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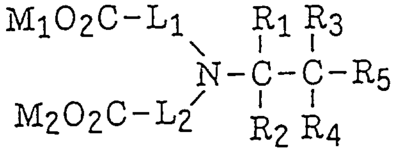
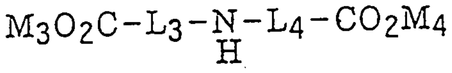
(54) Method for processing silver halide color photographic material

(57) A method for processing a silver halide color photographic material is disclosed, which comprises processing an imagewise exposed silver halide color photographic material with a processing solution having bleaching ability after color development, wherein said processing solution having bleaching ability contains at least one ferric complex salt of the compound represented by the following formula (I) or (II) and persulfate:



$$\begin{array}{l} M_1O_2C-L_1 \diagdown \quad \overset{R_1}{\underset{R_2}{|}} \; \overset{R_3}{\underset{R_4}{|}} \\ \qquad\qquad\quad N-C-C-R_5 \\ M_2O_2C-L_2 \diagup \end{array} \qquad (I)$$

wherein R_1, R_2, R_3, R_4 and R_5 each represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, a carboxyl group, a phosphono group, a hydroxy group or a sulfo group, provided that at least one of R_1, R_2, R_3, R_4 and R_5 represents a carboxyl group, a phosphono group, an aliphatic group substituted with a sulfo group or a carboxyl group, an aryl group substituted with a sulfo group or a carboxyl group or a heterocyclic group substituted with a sulfo group or a carboxyl group; L_1 and L_2 each represents a divalent aliphatic group, a divalent aromatic group or a divalent linking group containing these groups; and M_1 and M_2 each represents a hydrogen atom or a cation;



$$M_3O_2C-L_3-\underset{H}{N}-L_4-CO_2M_4 \qquad (II)$$

wherein L_3 and L_4 each represents a divalent aliphatic group, a divalent aromatic group or a divalent group containing these groups; and M_3 and M_4 each represents a hydrogen atom or a cation.

The method is excellent in biodegradability and bleaching ability.

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Description

FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic material excellent in rapid processing and the environmental protection. Particularly, a method for processing a silver halide color photographic material which is excellent in biodegradability and bleaching ability.

BACKGROUND OF THE INVENTION

In general, a silver halide black-and-white photographic material is subjected to, after exposure, processing steps such as black-and-white development, fixation, and washing, and a silver halide color photographic material (hereinafter referred to "a color photographic material") is subjected to, after exposure, color development, desilvering, washing, and stabilization. A silver halide color reversal photographic material is subjected to, after exposure, black-and-white development and reversal processing, then processed by color development, desilvering, washing and stabilization processing steps.

In a color development step, a sensitized silver halide grain is reduced by a color developing agent to be silver, and simultaneously the oxidized product of the color developing agent reacts with a coupler to form an image dye.

In the subsequent desilvering step, the developed silver produced in the development step is oxidized by a bleaching agent having an oxidizing action (an oxidizing agent) to be silver salt (bleaching), and, further, removed from the light-sensitive layer with the remaining silver halide by a fixing agent which acts to form soluble silver (fixation). Bleaching and fixation can be carried out independently as a bleaching step and a fixing step, respectively, or can be carried out simultaneously as a bleach-fixing step. The details about these processing steps and the constitution are disclosed in James, The Theory of Photographic Process, 4th Edition (1977), Research Disclosure, No. 17643, pp. 28 and 29, ibid., No. 18716, p. 651, from the left column to the right column, and ibid., No. 307105, pp. 880 and 881.

In addition to the above fundamental processing steps, various auxiliary steps can be used for maintaining photographic and physical qualities of color images or for maintaining processing safety, for example, a washing step, a stabilizing step, a hardening step and a stopping step.

The oxidizing agents for the processing solution which are used in the above bleach processing or reduction processing are usually ethylenediaminetetraacetic acid ferric complex salts or 1,3-diaminopropanetetraacetic acid ferric complex salts. 1,3-Diaminopropanetetraacetic acid ferric complex salts have been used in recent years as a bleaching agent for rapid bleaching for responding to rapid processing services for customers by a small size automatic processor called mini-labo. However, they have a fatal drawback such that they are hardly biodegraded. Harmless waste solutions generated from photographic processing have recently been desired from the viewpoint of the environmental protection and substitutions for the above bleaching agent which is hardly biodegradable have been studied.

Further, the lowering of the concentration of the metal chelating compounds used as a bleaching agent is also desired from the environmental protection.

As a means for solving the above problem, there are disclosed in EP 602,600A2 bleaching solutions containing persulfate and a picolinic acid or a 2,6-pyridinecarboxylic acid which are biodegradable compounds and a ferric ion. However, when such bleaching solutions as disclosed in the above patent are used, problems arise such that stain (Dmin) becomes large and the color densities of the color images formed by processing with a color developing solution are reduced by processing with the bleaching solution, and it is necessary to carry out stopping-washing process sufficiently after color development, therefore, the total processing time is prolonged.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a method for processing a silver halide color photographic material which causes no environmental problems concerning the waste solution.

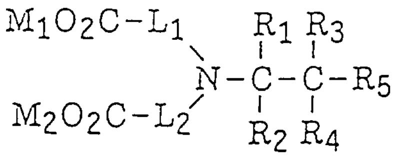
Another object of the present invention is to provide a method for processing a silver halide color photographic material using the processing solution having the bleaching ability which is preferably used from the viewpoint of the biodegradability and the environmental protection.

A further object of the present invention is to provide a method for processing a silver halide color photographic material using the processing solution having bleaching ability, which is excellent in desilvering even when iron concentration is low.

A still further object of the present invention is to provide a method for processing a silver halide color photographic material which causes less stain.

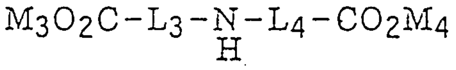
The above objects of the present invention have been attained by the following methods, that is:

(1) A method for processing a silver halide color photographic material which comprises processing an imagewise exposed silver halide color photographic material with the processing solution having the bleaching ability after color development, wherein said processing solution having bleaching ability contains at least one ferric complex salt of the compound represented by the following formula (I) or (II) and persulfate:



(I)

wherein R_1, R_2, R_3, R_4 and R_5 each represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, a carboxyl group, a phosphono group, a hydroxy group or a sulfo group, provided that at least one of R_1, R_2, R_3, R_4 and R_5 represents a carboxyl group, a phosphono group, an aliphatic group substituted with a sulfo group or a carboxyl group, an aryl group substituted with a sulfo group or a carboxyl group or a heterocyclic group substituted with a sulfo group or a carboxyl group; L_1 and L_2 each represents a divalent aliphatic group, a divalent aromatic group or a divalent linking group containing the aliphatic group and the aromatic group; and M_1 and M_2 each represents a hydrogen atom or a cation.

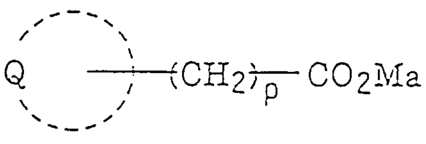


$$M_3O_2C-L_3-\underset{H}{N}-L_4-CO_2M_4 \qquad \text{(II)}$$

wherein L_3 and L_4 each represents a divalent aliphatic group, a divalent aromatic group or a divalent group containing the aliphatic group and the aromatic group; and M_3 and M_4 each represents a hydrogen atom or a cation.

(2) A method for processing a silver halide color photographic material as described in (1), wherein said processing solution having the bleaching ability contains at least one heterocyclic compound having a carboxyl group or the salt thereof in the molecule.

(3) A method for processing a silver halide color photographic material as described in (2), wherein said heterocyclic compound containing a carboxyl group or the salt thereof in the molecule is represented by the following formula (III):



(III)

wherein Q represents a non-metal atomic group necessary for forming a heterocyclic ring; p represents 0 or 1; and Ma represents a hydrogen atom or a cation.

(4) A method for processing a silver halide color photographic material as described in (1), (2) or (3), wherein said processing solution having the bleaching ability contains at least one hydrocarbon organic acid having two or more carboxyl groups.

DETAILED DESCRIPTION OF THE INVENTION

The compounds represented by formula (I) are described in detail below.

The aliphatic group represented by R_1, R_2, R_3, R_4 and R_5 is a straight chain, branched or cyclic alkyl group (preferably having from 1 to 6 carbon atoms), an alkenyl group (preferably having from 2 to 6 carbon atoms), or an alkynyl group (preferably having from 2 to 6 carbon atoms), and preferably an alkyl group. Examples of the aliphatic group include a methyl group, an ethyl group, a cyclohexyl group, a benzyl group or an allyl group. The aliphatic group may have a substituent, and examples of the substituents include, for example, an alkyl group (e.g., methyl, ethyl), an aralkyl group (e.g., phenylmethyl), an alkenyl group (e.g., allyl), an alkynyl group, an alkoxy group (e.g., methoxy, ethoxy), an aryl group (e.g., phenyl, p-methylphenyl), an acylamino group (e.g., acetylamino), a sulfonylamino group (e.g., methanesulfonylamino), a ureido group, an alkoxycarbonylamino group (e.g., methoxycarbonylamino), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino), an aryloxy group (e.g., phenoxy), a sulfamoyl group (e.g., methylsulfamoyl), a carbamoyl group (e.g., carbamoyl, methylcarbamoyl), an alkylthio group (e.g., methylthio, carboxymethylthio), an arylthio group (e.g., phenylthio), a sulfonyl group (e.g., methanesulfonyl), a sulfinyl group (e.g., methanesulfinyl), a hydroxyl group, a halogen atom (e.g., chlorine, bromine, fluorine), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (e.g., phenyloxycarbonyl), an acyl group (e.g., acetyl, benzoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), an acyloxy group (e.g., acetoxy), a nitro group, a hydroxamic acid group, a mercapto group, and a heterocyclic group (e.g., imidazolyl, pyridyl).

The aryl group represented by R_1, R_2, R_3, R_4 and R_5 may be monocyclic or bicyclic, and the carbon atom number is preferably from 6 to 20, for example, a phenyl group and a naphthyl group. The aryl group may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the aliphatic group represented by R_1 to R_5.

The heterocyclic group represented by R_1, R_2, R_3, R_4 and R_5 is a 3- to 10-membered heterocyclic group containing at least one of a nitrogen atom, an oxygen atom or a sulfur atom, which may be saturated or unsaturated, may be monocyclic, and may further form a condensed ring with other aromatic ring or a heterocyclic ring. A 5- or 6-membered unsaturated heterocyclic group is preferred as the heterocyclic ring, and more preferably a 5- or 6-membered aromatic heterocyclic group the hetero atom of which is a nitrogen atom. Preferred examples of the heterocyclic rings are pyridine, pyrazine, pyrimidine, pyridazine, thiophene, pyrrole, imidazole, pyrazole, thiazole, oxazole, and indole, and more preferably pyridine, imidazole, and indole.

At least one of R_1, R_2, R_3, R_4 and R_5 represents a carboxyl group, a phosphono group, an aliphatic group substituted with a sulfo group or a carboxyl group, an aryl group substituted with a sulfo group or a carboxyl group or a heterocyclic group substituted with a sulfo group or a carboxyl group.

R_1, R_2, R_3, R_4 and R_5 preferably represent a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, a phenyl group, a phenylmethyl group, a carboxyl group, a hydroxyl group, a carboxymethyl group, or a hydroxymethyl group, and more preferably there are cases (1) R_1, R_2, R_3 and R_5 each represents a hydrogen atom and R_4 represents a carboxyl group, (2) R_1, R_2 and R_3 each represents a hydrogen atom, R_4 represents a carboxyl group, and R_5 represents a phenyl group, (3) R_1, R_2 and R_3 each represents a hydrogen atom, R_4 represents a carboxyl group, and R_5 represents a phenylmethyl group, (4) R_1, R_3 and R_5 each represents a hydrogen atom, R_2 represents a phenyl group, and R_4 represents a carboxyl group, and (5) R_1, R_3 and R_5 each represents a hydrogen atom, R_2 represents a phenylmethyl group, and R_4 represents a carboxyl group.

