2-Benzoisothiazolin-3-one, 2-methyl-1,2-benzoisothiazolin-3-one, 2-ethyl-1,2-benzoisothiazolin-3-one, 2-(n-propyl)-1,2-benzoisothiazolin-3-one, 2-(n-butyl)-1,2-benzoisothiazolin-3-one, 2-(sec-butyl)-1,2-benzoisothiazolin-3-one, 2-(t-butyl)-1,2-benzoisothiazolin-3-one, 2-methoxy-1,2-benzoisothiazolin-3-one, 2-ethoxy-1,2-benzoisothiazolin-3-one, 2-(n-propyloxy)-1,2-benzoisothiazolin-3-one, 2-(n-butyloxy)-1,2-benzoisothiazolin-3-one, 5-chloro-1,2-benzoisothiazolin-3-one, 5-methyl-1,2-benzoisothiazolin-3-one, 6-ethoxy-1,2-benzoisothiazolin-3-one, 6-cyano-1,2-benzoisothiazolin-3-one and 5-nitro-1,2-benzoisothiazolin-3-one.

The addition amount of the compound is preferably from 0.001 to 1 g, more preferably from 0.01 to 0.5 g, still more preferably from 0.02 to 0.2 g, per ℓ of the bleaching solution. The compound may be added in the form of a salt, or two or more compounds may be used in combination.

The replenisher of the solution having bleaching ability fundamentally contains components each in a concentration calculated according to the following formula, whereby the concentration of each component in the mother solution can be kept constant:

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

wherein

C_R: concentration of the component in the replenisher
C_T: concentration of the component in the mother solution (processing tank solution)
C_P: concentration of the component consumed during the processing
V_1: replenishing amount (ml) of the replenisher having bleaching ability per m^2 of the light-sensitive material
V_2: amount (ml) of the solution carried over from the previous bath by 1 m^2 of the light-sensitive material

The color developer is described below.

The color developer may use the compounds described in JP-A-4-121739, from page 9, right upper column, line 1 to page 11, left lower column, line 4. Particularly, in conducting rapid processing, preferred as the color developing agent are 2-methyl-4-[N-ethyl-N-(2-hydroxyethyl)amino]aniline, 2-methyl-4-[N-ethyl-N-(3-hydroxypropyl)amino]aniline and 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl)amino]aniline.

The color developer contains the color developing agent in an amount of preferably from 0.01 to 0.08 mol/ℓ, more preferably from 0.015 to 0.06 mol/ℓ, still more preferably from 0.02 to 0.05 mol/ℓ. The replenisher of the color developer preferably contains the color developing agent in an amount of from 1.1 to 3 times the above-described amount.

The color developer usually contains a pH buffer agent such as a carbonate, a borate and a phosphate of an alkali metal, and a development inhibitor or antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole and a mercapto compound. Further, the color developer may contain a preservative such as hydroxylamines (e.g., hydroxylamine, diethylhydroxylamine, those represented by formula (I) of JP-A-3-144446 including N,N-bis(2-sulfonatoethyl)hydroxylamine), sulfites, hydrazines (e.g., N,N-bis-carboxymethylhydrazine), phenylsemicarbazides, triethanolamine and catecholsulfonic acids; an organic solvent such as ethylene glycol and diethylene glycol; a development accelerator such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines; a dye forming coupler; a competitive coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a tackifying agent; and a chelating agent represented by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid and phosphonocarboxylic acid, representative examples thereof including 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) and salts thereof.

In the present invention, the temperature in the processing with the color developer is generally from 20 to 55°C, preferably from 30 to 55°C. The processing time is, in the case of a light-sensitive material for photographing, generally from 20 seconds to 10 minutes, preferably from 30 seconds to 8 minutes, more preferably from 1 to 6 minutes, most preferably from 1 minute and 10 seconds to 3 minutes and 30 seconds, and in the case of a material for printing, it is generally from 10 seconds to 1 minute and 20 seconds, preferably from 10 to 60 seconds, more preferably from 10 to 40 seconds.

In carrying out reversal processing, the color development usually follows black-and-white development. The black-and-white developer may use a known black-and-white developing agent such as dihydroxybenzenes (e.g., hydroquinone, hydroquinone monosulfonate), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol), which may be used individually or in combination. Also, in the processing of a black-and-white light-sensitive material, the above-described black-and-white developer is used.

The color developer and the black-and-white developer each usually has a pH of from 9 to 12. The replenishing amount of these developers is, although it depends on the color photographic light-sensitive material to be processed, usually 3 ℓ or less per m^2 of the light-sensitive material and it may be reduced to 500 ml or less by reducing the bromide ion concentration in the replenisher. When the replenishing amount is reduced, the contact area of the processing tank with air is preferably made small so that evaporation or air oxidation of the solution can be prevented.

The contact area of a photographic processing solution with air in a processing tank can be expressed by an opening ratio defined below. Namely,

$$\text{Opening ratio} = [\text{contact area of the processing solution with air } (\text{cm}^2)] \div [\text{volume of the processing solution } (\text{cm}^3)]$$

The opening ratio as defined above is preferably 0.1 or less, more preferably from 0.001 to 0.05. The opening ratio can be reduced by providing a shielding material such as a floating lid on the surface of the photographic processing solution in the processing tank, by a method of using a movable lid described in JP-A-1-82033 or by a slit development method described in JP-A-63-216050. Also, a method of bringing into contact with the processing solution surface a liquid capable of covering the processing solution surface such as liquid paraffin or a low oxidative and/or non-oxidative gas may be used. The reduction in the opening ratio is preferably applied not only to the color development and the black-and-white development but also to all of subsequent steps such as bleaching, bleach-fixing, fixing, water washing and stabilization. Further, by using a means of suppressing accumulation of bromide ions in the developer, the replenishing amount can also be reduced.

When the replenishing amount is reduced or when the bromide ion concentration is set high, in order to increase the sensitivity, a pyrazolidone represented by 1-phenyl-3-pyrazolidone and 1-phenyl-2-methyl-2-hydroxymethyl-3-pyrazolidone, a thioether compound represented by 3,6-dithia-1,8-octanediol, a sodium thiosulfate or a potassium thiosulfate is preferably used as a development accelerator.

The above-described development accelerator is also preferably used in the color developer.

The shape and the structure of the container for housing a color developer constituting the color developer solution may be freely designed, but preferred are, for example, a container having a freely shrinkable structure such as bellows described in JP-A-58-97046, JP-A-63-50839, JP-A-1-235950 and JP-U-A-63-45555 (the term "JP-U-A" as used herein means an "unexamined published Japanese utility model application"), a container capable of housing a waste having a flexible partition described in JP-A-58-52065, JP-A-62-246061 and JP-A-62-134646, and a structure where a plurality of containers variable in the content volume are connected described in JP-A-2-264950.

In feeding the color developer from the above-described container to the processing solution tank in an automatic processor, the developer may be once placed in a supply tank and automatically or manually mixed and diluted with water there, or the liquid color developer and water may be separately transferred directly to the processing solution tank.

In view of working as described above, it is preferred that the cover of the container has a touch-and-open structure and examples thereof are described in JP-U-A-61-128646, JP-A-3-265849 and JP-A-4-240850.

The above-described color developer is preferably packed in a container made of a material having a carbon dioxide permeation rate of 25 ml/m^2 • 24 hrs • atm or less to give a void ratio of from 0.15 to 0.05.

Preferred examples of the material having the above-described carbon dioxide permeation rate include polyethylene terephthalate, polyvinyl chloride, polyvinylidene chloride, a laminate material of polyethylene or polypropylene and nylon, a laminate material of polyethylene or polypropylene and aluminum, and a glass having a thickness of front 300 to 2,000 μm. In particular, a polyethylene terephthalate and a laminate material of polyethylene and nylon, having a thickness of from 500 to 1,000 μm are most preferred because the carbon dioxide permeation rate, the mechanical strength and the weight are well balanced. Further, the material for the container used in the present invention preferably has an oxygen permeation rate of 20 ml/m^2 • 24 hrs • atm or less.

The void ratio as used herein means a value obtained by subtracting the packed amount (ml) of the color developer from the volume (ml) of the container housing the color developer and dividing the value obtained by the volume (ml) of the container. The liquid color developer of the present invention is preferably packed in the above-described container to give a void ratio of from 0.15 to 0.05.

The above-described color developer may be used directly as a color developer solution or a replenisher solution, however, it is preferably mixed and diluted with water before using it as a color developer solution or a replenisher solution. When the color developer is used as a color developer solution, a starter containing water, a pH adjusting agent and a bromide is preferably added thereto.

When the color developer is used as a replenisher solution, it may be previously mixed and diluted with water, stocked in a replenisher tank and supplied therefrom to the processing solution tank in a constant amount, or it may be supplied directly to the processing solution tank in a constant amount separately from water and mixed and diluted with water in the processing solution tank. Also, as a method middled therebetween, the color developer may be transferred to the processing solution tank while continuously mixing and diluting it with water. In this case, known methods such as disposition of a mixing tank in the middle may be used.

With respect to the water washing and the stabilization, the description in JP-A-4-125558, from page 12, right lower column, line 6 to page 13, right lower column, line 16, may be preferably applied. In particular, preferred in view of conservation of the working environment are the use of azolylmethylamines described in European Unexamined Patent Publication Nos. 504609 and 519190 or N-methylolazoles described in JP-A-4-362943, in place of formaldehyde in the stabilizing solution, and the formation of a surface active agent solution containing no image stabilizer such as formaldehyde by converting the magenta coupler into a two-equivalent coupler.

In the present invention, it is particularly preferred for improving the reading capability of magnetic recording information that the bath at the final step contains no image stabilizer.

In the processing solution, various ion components are present, such as calcium ion, magnesium ion, sodium ion and potassium ion, which components are dissolved out from the solution-conditioning water used for preparing a solution of the replenishing agent or eluted out from the light-sensitive material. However, in the present invention, the sodium ion concentration in the final bath at the water washing or stabilization step is preferably from 0 to 50 mg/ℓ, more preferably from 0 to 20 mg/ℓ.

In order to ensure the water washing or stabilization function and at the same time, to reduce the waste in view of environmental conservation, the replenishing amount of washing water or stabilizing solution is preferably from 80 to 1,000 ml, more preferably from 100 to 500 ml, still more preferably from 150 to 300 ml, per m^2 of the light-sensitive material. In the processing performed at the above-described replenishing rate, in order to prevent proliferation of bacteria and mold, a known antimold such as thiabendazole, 1,2-benzoisothiazolin-3-one and 5-chloro-2-methylisothiazolin-3-one, an antibiotic such as gentamicin, or water subjected to deionization treatment with an ion exchange resin is preferably used. The deionized water and the bactericide or antibiotic are more effective when they are used in combination.

Also, the solution in the washing water or stabilizing solution tank is preferably treated with a reverse osmosis membrane described in JP-A-3-46652, JP-A-3-53246, JP-A-3-121448 and JP-A-3-126030 to reduce the replenishing amount and in this case, the reverse osmosis membrane is preferably a low pressure reverse osmosis membrane.

In the processing of the present invention, the processing solution is preferably subjected to evaporation correction disclosed in JIII Journal of Technical Disclosure, No. 94-4992. In particular, a method of correcting evaporation using the temperature and humidity information of the environment where the automatic processor is installed, according to (formula-1) at page 2 of the above-described publication, is preferred. The water used in the evaporation correction is preferably sampled from the replenishing tank of washing water and in this case, deionized water is preferably used as the washing water replenisher.

The automatic processor for use in the present invention is preferably a film processor described in JIII Journal of Technical Disclosure, supra, page 3, right column, lines 22 to 28.

Specific examples of the processing agent, the automatic processor and the evaporation correction method preferred in practicing the present invention are described in JIII Journal of Technical Disclosure, supra, from page 5, right column, line 11 to page 7, right column, the last line.

The silver halide color photographic light-sensitive material to which the processing of the present invention is preferably applied is described below.

The silver halide color photographic light-sensitive material to which the present invention is preferably applied includes a color negative film and a color reversal film each coated with a silver iodobromide emulsion. A color negative film is more preferred and a color negative film comprising a support having thereon a magnetic recording layer is particularly preferred.

A light-sensitive material having a magnetic recording layer which is preferably processed in the present invention is described below.

The magnetic recording layer is provided by coating an aqueous or organic solvent-based coating solution containing a binder having dispersed therein magnetic particles, on a support. The magnetic particle includes ferromagnetic iron oxide (e.g., γFe_2O_3), Co-doped γFe_2O_3, Co-doped magnetite, Co-containing magnetite, ferromagnetic chromium dioxide, ferromagnetic metal, ferromagnetic alloy, hexagonal Ba ferrite, Sr ferrite, Pb ferrite and Ca ferrite. Among these, Co-doped ferromagnetic iron oxide such as Co-doped γFe_2O_3 is preferred.