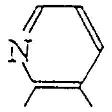
The divalent aliphatic group represented by L_1 and L_2 includes a straight chain, branched or cyclic alkylene (preferably having from 1 to 6 carbon atoms), alkenylene (preferably having from 2 to 6 carbon atoms), and alkynylene (preferably having from 2 to 6 carbon atoms) group. The divalent aliphatic group represented by L_1 and L_2 may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the aliphatic group represented by R_1 to R_5. Specific preferable examples of the aliphatic groups represented by L_1 and L_2 include a methylene group, an ethylene group, a 1-carboxymethylene group, a 1-carboxyethylene group, a 2-hydroxyethylene group, a 2-hydroxypropylene group, a 1-phosphonomethylene group, a 1-phenylmethylene group, and a 1-carboxybutylene group.

The divalent aromatic group represented by L_1 and L_2 include a divalent aromatic hydrocarbon group (arylene) and a divalent aromatic heterocyclic group.

The divalent aromatic hydrocarbon group (arylene) may be a monocyclic or bicyclic, and the carbon atom number is preferably from 6 to 20, for example, a phenylene group and a naphthylene group.

The divalent aromatic heterocyclic group is a 3- to 10-membered heterocyclic group containing at least one of a nitrogen atom, an oxygen atom or a sulfur atom, and may further form a condensed ring with other aromatic ring or a heterocyclic ring. The divalent aromatic heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic group the hetero atom of which is a nitrogen atom.

Examples of the divalent aromatic heterocyclic groups include, for example, the following.



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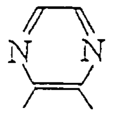

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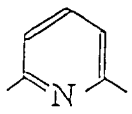

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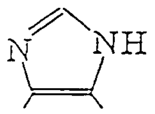

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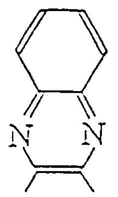
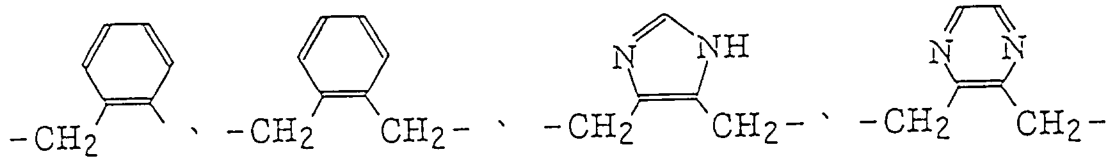


An arylene group (preferably having from 6 to 20 carbon atoms) is preferred as the divalent aromatic group, more preferably a phenylene group or a naphthylene group, and particularly preferably a phenylene group.

The divalent aromatic group represented by L_1 and L_2 may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the aliphatic group represented by R_1 to R_5.

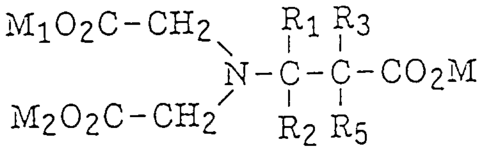
L_1 and L_2 may be a group combining the divalent aliphatic group and the divalent aromatic group, for example, the following can be cited as such examples.



L_1 and L_2 preferably represent an alkylene group having from 1 to 8 carbon atoms which may be substituted, or an o-phenylene group, more preferably a methylene or ethylene group which may be substituted, and particularly preferably a methylene group which may be substituted.

The cation represented by M_1 and M_2 is an organic or inorganic cation, for example, ammonium (e.g., ammonium, tetraethylammonium), pyridinium, or an alkali metal (e.g., lithium, sodium, potassium).

The compound represented by formula (I) is preferably represented by the following formula (IV):



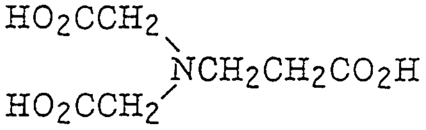
$$\begin{matrix} M_1O_2C-CH_2 \\ M_2O_2C-CH_2 \end{matrix} \Big> N-\overset{R_1}{\underset{R_2}{C}}-\overset{R_3}{\underset{R_5}{C}}-CO_2M \qquad (IV)$$

wherein M_1 and M_2 have the same meaning as M_1 and M_2 in formula (I); R_1, R_2, R_3 and R_5 each represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, a carboxyl group, a phosphono group, a hydroxyl group or a sulfo group; M has the same meaning as M_1 in formula (I).

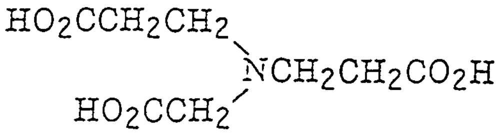
As R_1, R_2, R_3 and R_5, preferably (1) all of R_1, R_2, R_3 and R_5 represent hydrogen atoms, (2) R_1, R_2, R_3 each represents a hydrogen atom and R_5 represents a phenyl group, (3) R_1, R_2, R_3 each represents a hydrogen atom and R_5 represents a phenylmethyl group, (4) R_1, R_3, R_5 each represents a hydrogen atom and R_2 represents a phenyl group, or (4) R_1, R_3, R_5 each represents a hydrogen atom and R_2 represents a phenylmethyl group.

Specific examples of the compounds represented by formula (I) are shown below, but the present invention is not limited thereto.

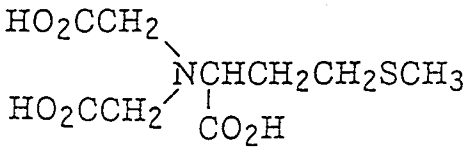
I-1



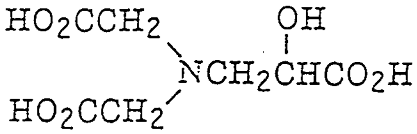
I-2



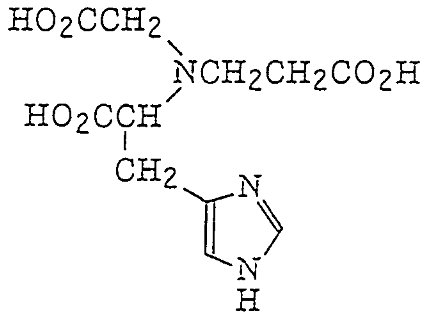
I-3



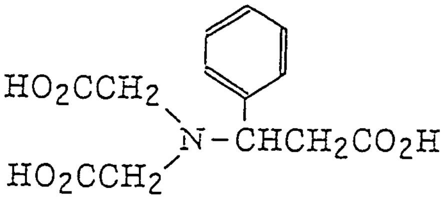
I-4



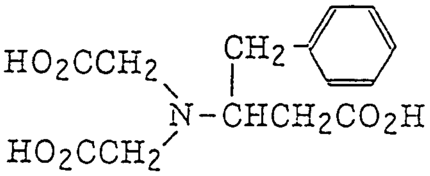
I-5



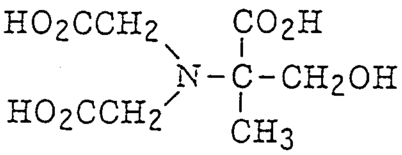
I-6



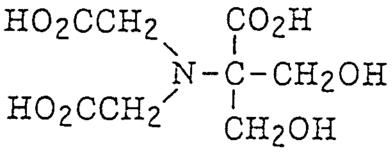
I-7



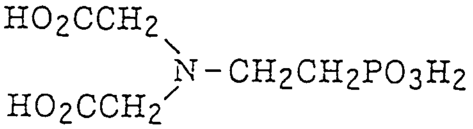
I-8



I-9



I-10



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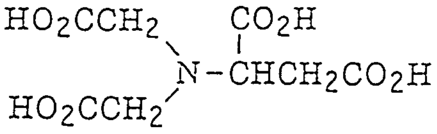

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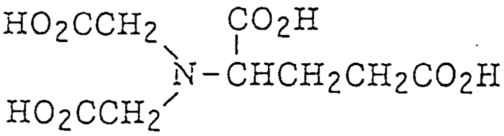

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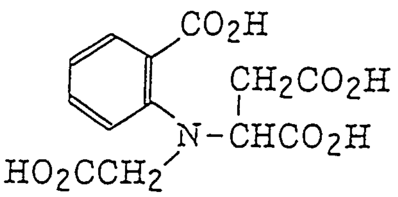

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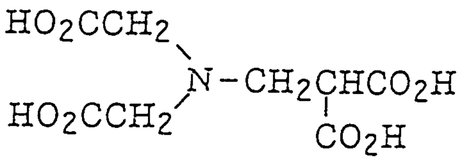
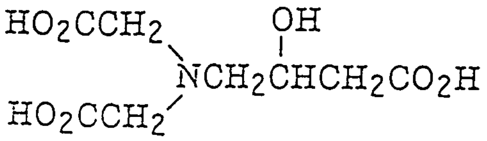
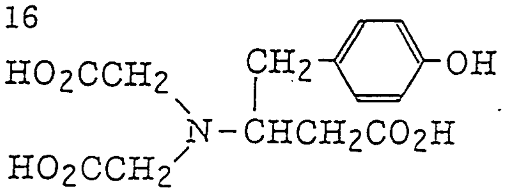


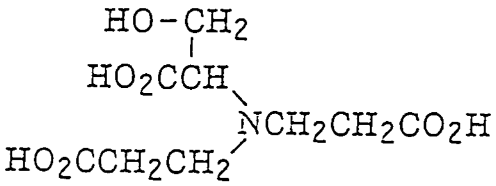
I-15



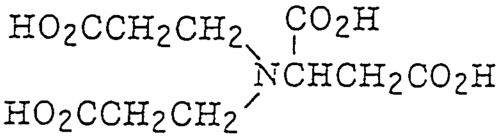
I-16



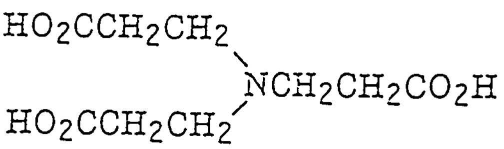
I-17



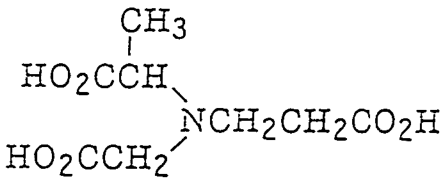
I-18



I-19



I-20



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

The above compounds represented by formula (I) can be synthesized according to the methods disclosed in JP-A-63-267750, JP-A-63-267751, JP-A-2-115172 and JP-A-2-295954 (the term "JP-A" as used herein means a "published unexamined Japanese patent application").

The compounds represented by formula (II) are described in detail below.

The divalent aliphatic group represented by L_3 and L_4 includes a straight chain, branched or cyclic alkylene group (preferably having from 1 to 6 carbon atoms), alkenylene group (preferably having from 2 to 6 carbon atoms), and alkynylene group (preferably having from 2 to 6 carbon atoms). The divalent aliphatic group represented by L_3 and L_4 may have a substituent, and examples of the substituents include, for example, an alkyl group (e.g., methyl, ethyl), an aralkyl group (e.g., phenylmethyl), an alkenyl group (e.g., allyl), an alkynyl group, an alkoxy group (e.g., methoxy, ethoxy), an aryl group (e.g., phenyl, p-methylphenyl), an acylamino group (e.g., acetylamino), a sulfonylamino group (e.g., methanesulfonylamino), a ureido group, an alkoxycarbonylamino group (e.g., methoxycarbonylamino), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino), an aryloxy group (e.g., phenyloxy), a sulfamoyl group (e.g., methylsulfamoyl), a carbamoyl group (e.g., carbamoyl, methylcarbamoyl), an alkylthio group (e.g., methylthio, carboxymethylthio), an arylthio group (e.g., phenylthio), a sulfonyl group (e.g., methanesulfonyl), a sulfinyl group (e.g., methanesulfinyl), a hydroxyl group, a halogen atom (e.g., chlorine, bromine, fluorine), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (e.g., phenyloxycarbonyl), an acyl group (e.g., acetyl, benzoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), an acyloxy group (e.g., acetoxy), a nitro group, a hydroxamic acid group, and a heterocyclic group (e.g., imidazolyl, pyridyl).

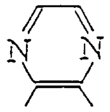
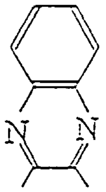
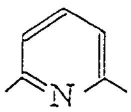
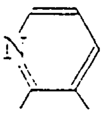
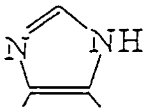
Specific examples of the aliphatic groups represented by L_3 and L_4 include a methylene group, an ethylene group, a 1-carboxymethylene group, a 1-carboxyethylene group, a 2-hydroxyethylene group, a 2-hydroxypropylene group, a 1-phosphonomethylene group, a 1-phenylmethylene group, and a 1-carboxybutylene group.

The divalent aromatic group represented by L_3 and L_4 include a divalent aromatic hydrocarbon group (arylene) and a divalent aromatic heterocyclic group.

The divalent aromatic hydrocarbon group (arylene) may be a monocyclic or bicyclic, and the carbon atom number is preferably from 6 to 20, for example, a phenylene group and a naphthylene group.

The divalent aromatic heterocyclic group is a 3- to 10-membered heterocyclic group containing at least one of a nitrogen atom, an oxygen atom or a sulfur atom, and may further form a condensed ring with other aromatic ring or a heterocyclic ring. The divalent aromatic heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic group the hetero atom of which is a nitrogen atom.

Examples of the divalent aromatic heterocyclic groups include, for example, the following.

 ,  ,  ,  , 

An arylene group (preferably having from 6 to 20 carbon atoms) is preferred as the divalent aromatic group, more preferably a phenylene group or a naphthylene group, and particularly preferably a phenylene group.

The divalent aromatic group represented by L_3 and L_4 may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the divalent aliphatic group represented by L_3 and L_4.

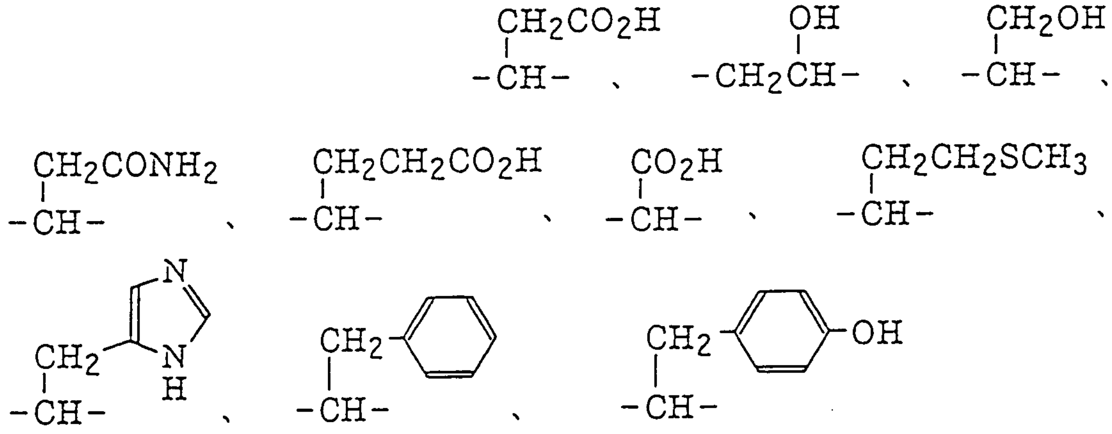
L_3 and L_4 may be a group combining the divalent aliphatic group and the divalent aromatic group, or may be combinations of -O-, -S-, -COO-, -N(R_0)-, -CO-N(R_0)- (R_0 represents a hydrogen atom, a hydroxyl group, an alkyl or aryl group which may be substituted) or -$SO_2N(R_{00})$- (R_{00} represents a hydrogen atom, an alkyl or aryl group which may be substituted) and a divalent aliphatic group or a divalent aromatic group. The substituents for the alkyl group and the aryl group represented by R_0 and R_{00} include, for example, the groups cited as substituents for the divalent aliphatic group represented by L_3 and L_4.

L_3 and L_4 are preferably represented by the following formula (L):

$$-La-(A)_n-(Lb)_m-(B)_p-(Lc)_q-^{*} \qquad \text{(L)}$$

wherein La, Lb and Lc each represents an alkylene group or an arylene group; A and B each represents -O-, -S-, -COO-, -N(R_{01})-, -CO-N(R_{02})- or -$SO_2N(R_{03})$- (R_{01}, R_{02} and R_{03} each represents a hydrogen atom, a hydroxyl group, or an alkyl or aryl group which may be substituted); m, n, p and q each represents 0 or 1; and * represents the connecting position with -$COOM_3$ or -$COOM_4$. The substituents for the alkyl group and the aryl group represented by R_{01}, R_{02} and R_{03} include, for example, the groups cited as substituents for the divalent aliphatic group represented by L_3 and L_4.

Preferred specific examples of L_3 and L_4 are shown below.
$-CH_2-$ 、 $-CH_2CH_2-$ 、



$\underset{-CH-}{\overset{CH_2CO_2H}{|}}$ 、 $\underset{-CH_2CH-}{\overset{OH}{|}}$ 、 $\underset{-CH-}{\overset{CH_2OH}{|}}$ 、

$\underset{-CH-}{\overset{CH_2CONH_2}{|}}$ 、 $\underset{-CH-}{\overset{CH_2CH_2CO_2H}{|}}$ 、 $\underset{-CH-}{\overset{CO_2H}{|}}$ 、 $\underset{-CH-}{\overset{CH_2CH_2SCH_3}{|}}$ 、

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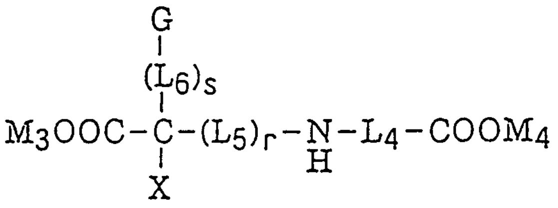
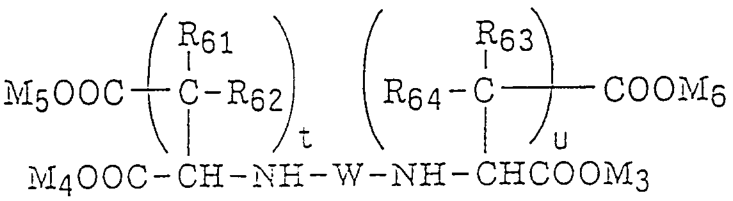
The cation represented by M_3 and M_4 is an organic or inorganic cation, for example, ammonium (e.g., ammonium, tetraethylammonium), pyridinium, or an alkali metal (e.g., lithium, sodium, potassium).

The compound represented by formula (II) is preferably represented by the following formula (V) or (VI):



$$M_3OOC-\underset{X}{\underset{|}{\overset{\overset{G}{|}}{\overset{(L_6)_s}{\overset{|}{C}}}}}-(L_5)_r-\underset{H}{N}-L_4-COOM_4 \qquad (V)$$

wherein L_4, M_3 and M_4 each has the same meaning as L_4, M_3 and M_4 in formula (II); L_5 and L_6 each represents a divalent aliphatic group, a divalent aromatic group or a divalent linking group combining these groups; r and s each represents 0 or 1; G represents a carboxyl group, a phosphono group, a sulfo group, a hydroxyl group, a mercapto group, an aryl group, a heterocyclic group, an alkylthio group, an amidino group, a guanidino group or a carbamoyl group; and X represents a hydrogen atom, an aliphatic group or an aromatic group.

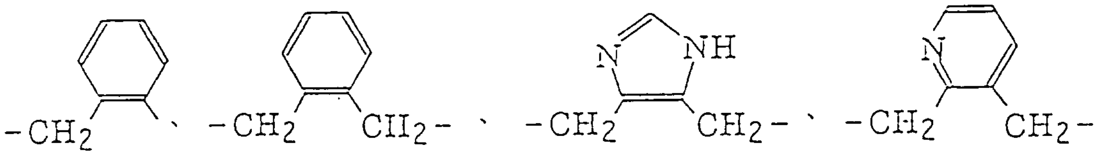


$$\begin{array}{c} M_5OOC\left(\overset{R_{61}}{\overset{|}{C}}-R_{62}\right)_t \qquad \left(R_{64}-\overset{R_{63}}{\overset{|}{C}}\right)_u COOM_6 \\ | \qquad\qquad\qquad\qquad | \\ M_4OOC-CH-NH-W-NH-CHCOOM_3 \end{array} \qquad (VI)$$

wherein M_3 and M_4 each has the same meaning as M_3 and M_4 in formula (II); M_5 and M_6 each represents a hydrogen atom or a cation; R_{61}, R_{62}, R_{63} and R_{64} each represents a hydrogen atom, a hydroxyl group, a carboxyl group, an aliphatic group or an aromatic group; t and u each represents 0 or 1; and W represents a divalent linking group containing a carbon atom.

Formula (V) is described in detail below.

The divalent aliphatic group and the divalent aromatic group represented by L_5 and L_6 have the same meaning as L_3 and L_4 in formula (II). L_5 and L_6 may be a group combining the divalent aliphatic group and the divalent aromatic group, for example, the following can be cited as such examples.



L_5 and L_6 preferably represents an alkylene group having from 1 to 3 carbon atoms or an o-phenylene group which may be substituted, and particularly preferably a methylene or ethylene group which may be substituted.

r and s each represents 0 or 1. r preferably represents 0 and s preferably represents 1.

The aryl group represented by G (an aromatic hydrocarbon group) may be a monocyclic or bicyclic, and the carbon atom number is preferably from 6 to 20, for example, a phenyl group and a naphthyl group. The aryl group may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the divalent aliphatic group represented by L_3 and L_4.

The heterocyclic group represented by G is a 3- to 10-membered heterocyclic group containing at least one of a nitrogen atom, an oxygen atom or a sulfur atom, which may be saturated or unsaturated, may be monocyclic ring or a condensed ring which may be formed by condensing the monocyclic ring with other aromatic ring or a heterocyclic ring. The preferred heterocyclic group preferably includes 5- or 6-membered unsaturated heterocyclic group, and more preferably 5- or 6-membered aromatic heterocyclic group the hetero atom of which is a nitrogen atom. Preferred examples of the heterocyclic rings are pyridine, pyrazine, pyrimidine, pyridazine, thiophene, pyrrole, imidazole, pyrazole, thiazole, and indole, and more preferably pyridine, imidazole and indole.

The alkylthio group represented by G is represented by -SRs (Rs represents an alkyl group). The alkyl group represented by Rs may be a straight chain, branched or cyclic alkyl group preferably having from 1 to 6 carbon atoms, particularly preferably a straight chain alkyl group having from 1 to 4 carbon atoms. The alkyl group represented by Rs may have a substituent, and examples of the substituents include, for example, the same groups enumerated as the substituents for the divalent aliphatic group represented by L_3 and L_4. Specific examples of the alkylthio group represented by G include, for example, a methylthio group, an ethylthio group, a hydroxyethylthio group, and a carboxymethylthio group, preferably a methylthio group and an ethylthio group.