The shape of the magnetic particle may be any of acicular, rice grain-like, spherical, cubic and platy forms. The specific surface area as S_{BET} is preferably 20 m^2/g or more, more preferably 30 m^2/g or more. The saturation magnetization (σs) of the ferromagnetic substance is preferably from 3.0×10^4 to 3.0×10^5 A/m, more preferably from 4.0×10^4 to 2.5×10^5 A/m. The ferromagnetic particle may be subjected to surface treatment with silica and/or alumina or with an organic material. Further, the ferromagnetic particle may be subjected to surface treatment with a silane coupling agent or a titanium coupling agent as described in JP-A-6-161032. Also, a magnetic particle having coated on the surface thereof an inorganic or organic material described in JP-A-4-259911 and JP-A-5-81652 may be used.

The binder for use in the magnetic particle includes a thermoplastic resin, a thermosetting resin, a radiation-curable resin, a reactive resin, an acid, alkali or biodegradable polymer, a natural polymer (e.g., cellulose derivative, saccharide derivative) and a mixture of these described in JP-A-4-219569. The above-described resin has a glass transition temperature (Tg) of from -40°C to 300°C and a weight average molecular weight of from 2,000 to 1,000,000. Examples of the resin include a vinyl copolymer, a cellulose derivative such as cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate and cellulose tripropionate, an acrylic resin and a polyvinyl acetal resin, and gelatin is also preferably used. Among these, cellulose di(tri)acetate is preferred. The binder may be cured by adding thereto an epoxy-based, aziridine-based or isocyanate-based cross-linking agent. Examples of the isocyanate-based cross-linking agent include isocyanates such as tolylenediisocyanate, 4,4'-diphenylmethanediisocyanate, hexamethylenediisocyanate and xylylenediisocyanate, a reaction product of these isocyanates with polyalcohol (e.g., a reaction product of 3 mol of tolylenediisocyanate with 1 mol of trimethylolpropane) and a polyisocyanate produced by the condensation of these isocyanates as described in JP-A-6-59357.

The ferromagnetic substance is dispersed into the binder by the method preferably using a kneader, a pin-type mill or an annular-type mill as described in JP-A-6-35092 and these may also be preferably used in combination. The dispersant described in JP-A-5-088283 and other known dipersants may be used.

The thickness of the magnetic recording layer is generally from 0.1 to 10 μm, preferably from 0.2 to 5 μm, more preferably from 0.3 to 3 μm. The weight ratio of the magnetic particle to the binder is preferably from 0.5:100 to 60:100, more preferably from 1:100 to 30:100. The coating amount of magnetic particles is from 0.005 to 3 g/m^2, preferably from 0.01 to 2 g/m^2, more preferably from 0.02 to 0.5 g/m^2.

The magnetic recording layer for use in the present invention may be provided throughout the entire surface of or stripedly on the back surface of the photographic support by coating or printing. The magnetic recording layer can be coated by using air doctor, blade, air knife, squeeze, soakage, reverse roller, transfer roller, gravure, kiss, cast, spray, dip, bar or extrusion, and the coating solution described in JP-A-5-341436 is preferred.

The magnetic recording layer may be designed to have additional functions such as improvement of lubricity, control of curl, electrostatic charge prevention, prevention of adhesion or head abrasion, or other functional layers may be provided to undertake these functions. It is preferred that at least one or more of particles is an abrasive as an aspheric inorganic particle having a Mhos' hardness of 5 or more. The composition of the aspheric inorganic particle is preferably an oxide such as aluminum oxide, chromium oxide, silicon dioxide or titanium dioxide, a carbide such as silicon carbide or titanium carbide, or a fine particle of diamond. The abrasive may be subjected to surface treatment with a silane coupling agent or a titanium coupling agent. The particle may be added to a magnetic recording layer or may be overcoated on the magnetic recording layer (for example, as a protective layer or a lubricant layer). The binder used here may be one selected from those described above and it is preferably the same as the binder in the magnetic recording layer. The light-sensitive material having a magnetic recording layer is described in U.S. Patents 5,336,589, 5,250,404, 5,229,259 and 5,215,874 and European Patent 466130.

The light-sensitive material which is processed in the present invention is preferably a light-sensitive material for photographing and the support thereof is preferably polyester. The details on polyester are described in JIII Journal of Technical Disclosure No. 94-6023 (March 15, 1994).

The polyester for use in the present invention is formed using diol and an aromatic dicarboxylic acid as essential components. Examples of the aromatic dicarboxylic acid include 2,6-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, a terephthalic acid, an isophthalic acid and a phthalic acid, and examples of the diol include diethylene glycol, triethylene glycol, cyclohexanedimethanol, bisphenol A and biphenol. The polymer includes a homopolymer such as polyethylene terephthalate, polyethylene naphthalate and polycyclohexanedimethanol terephthalate. Among these, preferred is a polyester containing from 50 to 100 mol% of 2,6-naphthalenedicarboxylic acid. Particularly preferred is polyethylene 2,6-naphthalate. The average molecular weight is approximately from 5,000 to 200,000. The polyester generally has a Tg of 50°C or higher, more preferably 90°C or higher.

The polyester support is preferably subjected to heat treatment to have an aversion to curling habit at a temperature of from 40°C to less than Tg, more preferably from (Tg - 20°C) to less than Tg. The heat treatment may be conducted either at a constant temperature within the above-described range or while cooling. The heat treatment time is from 0.1 to 1,500 hours, more preferably from 0.5 to 200 hours. The support may be subjected to heat treatment either in a state of roll or as a web on the way of conveyance. The surface may be made uneven (for example, by coating electrically conductive inorganic fine particles such as SnO_2 or Sb_2O_5)) to improve the surface state. Also, it is preferred to make some designs such that the edge is knurled to slightly increase the height only of the edge, thereby preventing the cut copy at the core portion. The heat treatment may be performed at any stage, such as after formation of support film, after surface treatment, after coating of a back layer (e.g., antistatic agent, slipping agent), or after coating of an undercoat layer. The preferred stage is after coating of an antistatic agent.

Into the polyester, an ultraviolet absorbent may be kneaded in. Or, for preventing light piping, a commercially available dye or pigment for polyester, such as Diaresin produced by Mitsubishi Chemicals Industries, Ltd. or Kayaset produced by Nippon Kayaku K.K., may be mixed so as to attain the object.

The light-sensitive material for use in the present invention is preferably subjected to surface treatment so that the support can be bonded to the light-sensitive constituent layer. Examples of the surface activation treatment include chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet light treatment, high frequency treatment, glow discharge treatment, active plasma treatment, laser treatment, mixed acid treatment and ozone oxidation treatment. Among these surface treatments, preferred are ultraviolet irradiation treatment, flame treatment, corona treatment and glow treatment.

The undercoating method is described below. The undercoating may be mono layer coating or two or more layer coating. The binder for the undercoat layer includes a copolymer starting from a monomer selected from vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid and maleic anhydride, and in addition, polyethyleneimine, epoxy resin, grafted gelatin, nitrocellulose and gelatin. The compound which swells the support include resorcinol and p-chlorophenol. The undercoat layer may contain a gelatin hardening agent and examples thereof include chromic salts (e.g., chrome alum), aldehydes (e.g., formaldehyde, glutaraldehyde), isocyanates, active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-S-triazine), epichlorohydrin resins and active vinyl sulfone compounds. Further, the undercoat layer may contain an inorganic fine particle such as SiO_2 and TiO_2 or a polymethyl methacrylate copolymer fine particle (0.01 to 10 μm) as a matting agent.

The light-sensitive material for use in the present invention preferably contains an antistatic agent. Examples of the antistatic agent include a high polymer containing a carboxylic acid, a carboxylate or a sulfonate, a cationic high polymer and an ionic surface active agent compound.

Most preferred antistatic agents are a fine particle of at least one crystalline metal oxide having a volume resistivity of 10^7 Ω-cm or less, more preferably 10^5 Ω-cm or less and a particle size of from 0.001 to 1.0 μm, selected from ZnO, TiO_2, SnO_2, Al_2O_3, In_2O_3, SiO_2, MgO, BaO, MoO_3 and V_2O_5 or of a composite oxide of these (e.g., Sb, P, B, In, S, Si, C) and a fine particle of a sol-like metal oxide or of a composite oxide of these. The content thereof in the light-sensitive material is preferably from 5 to 500 mg/m^2, more preferably from 10 to 350 mg/m^2. The ratio of the electrically conductive crystalline oxide or a composite oxide to the binder is preferably from 1/300 to 100/1, more preferably from 1/100 to 100/5.

The light-sensitive material preferably has a slipperiness. The slipping agent-containing layer is preferably present on both the light-sensitive layer surface and the back surface. The preferred slipperiness is in terms of a coefficient of dynamic friction, from 0.01 to 0.25. The value is determined using a stainless steel ball having a diameter of 5 mm by transporting the light-sensitive material at a speed of 60 cm/min (25°C, 60% RH). In this evaluation, even when the other party is changed to the light-sensitive layer surface, the value almost on the same level is obtained.

The slipping agent which can be used in the present invention includes polyorganosiloxane, a higher fatty acid amide, a higher fatty acid metal salt and an ester of a higher fatty acid with a higher alcohol. Examples of the polyorganosiloxane include polydimethylsiloxane, polydiethylsiloxane, polystyrylmethylsiloxane and polymethylphenylsiloxane. The layer to which the slipping agent is added is preferably an outermost layer of the emulsion layer or a back layer. In particular, polydimethylsiloxane and an ester having a long chain alkyl group are preferred.

Further, the light-sensitive material preferably contains a matting agent. The matting agent may be used either on the emulsion surface or on the back surface, but it is particularly preferably added to the outermost layer on the emulsion layer side. The matting agent may be either soluble in the processing solution or insoluble in the processing solution, and the combination use thereof are preferred. For example, polymethyl methacrylate, poly(methyl methacrylate/methacrylic acid = 9/1 or 5/5 (by mol)) and polystyrene particles are preferred. The particle size is preferably from 0.8 to 10 μm, the particle size distribution is preferably narrower, and 90% by number or more of all particles preferably have a size between 0.9 and 1.1 times the average particle size.

In order to increase the matting property, fine particles of 0.8 μm or less are preferably added at the same time and examples thereof include polymethyl methacrylate (0.2 μm), poly(methyl methacrylate/methacrylic acid = 9/1 (by mol) (0.3 μm), polystyrene particles (0.25 μm) and colloidal silica (0.03 μm).

The light-sensitive material for use in the present invention preferably includes those described in JP-A-4-125558, from page 14, left upper column, line 1 to page 18, left lower column, line 11. The silver halide emulsion is preferably a silver iodobromide emulsion having an average silver iodide content of from 3 to 20 mol%, which preferably comprises tabular grains having an aspect ratio of 5 or more or double structure grains different in the halogen composition between the inside and the outside. The inside and the outside of the grain may form a clear layer structure. The aspect ratio is preferably from 5 to 20, more preferably from 6 to 12.

The monodisperse emulsions described in U.S. Patents 3,574,628 and 3,655,394 are also preferably used.

The light-sensitive material for use in the present invention preferably has a layer containing light-insensitive fine grain silver halide having an average grain size of from 0.02 to 0.2 μm. The fine grain silver halide is preferably silver bromide having a silver iodide content of from 0.5 to 10 mol%.

The additives which can be used in the light-sensitive material for use in the present invention are described in the following publications.

	Kinds of Additives	RD17643	RD18716	RD307105
1.	Chemical sensitizer	p. 23	p. 648, right col.	p. 866
2.	Sensitivity increasing agent		p. 648, right col.	
3.	Spectral sensitizer, supersensitizer	pp. 23-24	p. 648, right col.-p. 649, right col.	pp. 866-868
4.	Whitening agent	p. 24	p. 647, right col.	p. 868
5.	Light absorbent, filter dye, UV absorbent	pp. 25-26	p. 649, right col.-p. 650, left col.	p. 873
6.	Binder	p. 26	p. 651, left col.	pp. 873-874
7.	Plasticizer, lubricant	p. 27	p. 650, right col.	p. 876
8.	Coating aid, surface active agent	PP 26-27	p. 650, right col.	pp. 875-876
9.	Antistatic agent	p. 27	p. 650, right col.	pp. 876-877
10.	Matting agent			pp. 878-879

Various dye-forming couplers can be used in the light-sensitive material of the present invention and the following couplers are particularly preferred.