The carbamoyl group represented by G may be substituted and can be prepresented by $-CONR_{a1}(R_{a2})$. R_{a1} and R_{a2} each represents a hydrogen atom, an alkyl or aryl group which may be substituted. The alkyl group represented by R_{a1} and R_{a2} is a straight chain, branched or cyclic alkyl group preferably having from 1 to 10 carbon atoms. The aryl group represented by R_{a1} and R_{a2} has preferably from 6 to 10 carbon atoms, more preferably a phenyl group. R_{a1} and R_{a2} may be linked to form a ring. R_{a1} and R_{a2} particularly preferably represent a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms which may be substituted, or an aryl group which may be substituted. As the substituents for the alky group and the aryl group represented by R_{a1} and R_{a2}, for example, the same groups enumerated as the substituents for the divalent aliphatic group represented by L_3 and L_4 can be applied. Specific examples of the carbamoyl group represented by G include, for example, a carbamoyl group, an N-methylcarbamoyl group, an N-phenylcarbamoyl group and a morpholinocarbamoyl group.

The aliphatic group represented by X is a straight chain, branched or cyclic alkyl group (preferably having from 1 to 6 carbon atoms), an alkenyl group (preferably having from 2 to 6 carbon atoms), or an alkynyl group (preferably having from 2 to 6 carbon atoms), preferably an alkyl group, for example, a methyl group, an ethyl group or a benzyl group. The aromatic group represented by X is an aromatic hydrocarbon group (aryl) or an aromatic heterocyclic group, for example, a phenyl group, a naphthyl group, a 2-pyridyl group, or a 2-pyrrole group, preferably an aryl group, and more preferably a phenyl group.

X preferably represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, more preferably a hydrogen atom.

Formula (VI) is described in detail below.

The aliphatic group and the aromatic group represented by R_{61}, R_{62}, R_{63} and R_{64} have the same meaning as the aliphatic group and the aromatic group in formula (V).

R_{61}, R_{62}, R_{63} and R_{64} preferably each represents a hydrogen atom or a hydroxyl group, more preferably a hydrogen atom.

t and u each represents 0 or 1.

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

$$-(W^1-D)_v-(W^2)_w- \qquad (W)$$

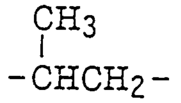
wherein W^1 and W^2 may be the same or different and each represents a straight chain or branched alkylene group having from 2 to 8 total carbon atoms which may be substituted (e.g., ethylene, trimethylene), a cycloalkylene group having from 5 to 10 total carbon atoms which may be substituted (e.g., 1,2-cyclohexylene), an arylene group having from 6 to 10 total carbon atoms which may be substituted (e.g., o-phenylene), an aralkylene group having from 7 to 10 total carbon atoms which may be substituted (e.g., o-xylenyl), 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 the hetero atom of which is a nitrogen atom, or a heterocyclic group in which W^1 and W^2 are linked to adjacent carbon atoms such as an imidazolyl group. D represents -O-, -S-, or $-N(R_w)-$. R_w represents a hydrogen atom or an alkyl group having from 1 to 8 total carbon atoms, e.g., methyl group, which may be substituted with a carboxyl group, a phosphono group, a hydroxyl group or a sulfo group, or an aryl group having from 6 to 10 total carbon atoms, e.g., phenyl group, which may be substituted with groups disclosed above.

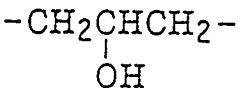
W^1 and W^2 preferably represent an alkylene group having from 2 to 4 total carbon atoms which may be substituted.

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

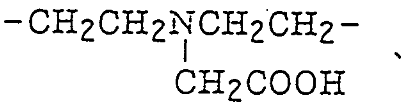
Examples of W are shown below.

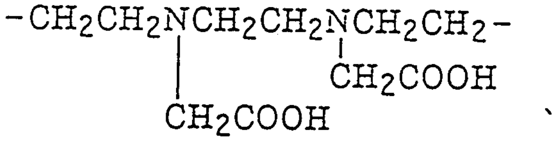
$(CH_2)_2$ 、 $(CH_2)_3$ 、 $(CH_2)_4$ 、

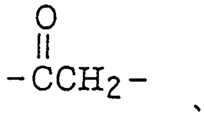

$-\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2-$ 、

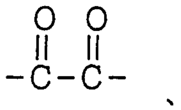

$-CH_2\underset{\underset{OH}{|}}{C}HCH_2-$ 、

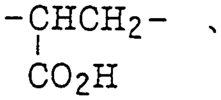
$-CH_2CH_2CH_2OCH_2CH_2-$ 、 $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ 、 $-CH_2CH_2SCH_2CH_2-$ 、
$-CH_2CH_2SCH_2CH_2SCH_2CH_2-$ 、

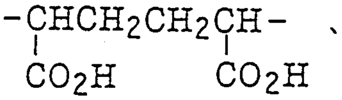

$-CH_2CH_2\underset{\underset{CH_2COOH}{|}}{N}CH_2CH_2-$ 、


$-CH_2CH_2\underset{\underset{CH_2COOH}{|}}{N}CH_2CH_2\underset{\underset{CH_2COOH}{|}}{N}CH_2CH_2-$ 、


$-\overset{\overset{O}{\|}}{C}CH_2-$ 、


$-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ 、


$-\underset{\underset{CO_2H}{|}}{C}HCH_2-$ 、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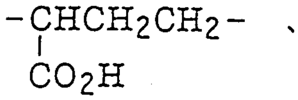
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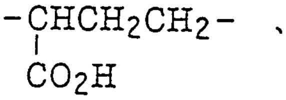
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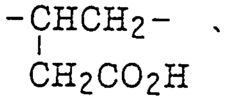
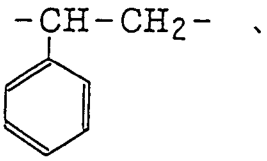

$-\underset{\underset{CH_2CO_2H}{|}}{C}HCH_2-$ 、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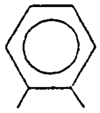
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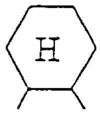
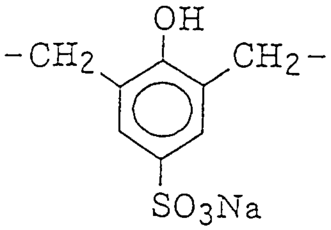
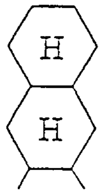
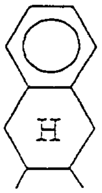

H
,

OH
-CH2
CH2-
SO3Na
,


H
H
,

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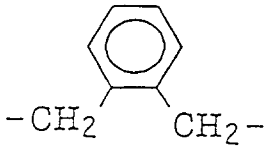
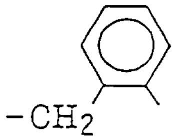
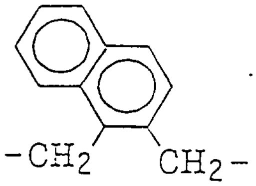
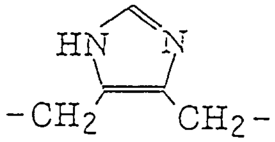

-CH2
CH2-
,


-CH2
,

-CH2
CH2-
,

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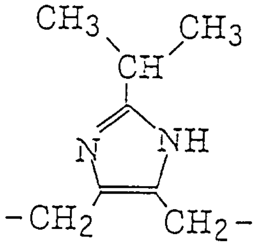
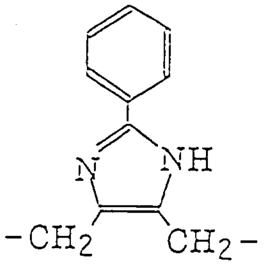
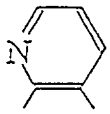
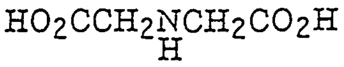
N
-CH2
CH2-
,


CH3
CH3
CH
N
NH
-CH2
CH2-
,

N
NH
-CH2
CH2-
,

N
,

$-CH_2-CH=CH-CH_2-$

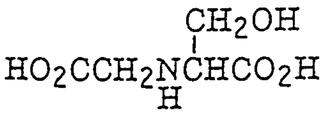
Specific examples of the compounds represented by formula (II) are shown below, but the present invention is not limited thereto.

II-1.



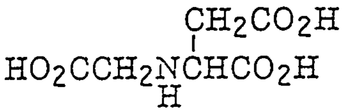
$\mathrm{HO_2CCH_2\underset{H}{N}CH_2CO_2H}$

II-2.



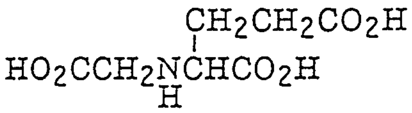
$\mathrm{HO_2CCH_2\underset{H}{N}\overset{CH_2OH}{C}HCO_2H}$

II-3.



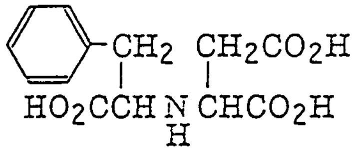
$\mathrm{HO_2CCH_2\underset{H}{N}\overset{CH_2CO_2H}{C}HCO_2H}$

II-4.

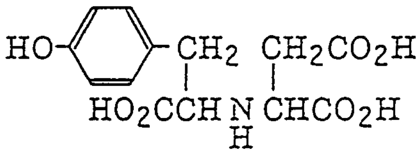


$\mathrm{HO_2CCH_2\underset{H}{N}\overset{CH_2CH_2CO_2H}{C}HCO_2H}$

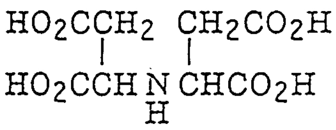
II-5.



II-6.

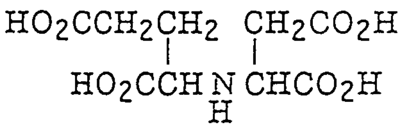


II-7.



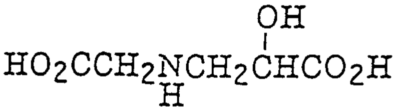
$\mathrm{HO_2C\overset{HO_2CCH_2}{C}H\,\underset{H}{N}\,\overset{CH_2CO_2H}{C}HCO_2H}$

II-8.



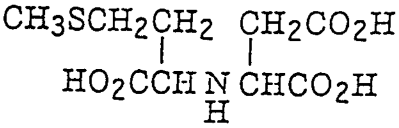
$\mathrm{HO_2C\overset{HO_2CCH_2CH_2}{C}H\,\underset{H}{N}\,\overset{CH_2CO_2H}{C}HCO_2H}$

II-9.



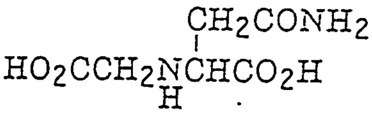
$HO_2CCH_2NHCH_2CH(OH)CO_2H$

II-10.



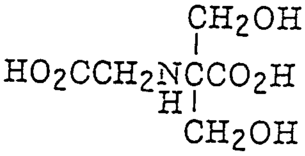
$HO_2CCH(CH_2CH_2SCH_3)NHCH(CH_2CO_2H)CO_2H$

II-11.



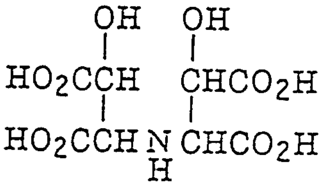
$HO_2CCH_2NHCH(CH_2CONH_2)CO_2H$

II-12.



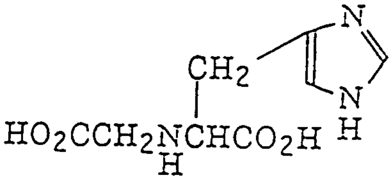
$HO_2CCH_2NHC(CH_2OH)_2CO_2H$

II-13.

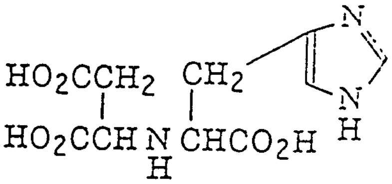


$HO_2CCH(OH)CH(CO_2H)NHCH(CO_2H)CH(OH)CO_2H$

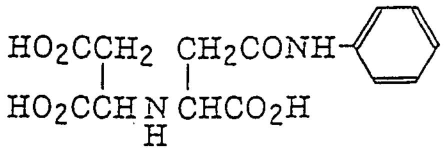
II-14.



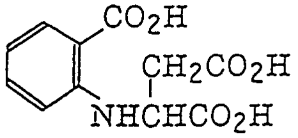
II-15.



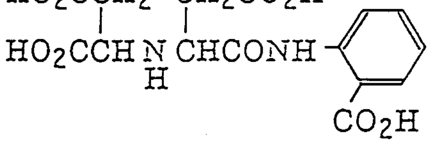
II-16.



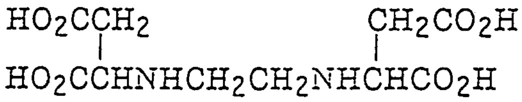
II-17.



II-18.

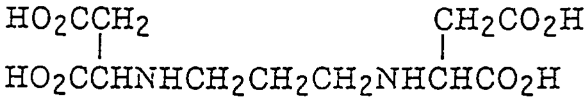


II-19.



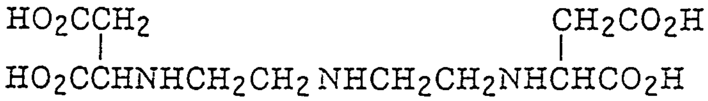
$HO_2CCH(CH_2CO_2H)NHCH_2CH_2NHCH(CH_2CO_2H)CO_2H$

II-20.



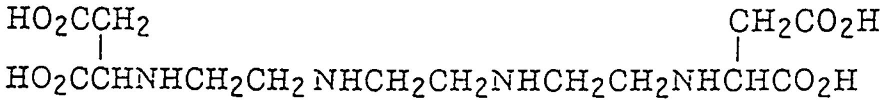
$HO_2CCH(CH_2CO_2H)NHCH_2CH_2CH_2NHCH(CH_2CO_2H)CO_2H$

II-21.



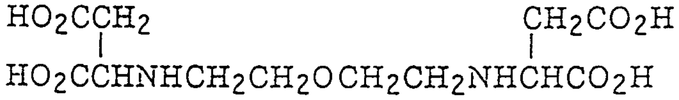
$HO_2CCH(CH_2CO_2H)NHCH_2CH_2NHCH_2CH_2NHCH(CH_2CO_2H)CO_2H$

II-22.



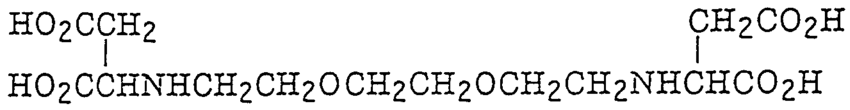
$HO_2CCH(CH_2CO_2H)NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH(CH_2CO_2H)CO_2H$

II-23.



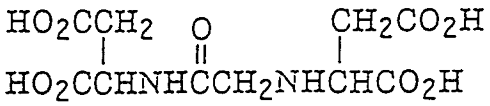
$HO_2CCH(CH_2CO_2H)NHCH_2CH_2OCH_2CH_2NHCH(CH_2CO_2H)CO_2H$

II-24.



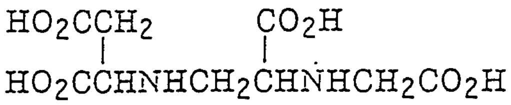
$$\mathrm{HO_2C\overset{\substack{HO_2CCH_2\\|}}{C}HNHCH_2CH_2OCH_2CH_2OCH_2CH_2NH\overset{\substack{CH_2CO_2H\\|}}{C}HCO_2H}$$

II-25.



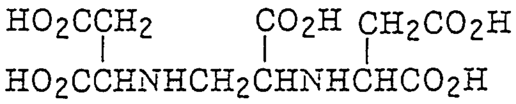
$$\mathrm{HO_2C\overset{\substack{HO_2CCH_2\\|}}{C}HNH\overset{\substack{O\\\|}}{C}CH_2NH\overset{\substack{CH_2CO_2H\\|}}{C}HCO_2H}$$

II-26.



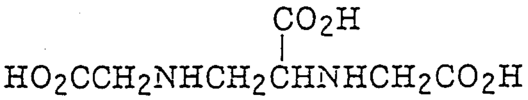
$$\mathrm{HO_2C\overset{\substack{HO_2CCH_2\\|}}{C}HNHCH_2\overset{\substack{CO_2H\\|}}{C}HNHCH_2CO_2H}$$

II-27.



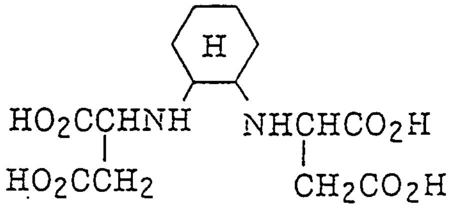
$$\mathrm{HO_2C\overset{\substack{HO_2CCH_2\\|}}{C}HNHCH_2\overset{\substack{CO_2H\\|}}{C}HNH\overset{\substack{CH_2CO_2H\\|}}{C}HCO_2H}$$

II-28.

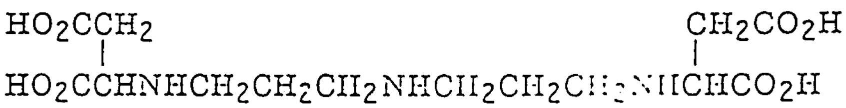


$$\mathrm{HO_2CCH_2NHCH_2\overset{\substack{CO_2H\\|}}{C}HNHCH_2CO_2H}$$

II-29.

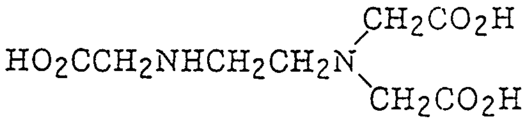


II-30.

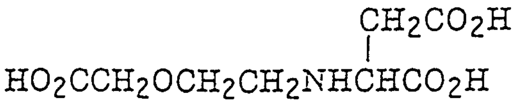


$$\mathrm{HO_2C\overset{\substack{HO_2CCH_2\\|}}{C}HNHCH_2CH_2CH_2NHCH_2CH_2CH_2NH\overset{\substack{CH_2CO_2H\\|}}{C}HCO_2H}$$

II-31.

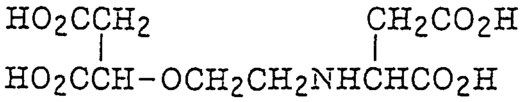


II-32.



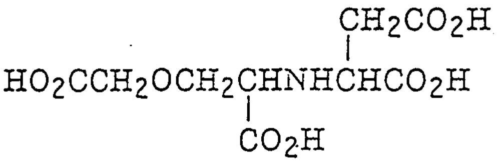
$$\mathrm{HO_2CCH_2OCH_2CH_2NH\overset{\overset{CH_2CO_2H}{|}}{C}HCO_2H}$$

II-33.



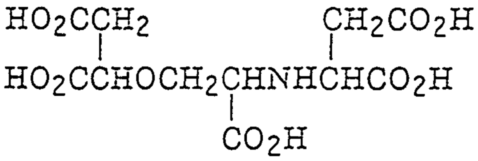
$$\mathrm{HO_2C\overset{\overset{HO_2CCH_2}{|}}{C}H-OCH_2CH_2NH\overset{\overset{CH_2CO_2H}{|}}{C}HCO_2H}$$

II-34.



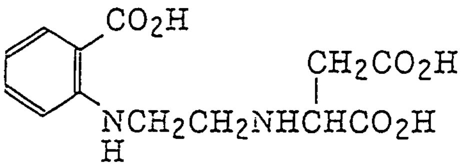
$$\mathrm{HO_2CCH_2OCH_2\underset{\underset{CO_2H}{|}}{C}HNH\overset{\overset{CH_2CO_2H}{|}}{C}HCO_2H}$$

II-35.

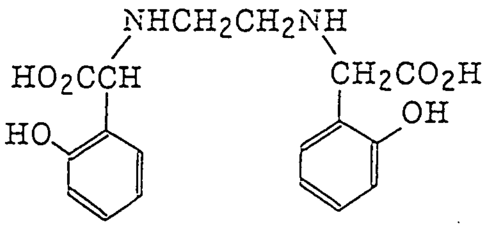


$$\mathrm{HO_2C\overset{\overset{HO_2CCH_2}{|}}{C}HOCH_2\underset{\underset{CO_2H}{|}}{C}HNH\overset{\overset{CH_2CO_2H}{|}}{C}HCO_2H}$$

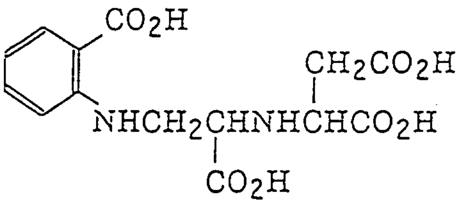
II-36.



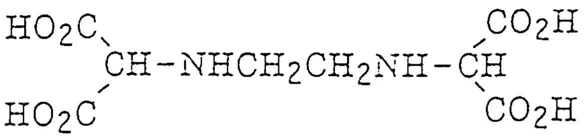
II-37.



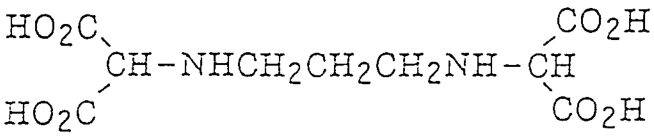
II-38.



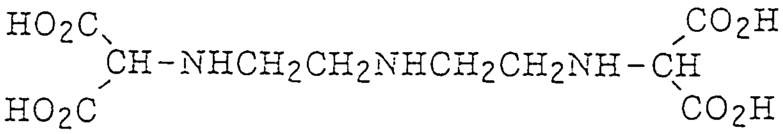
II-39.



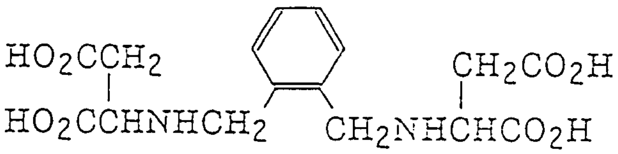
II-40.



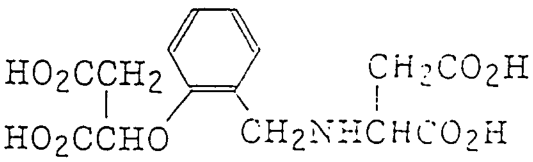
II-41.



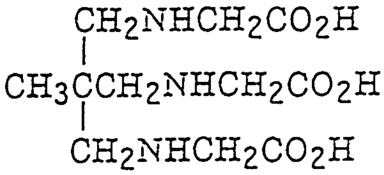
II-42.



II-43.

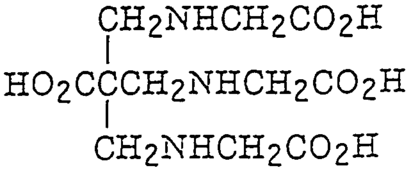


II-44.



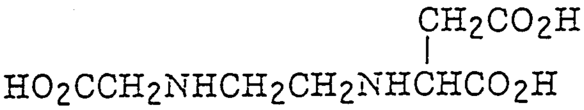
$$\mathrm{CH_3\underset{\underset{CH_2NHCH_2CO_2H}{|}}{\overset{\overset{CH_2NHCH_2CO_2H}{|}}{C}}CH_2NHCH_2CO_2H}$$

II-45.