Yellow Coupler:

Couplers represented by formulae (I) and (II) of EP 502424A; couplers represented by formulae (1) and (2) (particularly, Y-28 at page 18) of EP 513496A; couplers represented by formula (I) in claim 1 of EP 568037A; couplers represented by formula (I) in column 1, lines 45 to 55 of U.S. Patent 5,066,576; couplers represented by formula (I) in paragraph 0008 of JP-A-4-274425; couplers (particularly, D-35 at page 18) described in claim 1 at page 40 of EP 498381A1; couplers represented by formula (Y) at page 4 (particularly, Y-1 (page 17) and Y-54 (page 41)) of EP 447969A1; and couplers represented by formulae (II) to (IV) in column 7, lines 36 to 58 (particularly, II-17, II-19 (column 17) and II-24 (column 19)) of U.S. Patent 4,476,219.

Magenta Coupler:

L-57 (page 11, right lower column), L-68 (page 12, right lower column) and L-77 (page 13, right lower column) of JP-A-3-39737; A-4-63 (page 134), A-4-73 and A-4-75 (page 139) of European Patent 456257; M-4, M-6 (page 26) and M-7 (page 27) of European Patent 486965; M-45 (page 19) of EP 571959A; (M-1) (page 6) of JP-A-5-204106; and M-22 in paragraph 0237 of JP-A-4-362631.

Cyan Coupler:

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

Polymer Coupler:

P-1 and P-5 (page 11) of JP-A-2-44345.

As the coupler which provides a colored dye having an appropriate diffusibility, those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96873B and German Patent 3,234,533 are preferred.

As the coupler for correcting unnecessary absorption of a colored dye, yellow colored cyan couplers represented by formulae (CI), (CII), (CIII) and (CIV) described at page 5 of EP 456257A1 (particularly, YC-86 at page 84); Yellow Colored Magenta Couplers ExM-7 (page 202), EX-1 (page 249) and EX-7 (page 251) described in EP 456257A1; Magenta Colored Cyan Couplers CC-9 (column 8) and CC-13 (column 10) described in U.S. Patent 4,833,069; and colorless masking couplers represented by formula (2) (column 8) of U.S. Patent 4,837,136 and formula (A) in claim 1 of WO92/11575 (particularly, compounds described at pages 36 to 45) are preferred.

The container (patrone) for housing the light-sensitive material to be processed according to the method of the present invention is described below. The main material of the patrone may be either a metal or a synthetic plastic, however, preferred is a plastic material such as polystyrene, polyethylene, polypropylene and polyphenyl ether.

The patrone of the present invention may further contain various antistatic agents and preferred examples thereof include carbon black, a metal oxide particle, a nonionic, anionic, cationic or betaine surface active agent and a polymer. The patrone having the antistatic property is described in JP-A-1-312537 and JP-A-1-312538. In particular, the resistance at 25°C and 25% RH is preferably 10^{12} Ω or less. Usually, the plastic patrone is produced using a plastic having kneaded therein carbon black or a pigment so as to give light-shielding property. The patrone may have a currently used 135 size but it is also effective for achieving miniaturization of a camera to reduce the cartridge size from 25 mm in the current 135 size to 22 mm or less. The volume of the patrone case is preferably 30 cm^3 or less, more preferably 25 cm^3 or less. The weight of plastics used in the patrone and the patrone case is preferably from 5 to 15 g.

The patrone may send forth film by the rotation of a spool. Also, the patrone may have such a structure that a film leading end is housed in the patrone body and the film leading end is sent forth from the port part of the patrone towards the outside by rotating the spool shaft in the film delivery direction. These are disclosed in U.S. Patents 4,834,306, 5,226,613 and 5,296,887. A processed light-sensitive material may be again housed in a patrone and in this case, the patrone may be the same with or different from the patrone which had housed the light-sensitive material before development.

The present invention will be described in greater detail below with reference to Examples but the present invention should not be construed as being limited to these Examples.

EXAMPLE 1

A color negative film was prepared by coating layers each having the following composition one on another on a cellulose triacetate film support having an undercoat layer.

(Composition of light-sensitive layer)

The main materials used in each layer are classified as follows.

ExC: cyan coupler
ExM: magenta coupler
ExY: yellow coupler
ExS: sensitizing dye
UV: ultraviolet absorbent
HBS: high-boiling point organic solvent
H: gelatin hardening agent

Numerals corresponding to respective components show coating amounts expressed by the unit g/m^2 and in case of silver halide, they show coating amounts calculated in terms of silver. With respect to sensitizing dyes, the coating amount is shown by the unit mol per mol of silver halide in the same layer.

First Layer (Antihalation Layer)

Black colloidal silver	as silver 0.09
Gelatin	1.60
ExM-1	0.12
ExF-1	2.0×10^{-3}
Solid Disperse Dye ExF-2	0.030
Solid Disperse Dye ExF-3	0.040
HBS-1	0.15
HBS-2	0.02

Second Layer (Interlayer)

Silver Iodobromide Emulsion M	as silver 0.065
ExC-2	0.04
Polyethylacrylate latex	0.20
Gelatin	1.04

Third Layer (Low-sensitivity Red-sensitive Emulsion Layer)

Silver Iodobromide Emulsion A	as silver 0.25
Silver Iodobromide Emulsion B	as silver 0.25
ExS-1	6.9×10^{-5}
ExS-2	1.8×10^{-5}
ExS-3	3.1×10^{-4}
ExC-1	0.17
ExC-3	0.030
ExC-4	0.10
ExC-5	0.020
ExC-6	0.010
Cpd-2	0.025
HBS-1	0.10
Gelatin	0.87

Fourth Layer (Medium-sensitivity Red-sensitive Emulsion Layer)

Silver Iodobromide Emulsion C	as silver 0.70
ExS-1	3.5×10^{-4}
ExS-2	1.6×10^{-5}
ExS-3	5.1×10^{-4}
ExC-1	0.13
ExC-2	0.060
ExC-3	0.0070
ExC-4	0.090
ExC-5	0.015
ExC-6	0.0070
Cpd-2	0.023
HBS-1	0.10
Gelatin	0.75

Fifth Layer (High-sensitivity Red-sensitive Emulsion Layer)

Silver Iodobromide Emulsion D	as silver 1.40
ExS-1	2.4×10^{-4}
ExS-2	1.0×10^{-4}
ExS-3	3.4×10^{-4}
ExC-1	0.10
ExC-3	0.045
ExC-6	0.020
ExC-7	0.010
Cpd-2	0.050
HBS-1	0.22
HBS-2	0.050
Gelatin	1.10

Sixth Layer (Interlayer)

Cpd-1	0.090
Solid Disperse Dye ExF-4	0.030
HBS-1	0.050
Polyethylacrylate latex	0.15
Gelatin	1.10

Seventh Layer (Low-sensitivity Green-sensitive Emulsion Layer)

Silver Iodobromide Emulsion E	as silver 0.15
Silver Iodobromide Emulsion F	as silver 0.10
Silver Iodobromide Emulsion G	as silver 0.10
ExS-4	3.0×10^{-5}
ExS-5	2.1×10^{-4}
ExS-6	8.0×10^{-4}
ExM-2	0.33
ExM-3	0.086
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.73

Eighth Layer (Medium-sensitivity Green-sensitive Emulsion Layer)

Silver Iodobromide Emulsion H	as silver 0.80
ExS-4	3.2×10^{-5}
ExS-5	2.2×10^{-4}
ExS-6	8.4×10^{-4}
ExC-8	0.010
ExM-2	0.10
ExM-3	0.025
ExY-1	0.018
ExY-4	0.010
ExY-5	0.040
HBS-1	0.13
HBS-3	4.0×10^{-3}
Gelatin	0.80

Ninth Layer (High-sensitivity Green-sensitive Emulsion Layer)

Silver Iodobromide Emulsion I	as silver 1.25
ExS-4	3.7×10^{-5}
ExS-5	8.1×10^{-5}
ExS-6	3.2×10^{-4}
ExC-1	0.010
ExM-1	0.020
ExM-4	0.025
ExM-5	0.040
Cpd-3	0.040
HBS-1	0.25
Polyethylacrylate latex	0.15
Gelatin	1.33

Tenth Layer (Yellow Filter Layer)

Yellow colloidal silver	as silver 0.015
Cpd-1	0.16
Solid Disperse Dye ExF-5	0.060
Solid Disperse Dye ExF-6	0.060
Oil-Soluble Dye ExF-7	0.010
HBS-1	0.60
Gelatin	0.60

Eleventh Layer (Low-sensitivity Blue-sensitive Emulsion Layer)

Silver Iodobromide Emulsion J	as silver 0.09
Silver Iodobromide Emulsion K	as silver 0.09
ExS-7	8.6×10^{-4}
ExC-8	7.0×10^{-3}
ExY-1	0.050
ExY-2	0.22
ExY-3	0.50
ExY-4	0.020
Cpd-2	0.10
Cpd-3	4.0×10^{-3}
HBS-1	0.28
Gelatin	1.20

Twelfth Layer (High-sensitivity Blue-sensitive Emulsion Layer)

Silver Iodobromide Emulsion L	as silver 1.00
ExS-7	4.0×10^{-4}
ExY-2	0.10
ExY-3	0.10
ExY-4	0.010
Cpd-2	0.10
Cpd-3	1.0×10^{-3}
HBS-1	0.070
Gelatin	0.70

Thirteenth Layer (First Protective Layer)

UV-1	0.19
UV-2	0.075
UV-3	0.065
HBS-1	5.0×10^{-2}
HBS-4	5.0×10^{-2}
Gelatin	1.8

Fourteenth Layer (Second Protective Layer)

Silver Iodobromide Emulsion M	as silver 0.10
H-1	0.40
B-1 (diameter: 1.7 μm)	5.0×10^{-2}
B-2 (diameter: 1.7 μm)	0.15
B-3	0.05
S-1	0.20
Gelatin	0.70

Further, in order to provide good preservability, processability, pressure durability, antimold/bactericidal property, antistatic property and coatability, W-1, W-2, W-3, B-4, B-5, B-6, F-1, F-2, F-3, F-4, F-5, F-6, F-7, F-8, F-9, F-10, F-11, F-12, F-13, F-14, F-15, F-16, F-17, iron salt, lead salt, gold salt, platinum salt, palladium salt, iridium salt or rhodium salt was appropriately added to each layer.

TABLE 1

	Average AgI Content (%)	Coefficient of Variation in AgI Content among Grains (%)	Average Grain Size, Sphere-Corresponding Diameter (μm)	Coefficient of Variation in Grain Size (%)	Projected Area Size, Circle-Corresponding Diameter (μm)	Diameter/ Thickness Ratio
Emulsion A	1.7	10	0.46	15	0.56	5.5
Emulsion B	3.5	15	0.57	20	0.78	4.0
Emulsion C	8.9	25	0.66	25	0.87	5.8
Emulsion D	8.9	18	0.84	26	1.03	3.7
Emulsion E	1.7	10	0.46	15	0.56	5.5
Emulsion F	3.5	15	0.57	20	0.78	4.0
Emulsion G	8.8	25	0.61	23	0.77	4.4
Emulsion H	8.8	25	0.61	23	0.77	4.4
Emulsion I	8.9	18	0.84	26	1.03	3.7
Emulsion J	1.7	10	0.46	15	0.50	4.2
Emulsion K	8.8	18	0.64	23	0.85	5.2
Emulsion L	14.0	25	1.28	26	1.46	3.5
Emulsion M	1.0	-	0.07	15	-	1

In Table 1:

(1) Emulsions J to L were subjected to reduction sensitization at the grain preparation using thiourea dioxide and

thiosulfonic acid according to the example of JP-A-2-191938;

(2) Emulsions A to I were subjected to gold sensitization, sulfur sensitization and selenium sensitization in the presence of the spectral sensitizing dyes described in each light-sensitive layer and sodium thiocyanate according to the example of JP-A-3-237450;

(3) in the preparation of tabular grains, low molecular weight gelatin was used according to the example of JP-A-1-158426;

(4) in tabular grains, dislocation lines as described in JP-A-3-237450 were observed through a high-pressure electron microscope; and

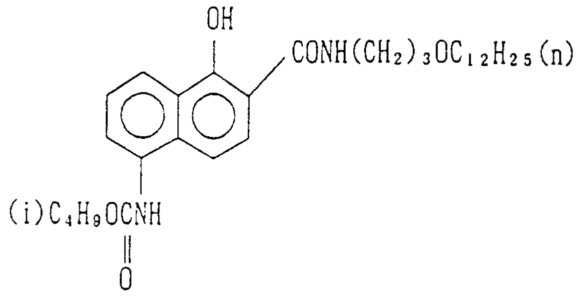
(5) Emulsion L is a double structure grain containing an inner high iodide core described in JP-A-60-143331.