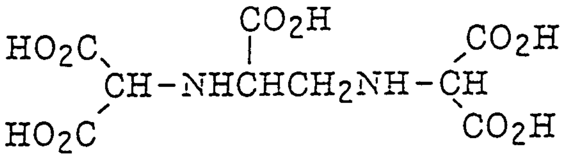
$$\mathrm{HO_2C\underset{\underset{CH_2NHCH_2CO_2H}{|}}{\overset{\overset{CH_2NHCH_2CO_2H}{|}}{C}}CH_2NHCH_2CO_2H}$$

II-46.

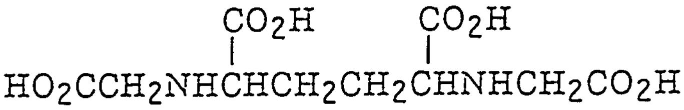


$$\mathrm{HO_2CCH_2NHCH_2CH_2NH\overset{\overset{CH_2CO_2H}{|}}{C}HCO_2H}$$

II-47.

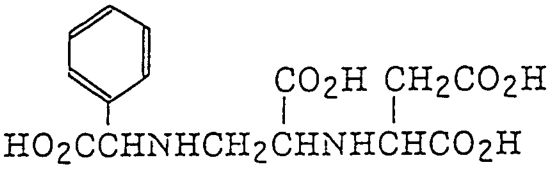


II-48.

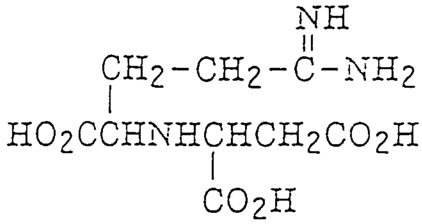


$$\mathrm{HO_2CCH_2NH\overset{\overset{CO_2H}{|}}{C}HCH_2CH_2\overset{\overset{CO_2H}{|}}{C}HNHCH_2CO_2H}$$

II-49.

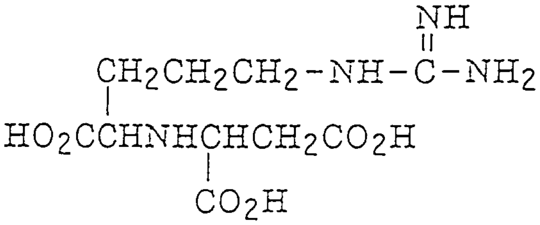


II-50.



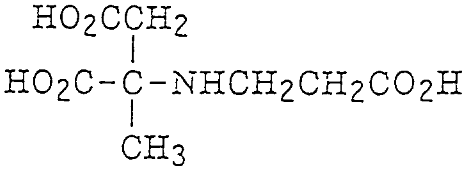
$HO_2CCH(CH_2-CH_2-C(=NH)-NH_2)NHCH(CO_2H)CH_2CO_2H$

II-51.



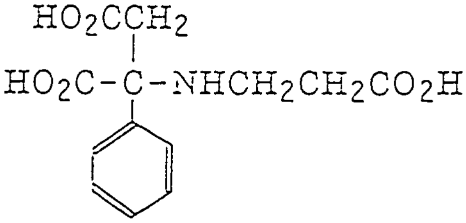
$HO_2CCH(CH_2CH_2CH_2-NH-C(=NH)-NH_2)NHCH(CO_2H)CH_2CO_2H$

II-52.



$HO_2C-C(CH_2CO_2H)(CH_3)-NHCH_2CH_2CO_2H$

II-53.



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

The compounds represented by the above formula (II) can be synthesized according to the methods disclosed in Journal of Inorganic and Nuclear Chemistry, Vol. 35, pp. 523 to 535 (1973), Swiss Patent 561,504, JP-A-63-199295, JP-A-3-173857, JP-A-6-161065, Zh. Neorg., Vol. 25 (6), pp. 1692 to 1694 (1980), and Bull. Soc. Chim. France, Vol. 11, pp. 2778 to 2782 (1964).

The ferric complex salt of the compound represented by formula (I) or (II) of the present invention may be used as the isolated metal chelate compound, or the compound represented by formula (I) or (II) may be used by reacting with iron salt (for example, ferric sulfate, ferric chloride, ferric nitrate, ferric phosphate) in the solution. Similarly, the ammonium salt or the alkali metal salt of the compound represented by formula (I) or (II) (e.g., a lithium salt, a sodium salt, a potassium salt) may be used by reacting with the salt of the above metal in the solution.

Of the ferric complex salts of the compounds represented by formula (I) or (II), preferred are the ferric complex salts of the compounds represented by formula (II).

The compound represented by formula (I) or (II) is used in the mol ratio of 1.0 or more to the iron ion. This mol ratio is preferably larger when the stability of the metal chelate compound is low, usually the mol ratio is from 1 to 30.

The ferric complex salt of the compound represented by formula (I) or (II) of the present invention (hereinafter sometimes referred to as "the ferric complex salt of the present invention") is preferably contained in an amount of from 0.001 to 1 mol, more preferably from 0.005 to 0.3 mol, and particularly preferably from 0.01 to 0.1 mol, per liter of the processing solution having bleaching ability (the bleaching solution or the bleach-fixing solution).

Further, the persulfate for use in the present invention is preferably used in an amount of from 0.001 to 2.0 mol, more preferably from 0.01 to 1.0 mol, and still more preferably from 0.05 to 0.50 mol, per liter of the processing solution having bleaching ability.

A lithium salt, a sodium salt, a potassium salt, an ammonium salt or a tertiary ammonium salt can be used as persulfate, and preferably a sodium salt.

It is preferred for the processing solution having the bleaching ability of the present invention to contain at least one heterocyclic compound having a carboxyl group or the salt thereof in the molecule.

The heterocyclic compound having a carboxyl group or the salt thereof in the molecule of the present invention is described in detail below.

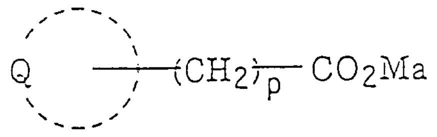
The heterocyclic group is a 3- to 10-membered saturated or unsaturated heterocyclic group containing at least one of a nitrogen atom, an oxygen atom or a sulfur atom, which may be monocyclic, and may further form a condensed ring with other ring.

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, and still more preferably a 5- or 6-membered aromatic heterocyclic group containing one or two nitrogen atoms.

Specific examples of the heterocyclic groups include, for example, pyrrolidine, piperidine, piperazine, morpholine, thiophene, furan, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyridazine, triazole, triazine, indole, indazole, purine, thiadiazole, oxadiazole, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, acridine, phenanthroline, phenazine, tetrazole, thiazole, and oxazole. The preferred of these are pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyridazine, triazole, triazine, indole, indazole, thiadiazole, oxadiazole, quinoline, phthalazine, quinoxaline, quinazoline, cinnoline, tetrazole, thiazole, and oxazole, and more preferably imidazole, pyrazole, pyridine, pyrazine, indole, indazole, thiadiazole, oxadiazole, quinoline, thiazole, and oxazole, still more preferably imidazole, pyridine, and quinoline, and particularly preferably imidazole and pyridine.

The heterocyclic group may have a substituent, and examples of the substituents include, for example, an alkyl group which preferably has from 1 to 12 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 3 carbon atoms, e.g., methyl, ethyl; an aralkyl group which preferably has from 7 to 20 carbon atoms, more preferably from 7 to 15 carbon atoms, and particularly preferably from 7 to 11 carbon atoms, e.g., phenylmethyl, phenylethyl; an alkenyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., allyl; an alkynyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., propargyl; an aryl group which preferably has from 6 to 20 carbon atoms, more preferably from 6 to 15 carbon atoms, and particularly preferably from 6 to 10 carbon atoms, e.g., phenyl, p-methylphenyl; an amino group which preferably has from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms, and particularly preferably from 0 to 6 carbon atoms, e.g., amino, methylamino, dimethylamino, diethylamino; an alkoxy group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy; an aryloxy group which preferably has from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, and particularly preferably from 6 to 8 carbon atoms, e.g., phenyloxy; an acyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., acetyl; an alkoxycarbonyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., methoxycarbonyl; an acyloxy group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., acetoxy; an acylamino group which preferably has from 2 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., acetylamino; a sulfonylamino group which preferably has from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino; a sulfamoyl group which preferably has from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, and particularly preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl; a carbamoyl group which preferably has from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl; an alkylthio group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio, an arylthio group which preferably has from 6 to 20 carbon atoms, more preferably from 6 to 10 carbon atoms, and particularly preferably from 6 to 8 carbon atoms, e.g., phenylthio; a sulfonyl group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl; a sulfinyl group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl; a ureido group; a hydroxyl group; a halogen atom (e.g., fluorine, chlorine, bromine, 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 further be substituted. When there are two or more substituents, they may be the same or different. Preferred substituents include an alkyl group, an amino group, an alkoxyl group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, and a mercapto group, more preferably an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxyl group, and a halogen atom, still more preferably an amino group, a carboxyl group, and a hydroxyl group, and particularly preferably a carboxyl group.

The heterocyclic compound having a carboxyl group or the salt thereof in the molecule is preferably represented by the following formula (III):



(III)

wherein Q represents a non-metal atomic group necessary for forming a heterocyclic ring; p represents 0 or 1; and Ma represents a hydrogen atom or a cation.

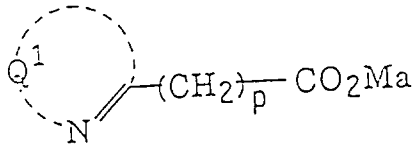
The heterocyclic ring formed by Q has the same meaning as the heterocyclic ring described above.

The preferred substituents for the heterocyclic ring formed by Q include an alkyl group having from 1 to 12 total carbon atoms, an amino group having from 0 to 20 total carbon atoms, an alkoxyl group having from 1 to 8 total carbon atoms, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, and a mercapto group, more preferably an amino group having from 0 to 10 total carbon atoms, a carboxyl group, a hydroxyl group, and a mercapto group, and particularly preferably a carboxyl group.

p represents 0 or 1, preferably 0.

The cation represented by Ma is an organic or inorganic cation, for example, an alkali metal ion (e.g., L_i^+, Na^+, K^+, Cs^+), an alkaline earth metal ion (e.g., Ca^{2+}, Mg^{2+}), ammonium (e.g., ammonium, tetraethylammonium), pyridinium, and phosphonium (e.g., tetrabutylphosphonium, tetraphenylphosphonium).

The compound represented by formula (III) is preferably represented by the following formula (III-a):



(III-a)

wherein p and Ma have the same meaning as those in formula (III); Q^1 represents a non-metal atomic group necessary for forming a nitrogen-containing heterocyclic ring.

The nitrogen-containing heterocyclic group represented by Q^1 is a 3- to 10-membered saturated or unsaturated heterocyclic group containing at least one nitrogen atom, which may be monocyclic, and may further form a condensed ring with other ring.

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

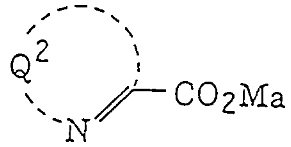
Specific examples of the nitrogen-containing heterocyclic group include, for example, pyrrolidine, piperidine, piperazine, morpholine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyridazine, triazole, triazine, indole, indazole, purine, thiadiazole, oxadiazole, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, acridine, phenanthroline, phenazine, tetrazole, thiazole, and oxazole. The preferred of these are pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyridazine, triazole, triazine, indole, indazole, thiadiazole, oxadiazole, quinoline, phthalazine, quinoxaline, quinazoline, cinnoline, tetrazole, thiazole, and oxazole, more preferably imidazole, pyrazole, pyridine, pyrazine, indole, indazole, thiadiazole, oxadiazole, quinoline, thiazole, and oxazole, still more preferably imidazole, pyridine, and quinoline, and particularly preferably imidazole and pyridine.