Preparation of Dispersion Product of Organic Solid Disperse Dye:

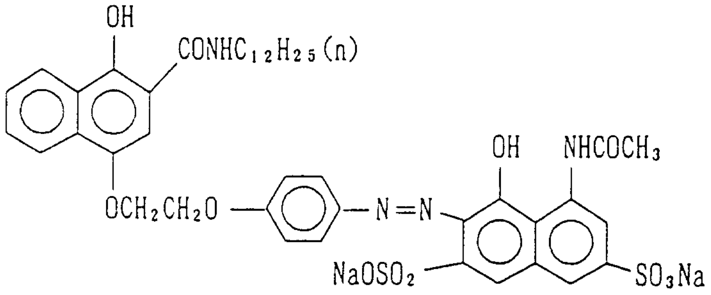
Solid Disperse Dye ExF-2 was dispersed as follows. That is, 21.7 ml of water, 3 ml of a 5% aqueous solution of sodium p-octylphenoxyethoxyethoxyethanesulfonate and 0.5 g of a 5% aqueous solution of p-octylphenoxypolyoxyethylene ether (polymerization degree: 10) were poured into a 700 ml-volume pot mill, then thereto 5.0 g of Dye ExF-2 and 500 ml of zirconium oxide beads (diameter: 1 mm) were added and the content was dispersed for 2 hours. In this dispersion, a BO-type vibration ball mill manufactured by Chuo Koki KK was used. After the dispersion, the content was taken out and added to 8 g of a 12.5% aqueous gelatin solution and the beads were removed by filtration to obtain a gelatin dispersion of the dye. The dye fine particles had an average particle size of 0.44 μm.

Solid dispersion products of ExF-3, ExF-4 and ExF-6 each was obtained in the same manner. The average particle size of dye fine particles was 0.24, 0.45 or 0.52 μm, respectively. ExF-5 was dispersed by the microprecipitation dispersion method described in Example 1 of EP 549489A. The average particle size was 0.06 μm.

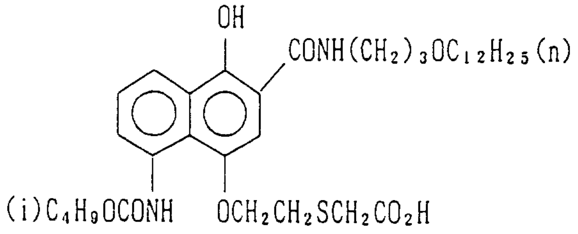
ExC－1



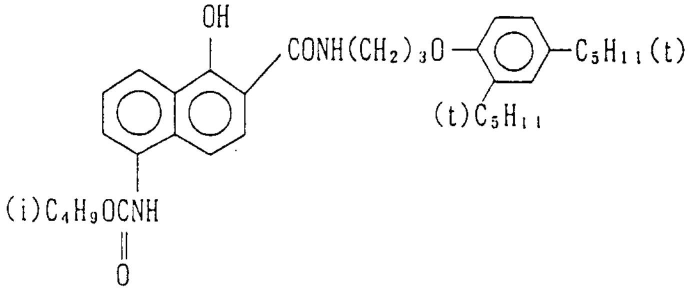
ExC－2



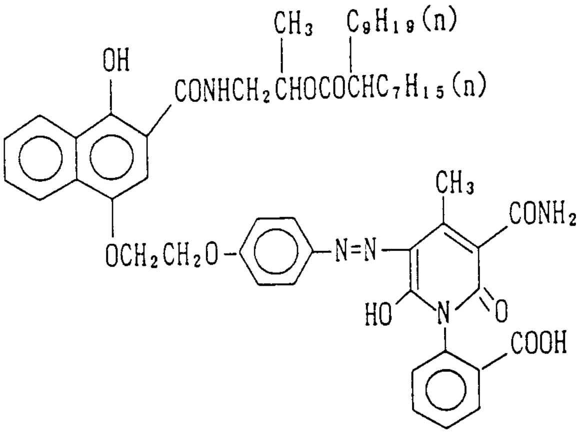
ExC－3



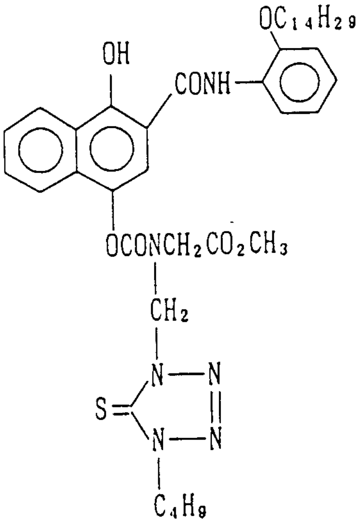
ExC－4



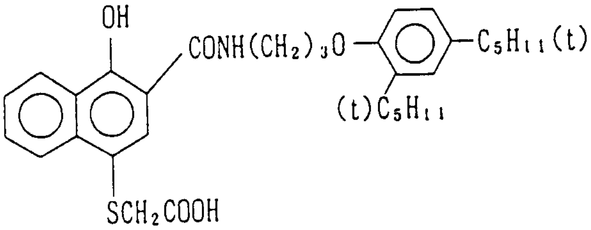
ExC−5



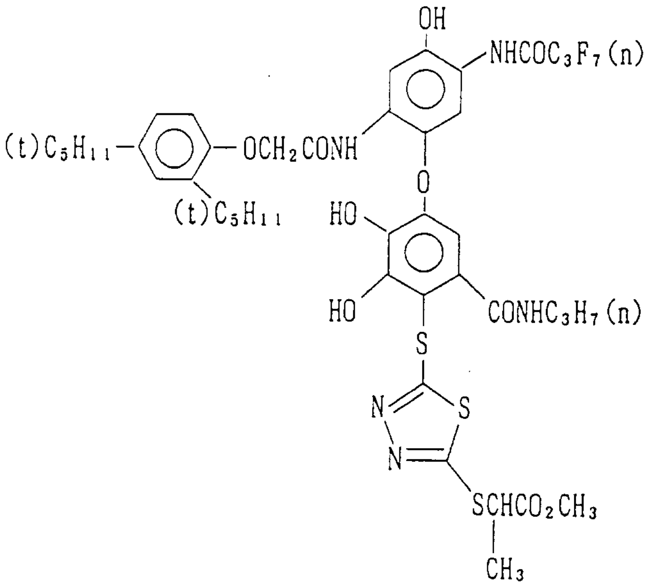
ExC−6



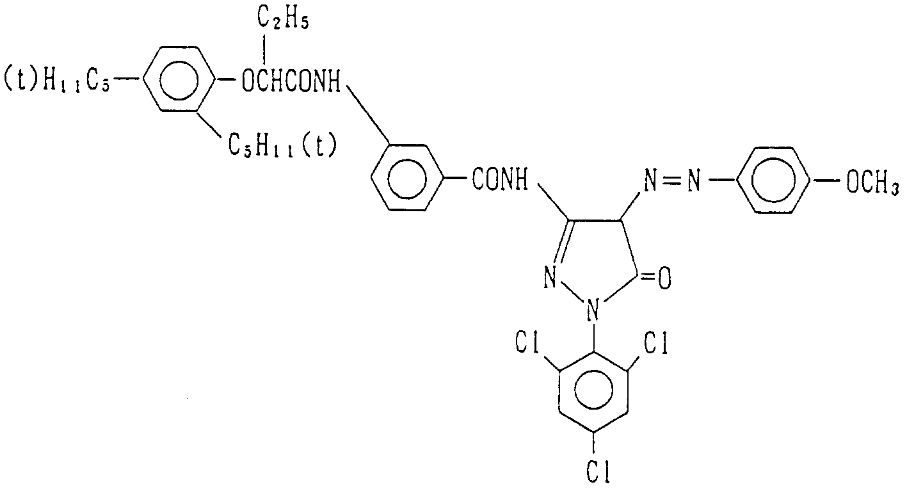
ExC−7



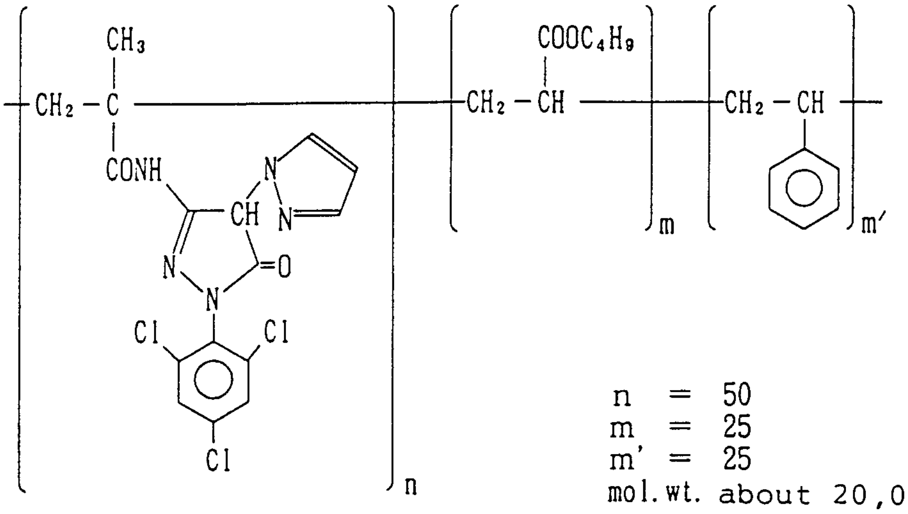
ExC-8


OH
NHCOC3F7(n)
(t)C5H11
OCH2CONH
(t)C5H11
O
HO
HO
CONHC3H7(n)
S
N
S
N
SCHCO2CH3
CH3

ExM-1

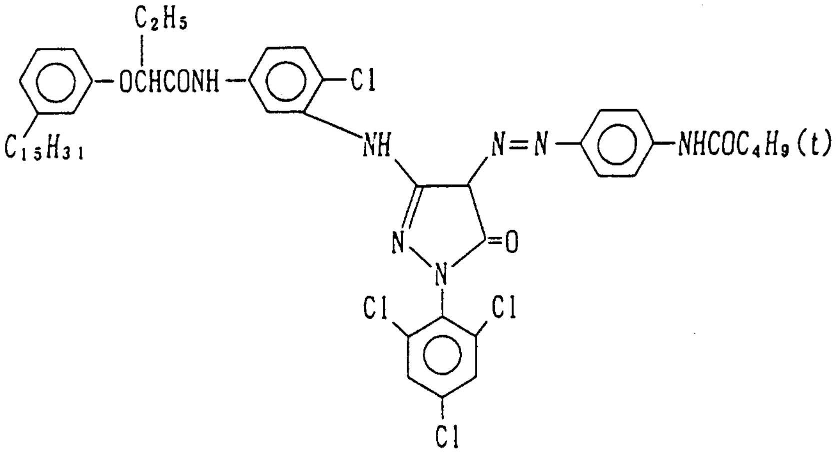

C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N=N
OCH3
N
N
=O
Cl
Cl
Cl

ExM-2

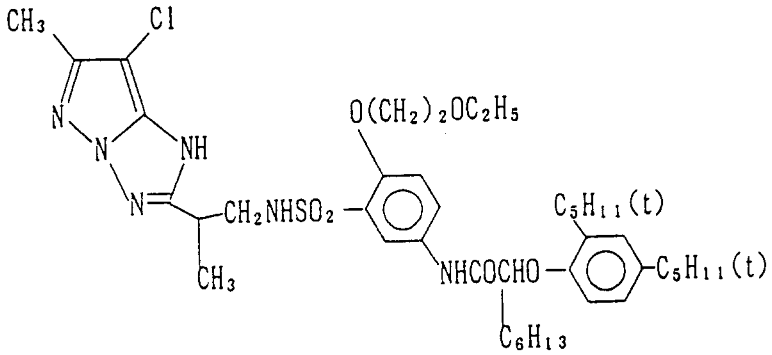


n = 50
m = 25
m' = 25
mol. wt. about 20,000

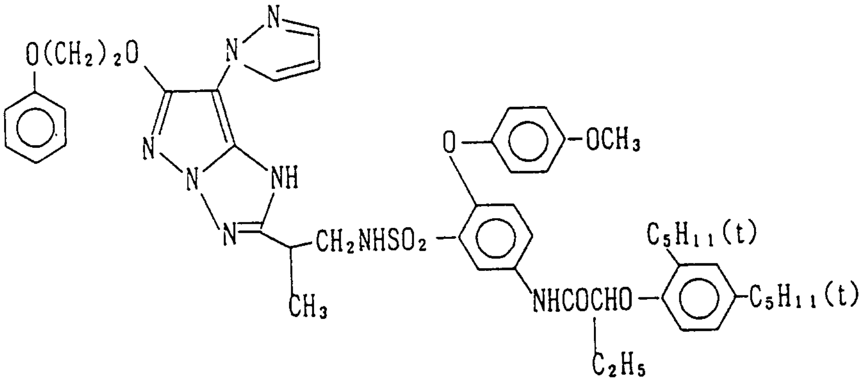
ExM-3



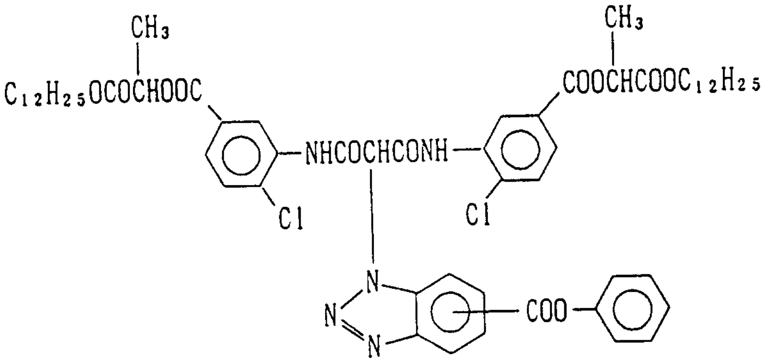
ExM－4



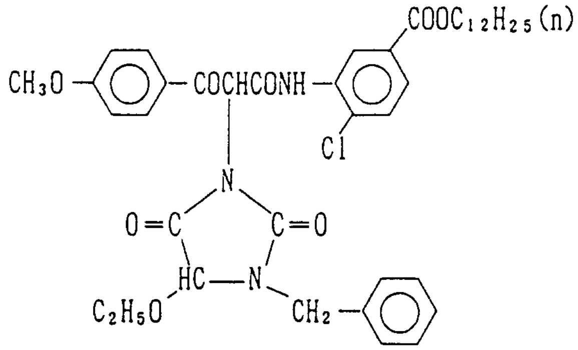
ExM－5



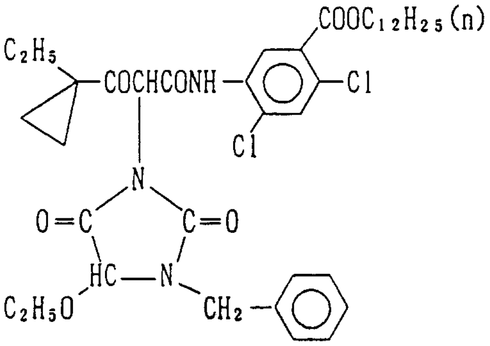
ExY－1



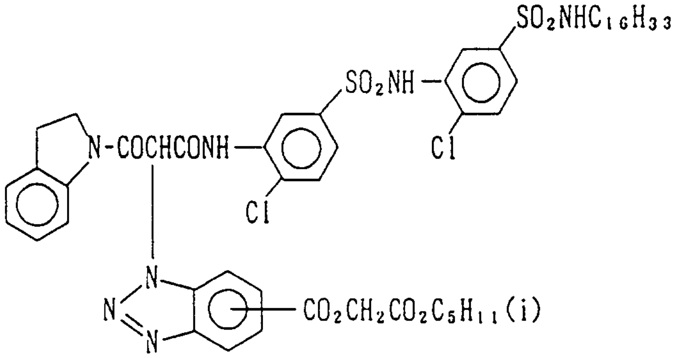
ExY－2



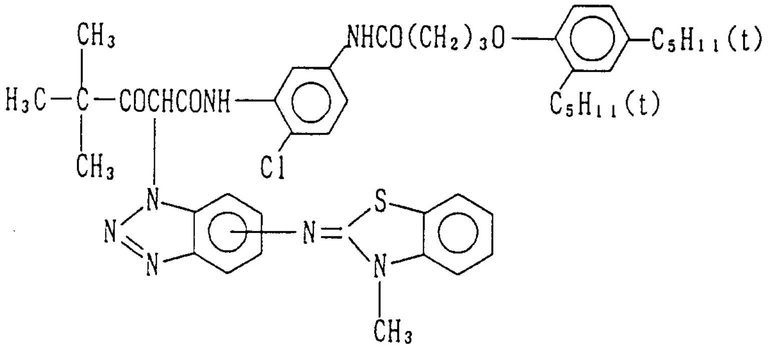
ExY－3



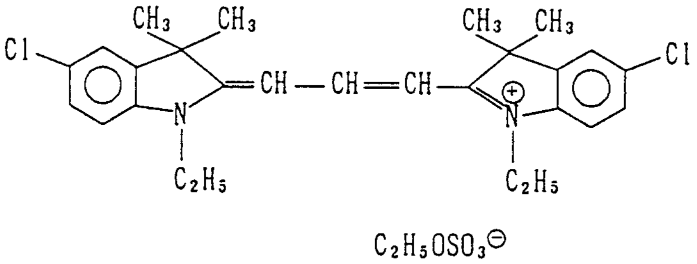
ExY－4



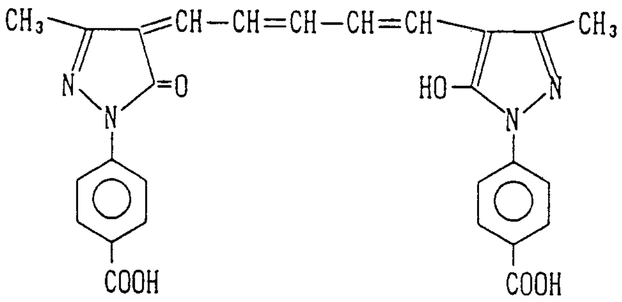
ExY－5



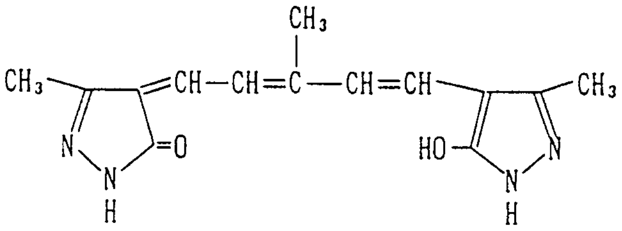
ExF－1



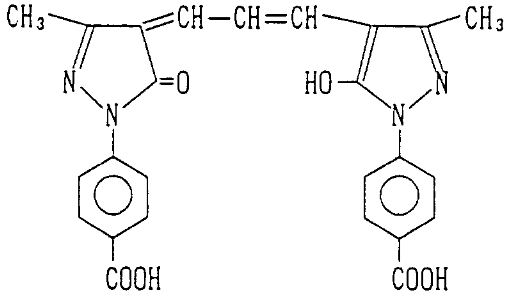
ExF－2



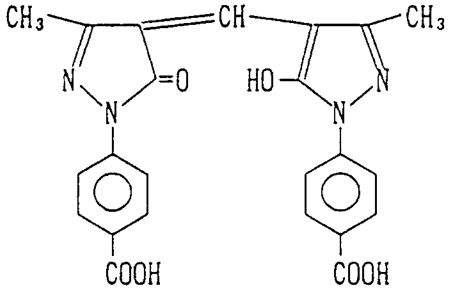
ExF－3



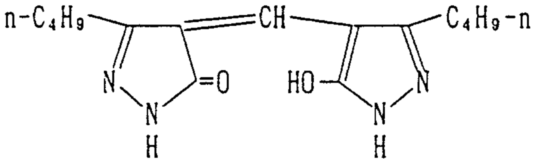
ExF－4



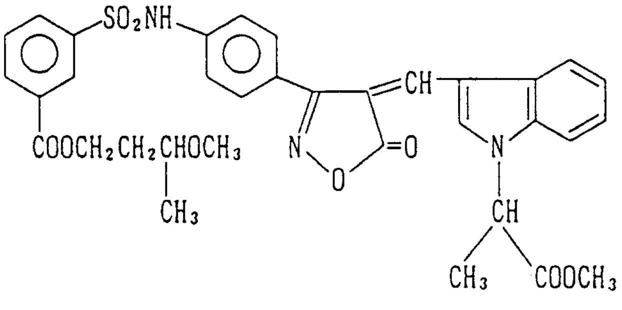
ExF－5



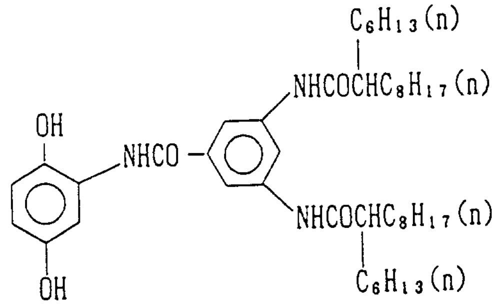
ExF－6



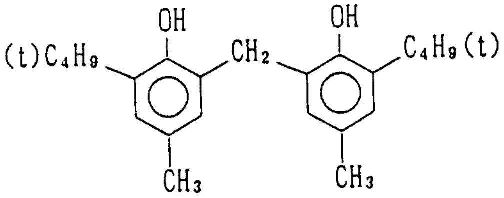
ExF－7



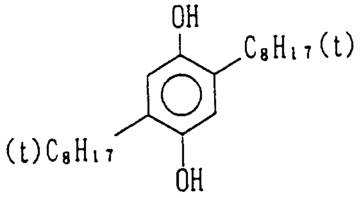
Cpd－1



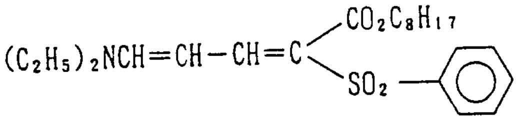
Cpd－2



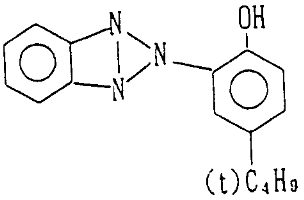
Cpd－3



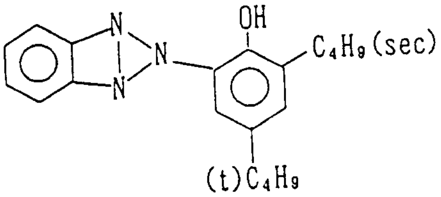
UV－1



UV－2



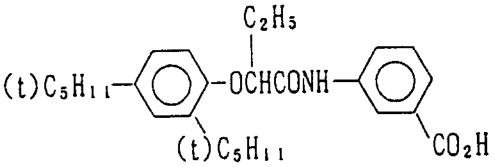
UV－3



HBS-1 Tricresyl phosphate

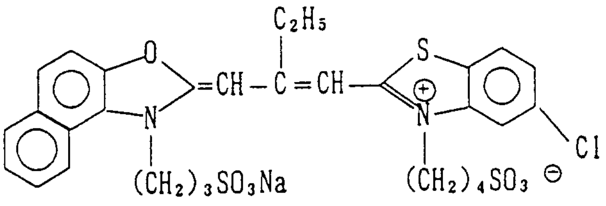
HBS-2 Di-n-butyl phthalate

HBS－3

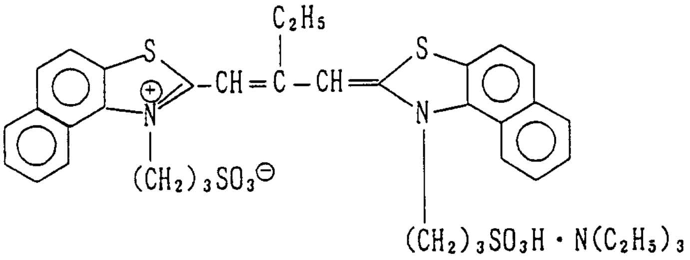


HBS-4 Tri(2-ethylhexyl) phosphate

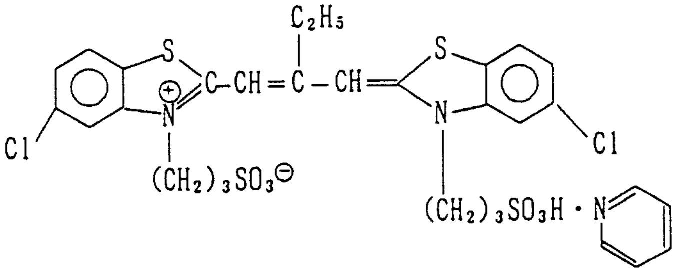
ExS－1



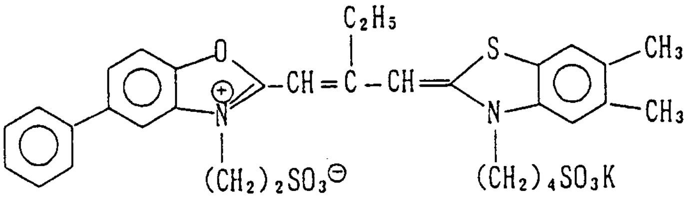
ExS－2



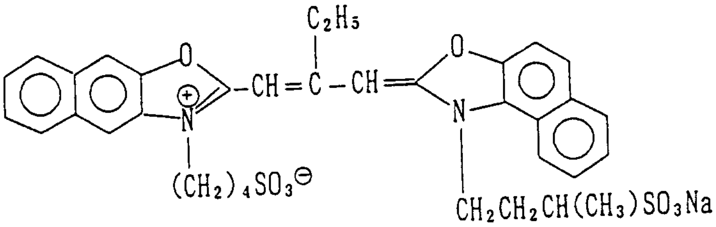
ExS－3



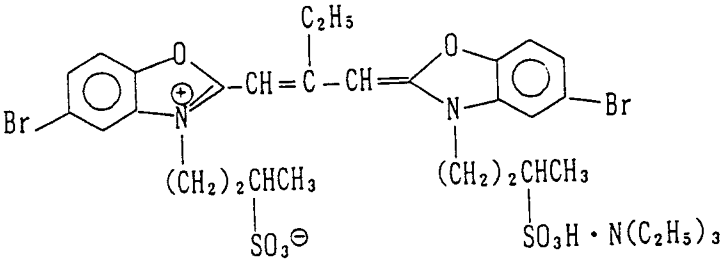
ExS－4



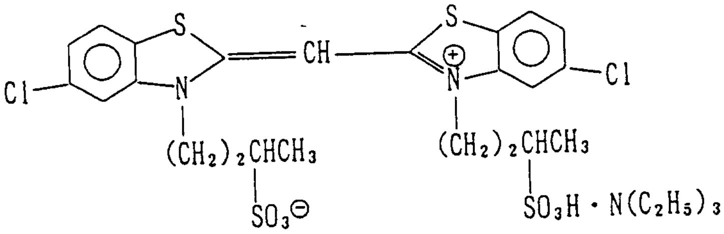
ExS-5



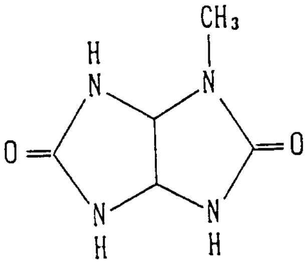
ExS-6



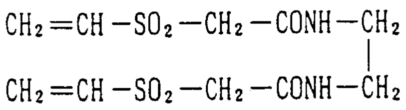
ExS-7



S-1

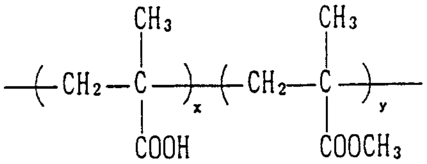


H－1



$$\begin{array}{l} CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

B－1

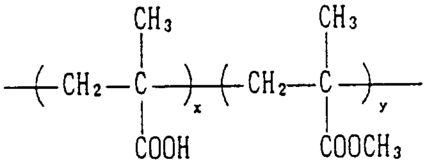


$$-\left(CH_2-\overset{CH_3}{\underset{COOH}{C}}\right)_x\left(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\right)_y-$$

x/y=10/90 (by weight)

Average molecular weight: about 35,000

B－2

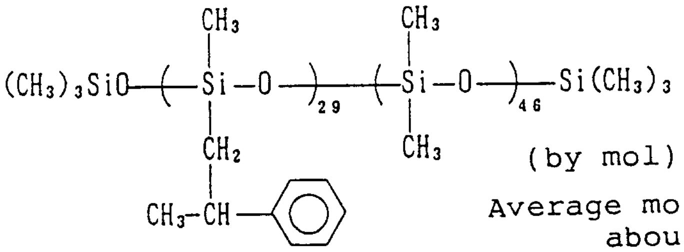


$$-\left(CH_2-\overset{CH_3}{\underset{COOH}{C}}\right)_x\left(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\right)_y-$$

x/y=40/60 (by weight)

Average molecular weight: about 20,000

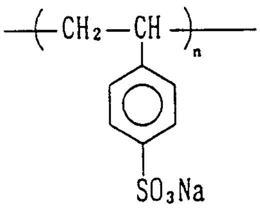
B－3



(by mol)

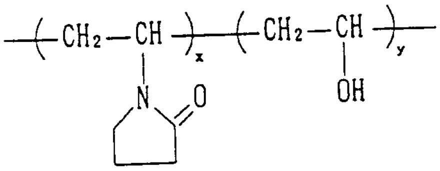
Average molecular weight: about 8,000

B－4



Average molecular weight: about 750,000

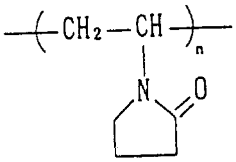
B-5



x/y=70/30 (by weight)

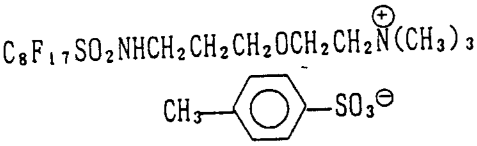
Average molecular weight: about 17,000

B-6

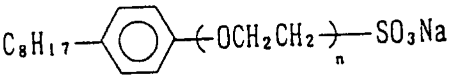


Average molecular weight: about 10,000

W-1

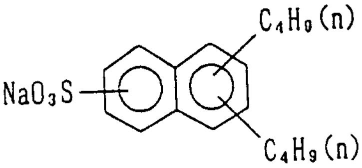


W-2

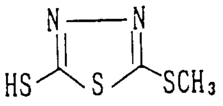


n=2 ~ 4

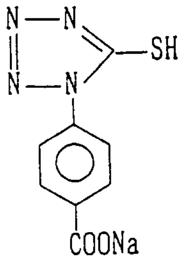
W-3



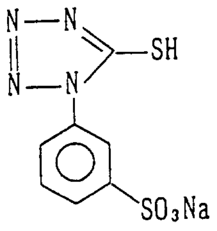
F - 1



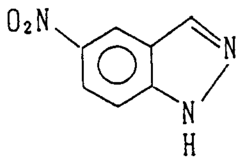
F - 2



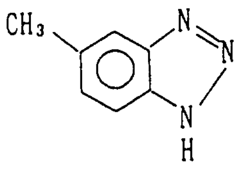
F - 3



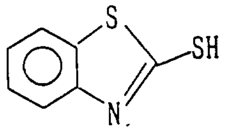
F - 4



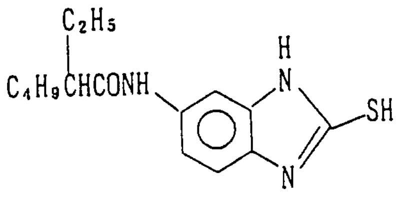
F - 5



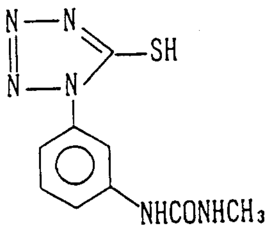
F - 6



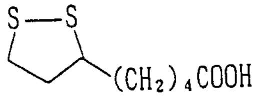
F - 7



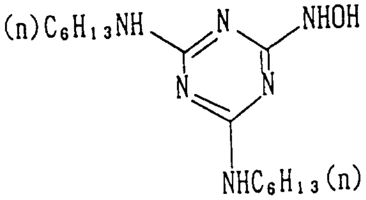
F - 8



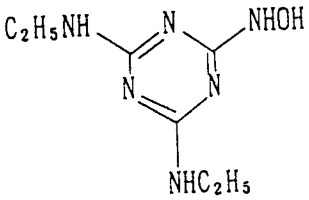
F－9



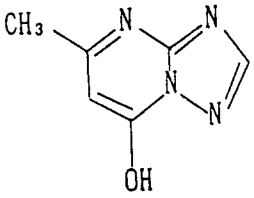
F－10



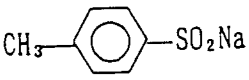
F－11



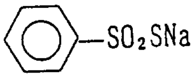