The nitrogen-containing heterocyclic group may have a substituent, and examples of the substituents include, for example, an alkyl group which preferably has from 1 to 12 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 3 carbon atoms, e.g., methyl, ethyl; an aralkyl group which preferably has from 7 to 20 carbon atoms, more preferably from 7 to 15 carbon atoms, and particularly preferably from 7 to 11 carbon atoms, e.g., phenylmethyl, phenylethyl; an alkenyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., allyl; an alkynyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., propargyl; an aryl group which preferably has from 6 to 20 carbon atoms, more preferably from 6 to 15 carbon atoms, and particularly preferably from 6 to 10 carbon atoms, e.g., phenyl, p-methylphenyl; an amino group which preferably has from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms, and particularly preferably from

0 to 6 carbon atoms, e.g., amino, methylamino, dimethylamino, diethylamino; an alkoxy group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy; an aryloxy group which preferably has from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, and particularly preferably from 6 to 8 carbon atoms, e.g., phenyloxy; an acyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., acetyl; an alkoxycarbonyl group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., methoxycarbonyl; an acyloxy group which preferably has from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, and particularly preferably from 2 to 8 carbon atoms, e.g., acetoxy; an acylamino group which preferably has from 2 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, and particularly preferably from 2 to 4 carbon atoms, e.g., acetylamino; a sulfonylamino group which preferably has from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino; a sulfamoyl group which preferably has from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, and particularly preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl; a carbamoyl group which preferably has from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl; an alkylthio group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio; an arylthio group which preferably has from 6 to 20 carbon atoms, more preferably from 6 to 10 carbon atoms, and particularly preferably from 6 to 8 carbon atoms, e.g., phenylthio; a sulfonyl group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl; a sulfinyl group which preferably has from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, and particularly preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl; a ureido group; a hydroxyl group; a halogen atom (e.g., fluorine, chlorine, bromine, 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 further be substituted. When there are two or more substituents, they may be the same or different. Preferred substituents include an alkyl group, an amino group, an alkoxyl group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, and a mercapto group, more preferably an alkyl group, an amino group, an alkoxyl group, a carboxyl group, a hydroxyl group, and a halogen atom, still more preferably an amino group, a carboxyl group, and a hydroxyl group, and particularly preferably a carboxyl group.

p and Ma have the same meaning as those in formula (III), and preferred range is also the same.

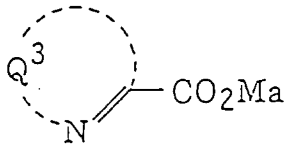
The compound represented by formula (III-a) is preferably represented by the following formula (III-b):



(III-b)

wherein Ma has the same meaning as Ma in formula (III); Q^2 represents a nitrogen-containing heterocyclic group and which may be substituted with an alkyl group, an amino group, an alkoxyl group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, or a mercapto group.

The compound represented by formula (III-b) is preferably represented by the following formula (III-c):

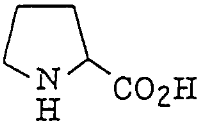


(III-c)

wherein Ma has the same meaning as Ma in formula (III); Q^3 represents an atomic group necessary for forming a pyridine ring or an imidazole ring, and which may be substituted with an alkyl group, an amino group, an alkoxyl group, a carboxyl group, a hydroxyl group, a halogen atom, a cyano group, a nitro group, or a mercapto group.

Specific examples of the compounds represented by formula (III) are shown below, but the present invention is not limited thereto.

1.



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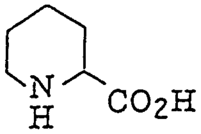

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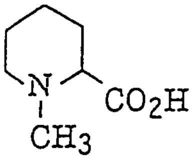

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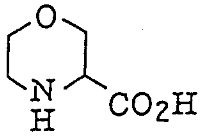

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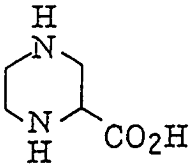

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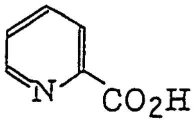

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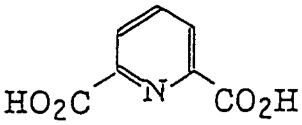

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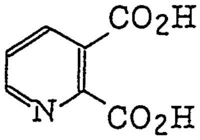

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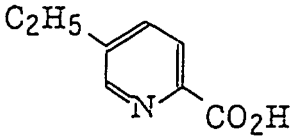

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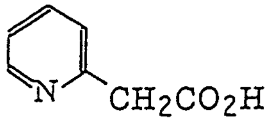

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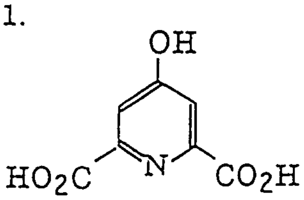

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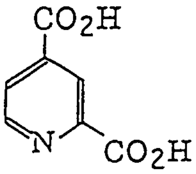

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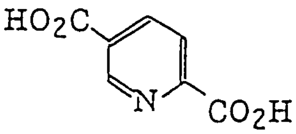

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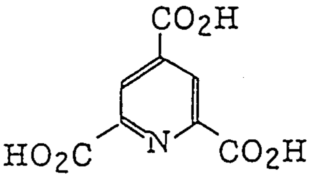

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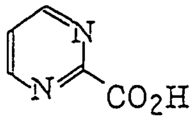

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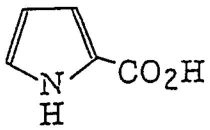

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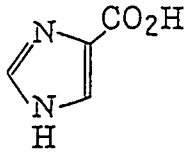

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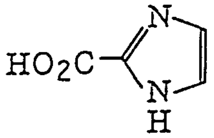

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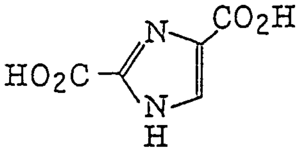

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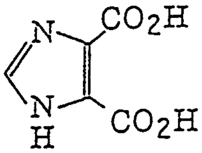

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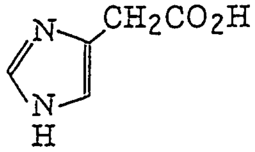

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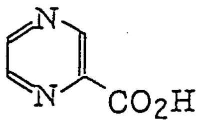

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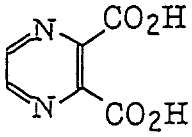

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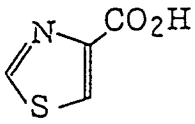

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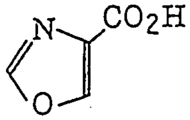

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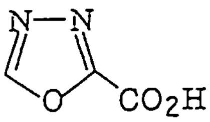

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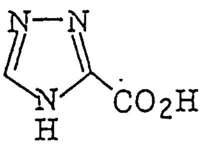

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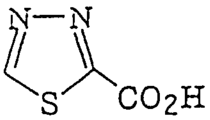

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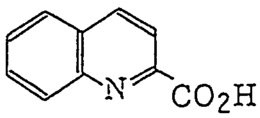

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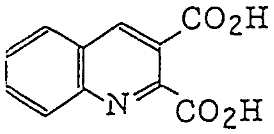

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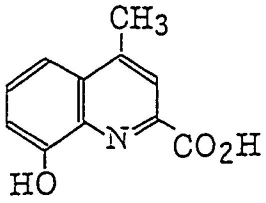

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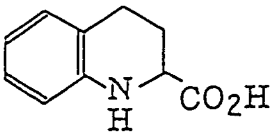

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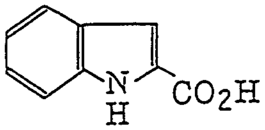

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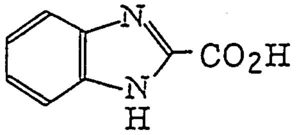

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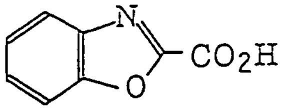

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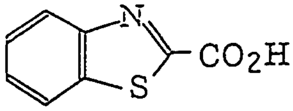

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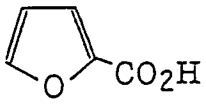

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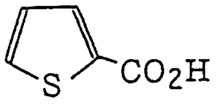

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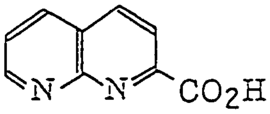

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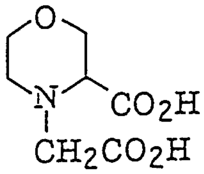

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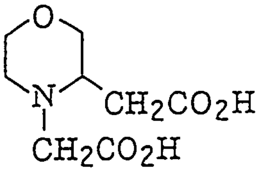

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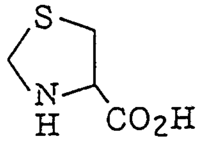

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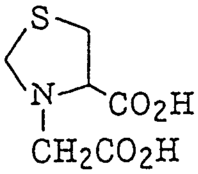

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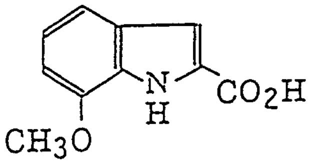

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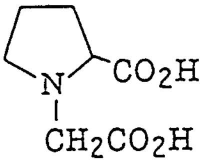

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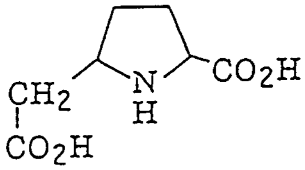

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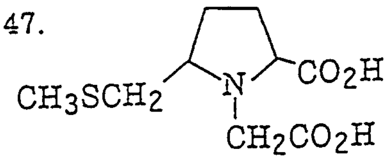

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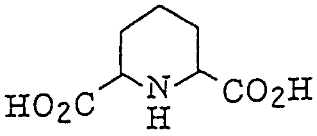

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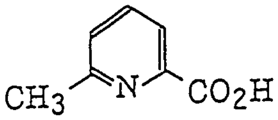

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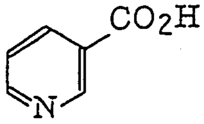

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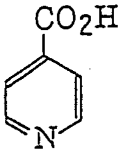

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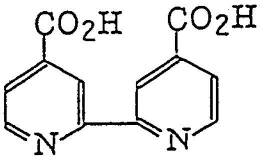

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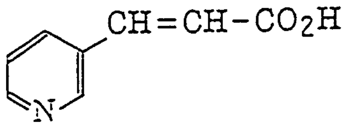

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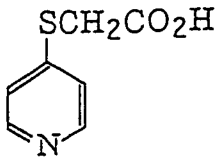

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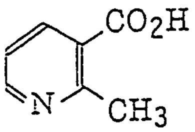

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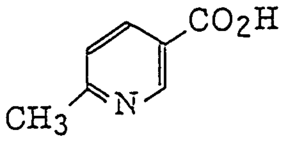

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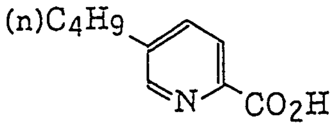

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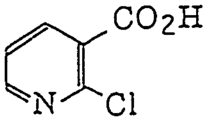

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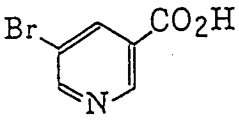

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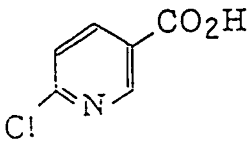

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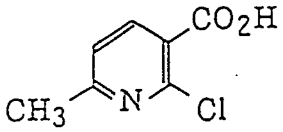

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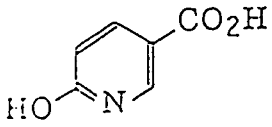

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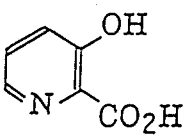

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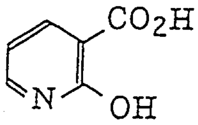

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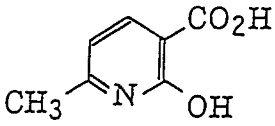