F－12



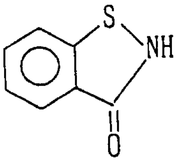
F－13



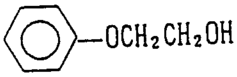
F－14



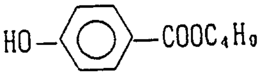
F－15



F－16



F－17



The thus-prepared Sample 101 was cut into a 135-type film size (corresponding International Standard: ISO 1007) and wedgewise exposed. Thereafter, the light-sensitive material was processed under the following conditions at a rate of 6 m^2 per day for two months. The processing machine used was Automatic Processor FNCP-300II manufactured by Fuji Photo Film Co., Ltd. The temperature of each processing solution was continuously set to the following processing temperature throughout the test period.

Processing Step

Step	Processing Time	Processing Temperature (°C)	Replenishing Amount* (ml/m^2)	Tank Volume (ℓ)
Color development	3 min 15 sec	38.0	550	82
Bleaching	3 min 00 sec	38.0	150	118
Water washing (1)	15 sec	24.0	counter-current piping system from (2) to (1)	20
Water washing (2)	15 sec	24.0	200	20
Fixing	3 min 00 sec	38.0	400	77
Water washing (3)	30 sec	24.0	counter-current piping system from (4) to (3)	40
Water washing (4)	30 sec	24.0	1,000	40
Stabilization	30 sec	38.0	300	40
Drying	4 min 20 sec	55		

The composition of each processing solution is shown below.

Color Developer

	Tank Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	1.0	1.2
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.2
Sodium sulfite	4.0	4.8
Potassium carbonate	30.0	39.0
Potassium bromide	1.4	0.3
Potassium iodide	1.5 mg	-
Hydroxylamine sulfate	2.4	3.3
Disodium N,N-bis(2-sulfonatoethyl)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

Bleaching Solution

	Tank Solution (g)	Replenisher (g)
1,3-Diaminopropane-N,N,N',N'-tetraacetic acid	0.17 mol	0.25 mol
Iron(III) nitrate nonahydrate	65.0	100.0
Ammonium bromide	80.0	120.0
Acetic acid (90%)	50.0	75.0
Water to make	1,000 ml	1,000 ml
pH (adjusted by aqueous ammonia and nitric acid)	4.3	3.8

Fixing Solution

	Tank Solution (g)	Replenisher (g)
Ammonium thiosulfinate	0.7 mol	1.0 mol
Ammonium sulfite	0.2 mol	0.3 mol
Compound of the Invention (shown in Table 2)	0.02 mol	0.03 mol
Acetic acid (90%)	3.0	4.0
Water to make	1,000 ml	1,000 ml
pH	shown in Table 2	

Stabilizing Solution

The tank solution and the replenisher were common.

	(g)
p-Nonylphenoxypolyglycidol (glycidol average polymerization degree: 10)	0.2
Ethylenediamine-N,N,N',N'-tetraacetic acid	0.05
1,2,4-Triazole	1.3
1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75
Glycolic acid	0.02
Gentamicin	0.01
Hydroxyethylcellulose (HEC SP-2000, produced by Dicel Chemical Industries, Ltd.)	0.1
1,2-Benzoisothiazolin-3-one	0.05
Water to make	1 ℓ
pH (adjusted by aqueous ammonia and nitric acid)	8.5

The light-sensitive materials after respective processings each was evaluated on the stains and image preservability according to the method described below.

Stains

The processed samples were subjected to the density measurement to obtain a characteristic curve and Dmin measured with red light (R light) was read from the characteristic curve.

Aging Change of Image

The processed samples were subjected to the density measurement to obtain a characteristic curve and Dmax measured with green light (G light) was read from the characteristic curve. Subsequently, the light-sensitive materials after the determination were stored under the following conditions and then Dmax after aging was determined. The aging change in Dmax of the magenta dye was obtained according to the following formula:

Storage condition:

70°C, relative humidity of 70%, 4 weeks

Aging change in Dmax (ΔDmax(G)) = (Dmax after storage) - (Dmax before storage)

Separately, a processing solution having the same composition as the tank solution of the above-described fixing solution was prepared except that 2,000 ppm of iron(III) ions, 400 ppm of calcium ions and 150 ppm of magnesium ions were added to the solution. After allowing the solution at 40°C for 4 weeks, generation of the precipitation was observed.

The results obtained are shown in Table 2.

TABLE 2

Additives of Fixing Solution <molar ratio>	pH of Fixing Solution	Observation of Aged Solution	Dmin (R)	ΔDmax (G)	Remarks
EDTA	5.4	turbidity	0.29	0.35	Comparison
"	6.0	"	0.29	0.37	"
"	6.1	slight turbidity	0.28	0.37	"
"	6.4	no turbidity	0.28	0.38	"
"	7.7	"	0.27	0.39	"
"	8.0	"	0.27	0.39	"
"	8.1	"	0.28	0.40	"
"	8.4	"	0.28	0.40	"
1,3-PDTA	6.4	slight turbidity	0.33	0.42	"
NTA	6.4	turbidity	0.30	0.51	"
I-7	6.4	turbidity	0.41	0.61	"
I-25	6.4	precipitation	0.31	0.57	"
II-1	6.4	precipitation	0.39	0.49	"
A-7	5.4	precipitation	0.24	0.45	Comparison
"	6.0	slight turbidity	0.24	0.38	"
"	6.1	no turbidity	0.24	0.33	Invention
"	6.4	"	0.23	0.27	"
"	7.7	"	0.24	0.28	"
"	8.0	"	0.26	0.31	"

TABLE 2 (continued)

Additives of Fixing Solution <molar ratio>	pH of Fixing Solution	Observation of Aged Solution	Dmin (R)	ΔDmax (G)	Remarks
A-7	8.1	slight turbidity	0.31	0.38	Comparison
"	8.4	"	0.34	0.38	"
A-6	6.4	no turbidity	0.24	0.28	Invention
A-14	6.4	"	0.25	0.33	"
A-22	6.4	slight turbidity	0.28	0.30	"
A-49	6.4	no turbidity	0.26	0.34	"
B-2	6.4	"	0.25	0.29	"
B-5	6.4	"	0.26	0.29	"
B-9	6.4	slight turbidity	0.28	0.30	"
B-11	6.4	no turbidity	0.28	0.33	"
EDTA:A-7 <1:1>	6.4	"	0.27	0.34	"
I-7:A-7 <1:1>	6.4	"	0.23	0.28	"
II-1:A-7 <1:1>	6.4	"	0.25	0.31	"
II-1:B-2 <1:1>	6.4	"	0.25	0.33	"

EDTA: Ethylenediamine-N,N',N'-tetraacetic acid
1,3-PDTA: 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid
NTA: Nitrilotriacetic acid

It is seen from Table 2 that in the processing of the present invention, excellent results were provided with respect to the solution stability, stains and aging change of magenta dye.

EXAMPLE 2

The processing was performed in the same manner as in Example 1 except for changing the bleaching solution, the fixing solution and the stabilizing solution as follows, and stains and aging change of the magenta dye were determined. The results obtained are shown in Table 3.

Bleaching Solution

	Tank Solution (g)	Replenisher (g)
Chelating agent for bleaching solution (shown in Table 3)	0.17 mol	0.25 mol
Iron(III) nitrate nonahydrate	65.0	100.0
Sodium bromide	80.0	120.0
Glycolic acid	40.0	65.0
Succinic acid	20.0	30.0
Water to make	1,000 ml	1,000 ml
pH (adjusted by NaOH and nitric acid)	shown in Table 3	

Fixing Solution

	Tank Solution (g)	Replenisher (g)
Sodium thiosulfate	0.7 mol	1.0 mol
Sodium sulfite	0.2 mol	0.3 mol
Compound of the Invention (shown in Table 3)	0.05 mol	0.08 mol
Acetic acid (90%)	3.0	4.0
Water to make	1,000 ml	1,000 ml
pH (adjusted by NaOH and nitric acid)	6.4	6.6

Stabilizing Solution

The tank solution and the replenisher were common.

	(g)
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10)	0.2
1,2,4-Triazole	1.3
1-Hydroxymethyl-1,2,4-triazole	0.75
Gentamicin	0.01
1,2-Benzoisothiazolin-3-one	0.05
Water to make	1 ℓ
pH (adjusted by aqueous ammonia and nitric acid)	8.5

TABLE 3

Bleaching Solution	pH	Fixing Solution	Dmin (R)	ΔDmax (G)	Remarks
1,3-PDTA	5.0	-	0.35	0.47	Comparison
"	5.0	A-6	0.26	0.35	Invention
"	2.0	A-7	0.28	0.38	"
"	3.0	"	0.26	0.35	"
"	3.5	"	0.26	0.34	"
"	5.0	"	0.26	0.33	"
"	7.0	"	0.28	0.36	"
"	8.0	"	0.32	0.39	"
"	5.0	B-5	0.28	0.37	"
I-28	5.0	-	0.33	0.57	Comparison
"	5.0	A-6	0.23	0.30	Invention
"	2.0	A-7	0.22	0.38	"
"	3.0	"	0.23	0.36	"
"	3.5	"	0.23	0.30	"
"	5.0	"	0.22	0.31	"
"	7.0	"	0.23	0.35	"
"	8.0	"	0.25	0.39	"
"	5.0	B-5	0.23	0.33	"
I-40	5.0	-	0.32	0.61	Comparison
"	5.0	A-6	0.22	0.30	Invention
"	5.0	A-7	0.21	0.29	"
"	5.0	B-5	0.23	0.31	"
II-15	5.0	-	0.33	0.52	Comparison
"	5.0	A-6	0.23	0.31	Invention
"	5.0	A-7	0.22	0.31	"
"	5.0	B-5	0.24	0.32	"

TABLE 3 (continued)

Bleaching Solution	pH	Fixing Solution	Dmin (R)	ΔDmax (G)	Remarks
I-7	5.0	A-7	0.19	0.29	Invention
I-7 + A-7 (50 mM)	5.0	A-7	0.15	0.24	"
I-7 + B-5 (50 mM)	5.0	A-7	0.17	0.26	"
I-54	5.0	-	0.33	0.55	Comparison
I-54	5.0	A-7	0.21	0.28	Invention
I-54 + A-7 (50 mM)	5.0	A-7	0.18	0.25	"
I-54 + A-7 (50 mM)	5.0	B-5	0.18	0.24	"

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

It is seen from Table 3 that in the processing of the present invention, when the compound represented by formula (I) or (II) was used as the bleaching agent and in particular, when the compound represented by formula (A) or (B) was used in the bleaching solution, the effect was provided.

EXAMPLE 3

A support and a back layer for a light-sensitive material were prepared as follows and thereon light-sensitive layers described in Example 1 were provided to prepare Light-Sensitive Material Sample 102.

1) Support

The support used in this example was prepared according to the following method.

Polyethylene-2,6-naphthalate polymer (100 parts by weight) and 2 parts by weight of Tinuvin P.326 (produced by Ciba Geigy AG) as an ultraviolet absorbent were dried, melted at 300°C, extruded from a T-die, longitudinally stretched at 140°C to 3.3 times, then transversely stretched at 130°C to 3.3 times and further heat set at 250°C for 6 seconds to obtain a PEN film having a thickness of 90 μm. To the resulting PEN film, a blue dye, a magenta dye and a yellow dye (Compounds I-1, I-4, I-6, I-24, I-26, I-27 and II-5 described in JIII Journal of Technical Disclosure, No. 94-6023) were added in an appropriate amount. Further, the film was wound around a stainless steel core having a diameter of 20 cm and heat history of 110°C for 48 hours was given to the film to obtain a support difficult of curling habit.

2) Coating of Undercoat layer

Both surfaces of the support obtained above was subjected to corona discharge treatment, UV discharge treatment and glow discharge treatment, and an undercoating solution containing 0.1 g/m^2 of gelatin, 0.01 g/m^2 of sodium α-sulfodi-2-ethylhexylsuccinate, 0.04 g/m^2 of salicylic acid, 0.2 g/m^2 of p-chlorophenol, 0.012 g/m^2 of $(CH_2{=}CHSO_2CH_2CH_2NHCO)_2CH_2$ and 0.02 g/m^2 of a polyamido-epichlorohydrin polycondensate was coated (10 ml/m^2, using a bar coater) on each surface to provide undercoat layers. The drying was conducted at 115°C for 6 minutes (rollers and the conveyance device in the drying zone all were heated to 115°C).

3) Coating of Back Layer

On one surface of the undercoated support, an antistatic layer, a magnetic recording layer and a slipping layer each having the following composition were coated as a back layer.

3-1) Coating of Antistatic Layer

A fine particle powder dispersion having a resistivity of 5 Ω • cm of a tin oxide-antimony oxide composite having an average particle diameter of 0.005 μm (secondary aggregate particle size: about 0.08 μm) was coated in an amount of 0.2 g/m^2 together with 0.05 g/m^2 of gelatin, 0.02 g/m^2 of $(CH_2{=}CHSO_2CH_2CH_2NHCO)_2CH_2$, 0.005 g/m^2 of poly(polymerization degree: 10)oxyethylene-p-nonylphenol and resorcin.

3-2) Coating of Magnetic Recording Layer

Co-γ-iron oxide (0.06 g/m^2) (specific surface area: 43 m^2/g; major axis: 0.14 μm; minor axis: 0.03 μm; saturated magnetization: 89 emu/g; Fe^{+2}/Fe^{+3}=6/94; the surface being treated with aluminum oxide and silicon oxide each in an amount of 2 wt% based on iron oxide) subjected to covering treatment with 3-poly(polymerization degree: 15)oxyethylene-propyloxytrimethoxysilane (15 wt%) and dispersed in 1.2 g/m^2 of diacetyl cellulose (the iron oxide being dispersed by an open kneader and sand mill) and 0.3 g/m^2 of $C_2H_5C(CH_2OCONH\text{-}C_6H_3(CH_3)NCO)_3$ as a hardening agent were coated using acetone, methyl ethyl ketone and cyclohexanone as solvents by means of a bar coater to obtain a magnetic recording layer having a thickness of 1.2 μm. Silica particles (0.3 μm) as a matting agent and an alumina oxide (0.15 μm) as an abrasive subjected to covering treatment with 3-poly(polymerization degree: 15)oxyethylene-propyloxytrimethoxysilane (15 wt%) each was added to give a coverage of 10 mg/m^2. The drying was conducted at 115°C for 6 minutes (rollers and the conveyance device in the drying zone all were heated to 115°C). Increase in the color density of D^B of the magnetic recording layer with X-Rite (blue filter) was about 0.1, the saturated magnetization moment of the magnetic recording layer was 4.2 emu/m^2, the coercive force was 7.3×10^4 A/m and the angular ratio was 65%.

3-3) Preparation of Slipping Layer

Diacetyl cellulose (25 mg/m^2) and a mixture of $C_6H_{13}CH(OH)C_{10}H_{20}COOC_{40}H_{81}$ (Compound a, 6 mg/m^2)/$C_{50}H_{101}O(CH_2CH_2O)_{16}H$ (Compound b, 9 mg/m^2) were coated. The mixture was prepared by melting the compounds in xylene/propylene monomethyl ether (1/1) at 105°C and pouring-dispersing the melt in propylene monomethyl ether (10-fold amount) at normal temperature. The resulting mixture was formed into a dispersion (average particle size: 0.01 μm) in acetone and then added. Silica particles (0.3 μm) as a matting agent and aluminum oxides (0.15 μm) as an abrasive covered with 3-poly(polymerization degree: 15)oxyethylenepropyloxytrimethoxysilane (15 wt%) each was added to give a coverage of 15 mg/m^2. The drying was conducted at 115°C for 6 minutes (rollers and the conveyance device in the drying zone all were heated to 115°C). The thus-provided slipping layer had excellent capabilities such that the coefficient of dynamic friction was 0.06 (stainless steel ball: 5 mm∅; load: 100 g; speed: 6 cm/min), the coefficient of static friction was 0.07 (by clip method) and the coefficient of dynamic friction between the emulsion surface and the slipping layer, which will be described later, was 0.12.

The thus-prepared Sample 102 was cut into a size of 24 mm (width) × 160 cm. At the portion 0.7 mm inside from one side width direction in the length direction of the light-sensitive material, two perforations of 2 mm square were provided at a distance of 5.8 mm. A pair of two perforations was provided at a distance of 32 mm. Then, the sample was housed in a plastic-made film cartridge described in Figs. 1 to 7 of U.S. Patent 5,296,887.

Sample 102 was wedgewise exposed, loaded in a camera equipped with a Permalloy-made magnetic recording device having a head gap of 5 μm and a turn number of 50, and subjected to digital saturation recording at a recording wavelength of 50 μm.

Sample 102 on which magnetic information was written as above was mixed with Sample 101 described in Example 1 and the light-sensitive materials were processed under the following conditions at a processing rate of 4 m^2 in total per day for 3 months. The processing amount of Sample 101 to Sample 102 was 5:2. The automatic processor used was FP-560B manufactured by Fuji Photo Film Co., Ltd. The automatic processor was modified so that the overflow solution of the bleaching bath did not flow into the post-bath but all was discharged to the waste water tank. On this FP-560B, an evaporation correcting means described in JIII Journal of Technical Disclosure, No. 94-4992 was mounted.

The processing steps and the composition of each processing solution are described below.

Processing Step

Step	Processing Time	Processing Temperature (°C)	Replenishing Amount* (ml/m^2)	Tank Volume (ℓ)
Color development	3 min 05 sec	37.8	400	17
Bleaching	50 sec	38.0	100	5
Fixing (1)	50 sec	38.0	-	5
Fixing (2)	50 sec	38.0	300	5
Water washing	30 sec	38.0	500	3.5
Stabilization (1)	20 sec	38.0	-	3
Stabilization (2)	20 sec	38.0	500	3
Drying	1 min 30 sec	60		

The stabilizing solution and the fixing solution each was in a countercurrent system of from (2) to (1) and the overflow solution of washing water was all introduced into the fixing bath (2). The carried-over amounts of color developer into the bleaching step, of bleaching solution into the fixing step, of fixing solution into the water washing step were 65 ml, 50 ml and 50 ml, respectively, per 1 m^2 of the 35 mm-width light-sensitive material. The cross-over time was 6 seconds in each interval and this time is included in the processing time of the previous step.

The open area of the above-described processor was 100 cm^2 for the color developer, 120 cm^2 for the bleaching solution and about 100 cm^2 for other processing solutions.

The composition of each processing solution is shown below.

Color Developer

	Tank Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	3.0	3.0
Disodium catechol-3,5-disulfonate	0.3	0.3
Sodium sulfite	3.9	5.3
Potassium carbonate	39.0	39.0
Disodium N,N,-bis(sulfonatoethyl)hydroxylamine	4.5	6.0
Potassium bromide	1.3	-
Potassium iodide	1.3 mg	-
4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene	0.05	-
2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline sulfate	4.5	6.5
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted by potassium hydroxide and sulfuric acid)	10.05	10.21

Bleaching Solution

	Tank Solution (g)	Replenisher (g)
Chelating agent for bleaching solution (shown in Table 4)	0.30 mol	0.40 mol
Iron(III) nitrate nonahydrate	0.30 mol	0.40 mol
Sodium bromide	70.0	105.0
Sodium 1,2-benzoisothiazolin-3-one	0.03	0.05
Compound (A-7) of the Invention	0.08 mol	0.13 mol
Succinic acid	20.0	30.0
Glycolic acid	60.0	90.0
Water to make	1,000 ml	1,000 ml
pH (adjusted by NaOH and nitric acid)	4.6	4.0

Fixing Solution

	Tank Solution (g)	Replenisher (g)
Aqueous solution of ammonium thiosulfate (750 g/ℓ)	240.0 ml	720.0 ml
Ammonium methanethiosulfonate	5.0	15.0
Ammonium methanesulfinate	10.0	30.0
Compound of the Invention (shown in Table 4)	0.07 mol	0.2 mol
Imidazole	7.0	20.0
Water to make	1,000 ml	1,000 ml
pH (adjusted by aqueous ammonia and acetic acid)	7.4	7.5

Washing Water

The tank solution and the replenisher were common.

Tap water was passed through a mixed bed column filled with an H-type strongly acidic cation exchange resin (Amberlite IR-120B, produced by Rhom and Haas) and an OH-type strongly basic anion exchange resin (Amberlite IRA-400, produced by the same company) to reduce the calcium and magnesium ion concentrations each to 3 mg/ℓ or less and then thereto 20 mg/ℓ of sodium isocyanurate dichloride and 150 mg/ℓ of sodium sulfate were added. The resulting solution had a pH of from 6.5 to 7.5.

Stabilizing Solution

The tank solution and the replenisher were common.

1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.4 g
1,2,4-Triazole	0.5 g
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10)	0.2 g
Sodium 1,2-benzoisothiazolin-3-one	0.10 g
Water to make	1.0 ℓ
pH (adjusted by aqueous ammonia and nitric acid)	8.5

After the processing, the sodium ion concentration of stabilizing solution (2) was measured and found to be 18 mg/ℓ.

After the processing under respective conditions, Sample 102 in the portion 150 m traced back from the processing end was measured on the output signal level of isolated frequency using a Sendust-made magnetic reproducing head having a head gap of 2.5 μm and a turn number of 2,000. The results obtained are shown in Table 4. The magnetic output results are shown in terms of the ratio of an average output in the final 1 m portion to the average output in the 1 m portion at the starting of measurement by the unit % taking the latter as 100.

TABLE 4

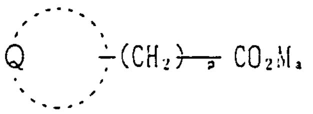
Bleaching Solution	Fixing Solution	Magnetic Output (%)	Remarks
1,3-PDTA	-	86	Comparison
"	A-6	93	Invention
"	A-7	96	"
"	B-5	94	"
I-7	-	78	Comparison
"	A-6	97	Invention
"	A-7	99	"
"	B-5	96	"
II-15	-	83	Comparison
"	A-6	95	Invention
"	A-7	96	"
"	B-5	94	"
1,3-PDTA: 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid			

As shown in Table 4, the present invention provided effective effect on the magnetic output.

According to the present invention, a processing composition and a processing method, improved in the stability of the processing solution having fixing ability and the photographic capabilities, can be provided and further, magnetic output of a light-sensitive material having a magnetic recording layer can be improved.

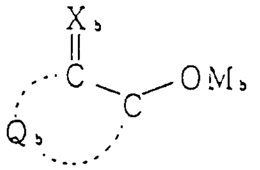
Claims

1. A method for processing a silver halide color light-sensitive material which comprises a support provided thereon at least one light-sensitive layer, comprising color development, desilvering and water washing and/or processing with a stabilizing solution, wherein a processing solution having fixing ability for use in said desilvering contains at least one compound represented by formula (A) or (B) and has a pH of from 6.1 to 8.0:



(A)

wherein Q represents a nonmetallic atom group necessary for forming a heterocyclic ring, p represents 0 or 1 and M_a represents a hydrogen atom or a cation;



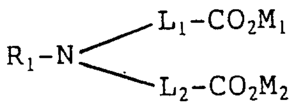
(B)

wherein Q_b represents a nonmetallic atom group necessary for forming a cyclic structure, X_b represents an oxygen atom, a sulfur atom or N-R_b, wherein R_b represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group, and M_b represents a hydrogen atom or a cation.

2. The method for processing a silver halide color light-sensitive material of claim 1, wherein the content of the compound represented by formula (A) or (B) is 0.001 to 0.3 mol per liter of the processing solution.

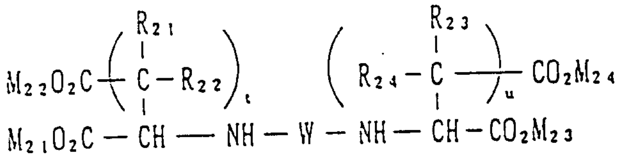
3. The method for processing a silver halide color light-sensitive material of claim 1, wherein the processing solution has a pH of 6.4 to 7.7.

4. The method for processing a silver halide color light-sensitive material of claim 1, wherein a processing solution having bleaching ability for use in said desilvering contains at least one iron(III) complex salt of a compound represented by formula (I) or (II) and has a pH of from 3 to 7:



(I)

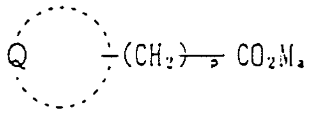
wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group, L_1 and L_2 each represents an alkylene group, and M_1 and M_2 each represents a hydrogen atom or a cation;



(II)

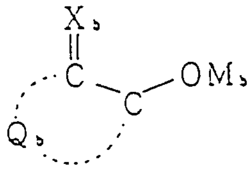
wherein R_{21}, R_{22}, R_{23} and R_{24} each represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, a hydroxy group or a carboxy group, t and u each represents 0 or 1, W represents a divalent linking group including carbon atom(s), and M_{21}, M_{22}, M_{23} and M_{24} each represents a hydrogen atom or a cation.

5. The method for processing a silver halide color light-sensitive material of claim 4, wherein said processing solution having bleaching ability contains a compound represented by formula (A) or (B):



(A)

wherein Q represents a nonmetallic atom group necessary for forming a heterocyclic ring, p represents 0 or 1 and M_a represents a hydrogen or a cation;



(B)

wherein Q_b represents a nonmetallic atom group necessary for forming a cyclic structure, X_b represents an oxygen atom, a sulfur atom or N-R_b, wherein R_b represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group, and M_b represents a hydrogen atom or a cation.

6. The method for processing a silver halide color light-sensitive material of claim 1, wherein said silver halide color light-sensitive material has a magnetic recording layer containing magnetic particles on the opposite side to the side of the support having the light-sensitive layer.

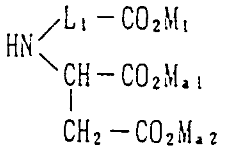
7. The method for processing a silver halide color light-sensitive material of claim 4, wherein the processing solution having bleaching ability is a bleaching solution and the processing solution having fixing ability is a fixing solution.

8. The method for processing a silver halide color light-sensitive material of claim 7, wherein the bleaching solution contains an iron(III) complex salt of the compound represented by formula (I) or (II) and the compound represented by formula (A) or (B), and the fixing solution contains the compound represented by formula (A) or (B).

9. The method for processing a silver halide color light-sensitive material of claim 8, wherein the bleaching solution contains an iron(III) complex salt of the compound represented by formula (I) and the compound represented by formula (A), and the fixing solution contains the compound represented by formula (A).

10. The method for processing a silver halide color light-sensitive material of claim 8, wherein the bleaching solution contains an iron(III) complex salt of the compound represented by formula (I) and the compound represented by formula (A), and the fixing solution contains the compound represented by formula (B).

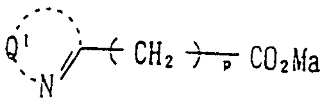
11. The method for processing a silver halide color light-sensitive material of claim 4, wherein the compound represented by formula (I) is one represented by formula (I-a):



(I-a)

wherein L_1 represents an alkylene group and M_1, M_{a1} and M_{a2} each represents a hydrogen atom or a cation.

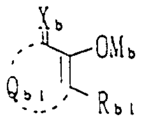
12. The method for processing a silver halide color light-sensitive material of claim 1, wherein the compound represented by formula (A) is one represented by formula (A-a):



(A-a)

wherein Q^1 represents a nonmetallic atom group necessary for forming a nitrogen-containing heterocyclic ring; p represents 0 or 1; and M_a represents a hydrogen atom or a cation.

13. The method for processing a silver halide color light-sensitive material of claim 1, wherein the compound represented by formula (B) is one represented by formula (B-a):



(B-a)

wherein Q_{b1} represents a nonmetallic atom group necessary for forming a ring structure; X_b represents an oxygen atom, a sulfur atom or N-R_b where R_b represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group; M_b represents a hydrogen atom or a cation; and R_{b1} represents a hydrogen atom, a carboxy group, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 3549

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.6)
X Y	EP-A-0 657 777 (FUJI) * page 3, line 3 - line 16 * * page 9, line 16 - page 12, line 19 * * page 13, line 10 - line 14 * * page 14, line 1 - page 15, line 42 * * page 44, line 54 * * page 45, line 13 * ---	1-5,11, 12 6-10,13	G03C7/42
D,Y	JP-A-51 007 930 (KONISHIROKU) * abstract * * page 2, left-hand column, line 21 - line 30 * * page 2, right-hand column, line 25 - line 40 * ---	7-9	
Y	EP-A-0 595 102 (FUJI) * page 2, line 49 - line 53 * * page 6, line 1 - page 10, line 51 * * page 33, line 47 - line 52 * * page 53, line 55 * * page 54, line 8 * ---	6	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
Y	EP-A-0 426 193 (FUJI) * page 3, line 54 - page 4, line 6 * * page 21, line 25 - line 50 * * page 83, line 13 * * page 83, line 28 * ---	10,13	
Y	BE-A-665 814 (DU PONT) * page 4, line 21 - page 7, line 3 * --- -/--	10,13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 November 1996	Magrizos, S

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EUROPEAN SEARCH REPORT

Application Number
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP-A-0 695 969 (FUJI) * page 2, line 47 - line 56 * * page 13, line 1 - page 20, line 54 * * page 24, line 1 - page 29, line 28 * * page 37, line 51 - line 53 * * page 69, line 19 * * page 69, line 34 * -----	1-6,11, 12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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