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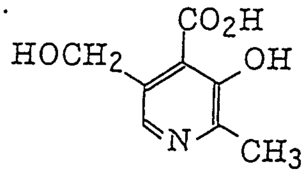

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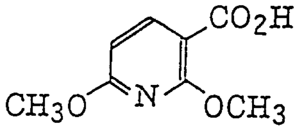

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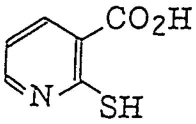

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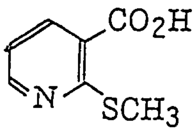

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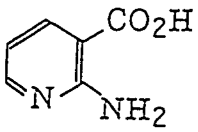

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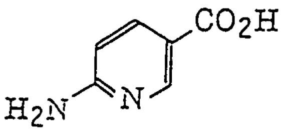

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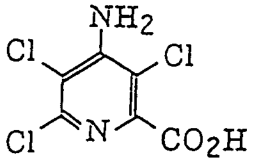

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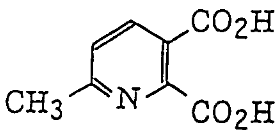

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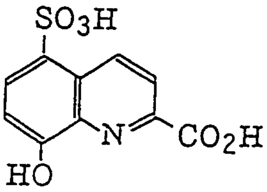

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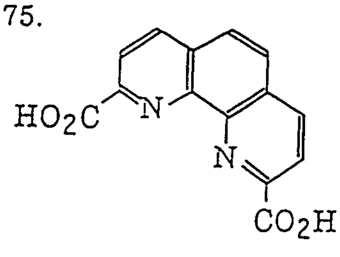

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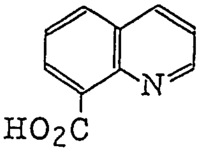

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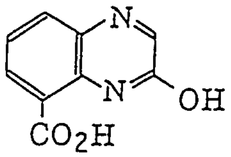

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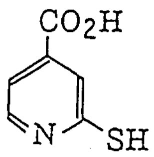

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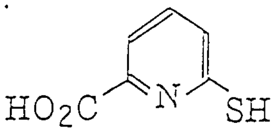

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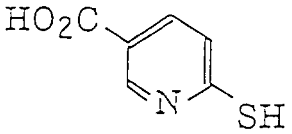

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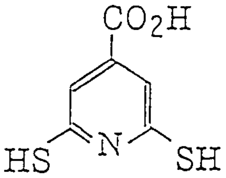


The above compounds can be used in the form of an ammonium salt or an alkali metal salt.

The compounds represented by formula (III) can be synthesized according to the methods disclosed in Organic Syntheses, Collective Volume 3, p. 740, or they are commercially available.

Of the compounds represented by formula (III), particularly preferred are 2-carboxypyridine, 2,6-pyridinedicarboxylic acid, 2-carboxyimidazole, 4-carboxyimidazole and derivatives thereof, more preferably 2-carboxypyridine and 2,6-pyridinedicarboxylic acid.

The addition amount of the compound represented by formula (III) of the present invention is preferably from 0.0001 to 1.0 mol, more preferably from 0.001 to 0.3 mol, and still more preferably from 0.01 to 0.2 mol, per liter of the processing solution having the bleaching ability. The present invention can exhibit excellent performances in the above range of the processing solution.

Further, it is preferred for the processing solution having the bleaching ability to contain the hydrocarbon organic acid having two or more carboxyl groups in the molecule. This organic acid means saturated hydrocarbon carboxylic acid, unsaturated hydrocarbon carboxylic adid, aromatic hydrocarbon carboxylic acid which have two or more carboxylic acid in one molecule, or alkali metal salts thereof and ammonium salts thereof. The dicarboxylic acid and the salt thereof represented by the following formula (B) are preferably used in the present invention as such hydrocarbon organic acid.

$$\text{HOOC-Q'-COOH} \qquad (B)$$

wherein Q' represents a single bond or a saturated or unsaturated aliphatic group having from 1 to 4 carbon atoms.

The aliphatic group represented by Q' in formula (B) is a straight chain or branched saturated or unsaturated aliphatic group having from 1 to 4 carbon atoms. The aliphatic group represented by Q' may be substituted or unsubstituted, and the substituents for the aliphatic group may be any substituent which can be substituted, preferably a hydroxyl group, a halogen atom (e.g., chlorine, bromine, fluorine), an amino group, an alkoxyl group (e.g., methoxy, ethoxy).

The addition amount of the compound represented by formula (B) is preferably in the range of from 0.1 to 2.0 mol, more preferably from 0.3 to 1.5 mol, per liter of the processing solution having the bleaching ability.

Preferred examples of the carboxylic acids are shown below, but the present invention is not limited thereto. There are cited oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, malic acid, tartaric acid, aspartic acid, glutamic acid and citric acid. Particularly preferred of them are malonic acid, succinic acid, glutaric acid, and maleic acid, and the use of two or more of them in combination is preferred, the use of two or three of them in combination is more preferred, and the combination of succinic acid and maleic acid, or the combination of succinic acid and glutaric acid is most preferred.

It is preferred to incorporate gelatin and a nitrogen-containing heterocyclic compound into the processing solution having the bleaching ability to inhibit the generation of harmful gas. Particularly preferred compounds are imidazole compounds. Above all, imidazole and lower (having 1 to 3 carbon atoms) alkyl-substituted imidazole (e.g., 2-methylimidazole, 2,4-dimethylimidazole, 2-ethylimidazole, 2-propylimidazole) are preferred.

The addition amount of these compounds of gelatin and the nitrogen-containing heterocyclic compounds is preferably from 0.001 to 0.3 mol, more preferably from 0.003 to 0.1 mol, still more preferably from 0.005 to 0.05 mol, per liter of the processing solution having the bleaching ability.

The lower the concentration of the ammonium ion in the processing solution having the bleaching ability, the less is the reduction of the color density of color images. The concentration of the ammonium ion in the processing solution having the bleaching ability is preferably from 0% to 20%, more preferably from 0% to 10%, of all the cations, and most preferably do not contain ammonium ion at all.

The lower concentration of the ammonium ion is also preferred in the processing solution having the fixing ability. The concentration of the ammonium ion in the processing solution having the fixing ability is preferably from 0% to 50%, more preferably from 0% to 20%, of all the cations, and most preferably do not contain ammonium ion at all.

The bleach of the developed silver can be carried out extremely rapidly according to the processing method of the present invention without containing the bleaching agent which is hardly biodegradable, and the photographically adverse influences such as stain can be reduced.

The present invention is characterized by processing of the silver halide color photographic material using the processing solution having the bleaching ability, and other requisites such as materials, etc., can be arbitrarily selected out of generally used materials and the like.

When the ferric complex salt of the present invention is used in the processing solution having the bleaching ability, other bleaching agents can be used in combination therewith, within the scope of the present invention (preferably 0.01 mol or less, more preferably 0.005 mol or less, per liter of the processing solution). The Fe(III), Co(III) or Mn(III) chelate bleaching agent of the following compounds can be cited as such a bleaching agent which can be used in combination.

The compounds which form the above chelate bleaching agents include ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine-N-(β-hydroxyethyl)N,N',N'-triacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, iminodiacetic acid, dihydroxyethylglycine, ethyl ether diaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrapropionic acid, phenylenediaminetetraacetic acid, N-(2-carboxymethoxyphenyl)iminodiacetic acid, β-alaninediacetic acid, glycinedipropionic acid, ethylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, 1,3-diaminopropane-N,N,N',N'-tetramethylenephosphonic acid, nitrilodiacetic acid monopropionic acid, nitrilomonoacetic acid dipropionic acid, 2-hydroxy-3-aminopropionic acid-N,N-diacetic acid, serine-N,N-diacetic acid, 2-methylserine-N,N-diacetic acid, 2-hydroxymethylserine-N,N-diacetic acid, hydroxyethyliminodiacetic acid, methyliminodiacetic acid, N-(2-acetamido)iminodiacetic acid, nitrilotripropionic acid, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, 1,4-diaminobutanetetraacetic acid, 2-methyl-1,3-diaminopropanetetraacetic acid, 2,2-dimethyl-1,3-diaminopropanetetraacetic acid, succinic acid and alkali metal salts (e.g., a lithium salt, a sodium salt, a potassium salt) and ammonium salts of these compounds. The bleaching agents as disclosed in JP-A-63-80256, JP-A-63-97952, JP-A-63-97953, JP-A-63-97954, JP-A-1-93740, JP-A-3-216650, JP-A-3-180842, JP-A-4-73645, JP-A-4-73647, JP-A-4-127145, JP-A-4-134450, JP-A-4-174432, European Patent Publication No. 430,000A1, and German Patent Publication No. 3,912,551 can also be enumerated but the present invention is not limited thereto.

It is preferred to incorporate halides such as chloride, bromide and iodide to the processing solution having the bleaching ability of the present invention as a rehalogenating agent to accelerate the oxidation of silver. Further, an organic ligand which forms a hardly soluble silver salt may be added in place of halides. Halides are added in the form of an alkali metal salt or an ammonium salt, or the salt of guanidine or amine. Specifically, there are sodium bromide, ammonium bromide, potassium chloride, guanidine hydrochloride, potassium bromide, and potassium chloride. The amount of the rehalogenating agent to be added to the processing solution having the bleaching ability is preferably 2 mol/liter or less. When the rehalogenating agent is added to the bleaching solution, the addition amount is preferably from 0.01 to 2.0 mol/liter, more preferably from 0.1 to 1.7 mol/liter, and particularly preferably from 0.1 to 0.6 mol/liter, and when added to the bleach-fixing solution, preferably from 0.001 to 2.0 mol/liter, more preferably from 0.001 to 1.0 mol/liter, and particularly preferably from 0.001 to 0.5 mol/liter.

A compound represented by formula (I) or (II) in addition to the compound of the ferric complex salt of the present invention can be incorporated into the processing solution having the bleaching ability of the present invention, and it is preferred that the lower the stability of the metal chelate compound is, the larger is the addition amount, generally used in the range of 30 mol times or less.

In addition to the foregoing, a bleaching accelerator, a corrosion inhibitor for preventing the corrosion of the processing baths, a fluorescent brightening agent, and a defoaming agent are added to the processing solution having the bleaching ability or the prebath thereof of the present invention according to the necessity.

Examples of the bleaching accelerators which can be used in the present invention include the compounds having a mercapto group or a disulfide group disclosed in U.S. Patent 3,893,858, German Patent 1,290,812, British Patent 1,138,842, JP-A-53-95630, and Research Disclosure, No. 17129 (1978), the thiazolidine derivatives disclosed in JP-A-50-140129, the thiourea derivatives disclosed in U.S. Patent 3,706,561, the iodides disclosed in JP-A-58-16235, the polyethylene oxides disclosed in German Patent 2,748,430, the polyamine compounds disclosed in JP-B-45-8836 (the term "JP-B" as used herein means an "examined Japanese patent publication"), and the imidazole compounds disclosed in JP-A-49-40493. Above all, the mercapto compounds disclosed in British Patent 1,138,842 are preferred.

Further, nitrate is preferred as a corrosion inhibitor, for example, ammonium nitrate, sodium nitrate and potassium nitrate are preferably used. The addition amount thereof is from 0.01 to 2.0 mol/liter, preferably from 0.05 to 0.5 mol/liter.

The pH of the bleaching solution or the bleach-fixing solution of the present invention is in the range of from 2.0 to 8.0, preferably from 3.0 to 6.0. When bleaching or bleach-fixing is carried out immediately after color development in the photographic material for photographing, pH is 7.0 or less, preferably 6.0 or less, for inhibiting bleaching fog. Particularly, in the case of the bleaching solution, pH is preferably from 3.0 to 5.0.

For this purpose, compounds which are difficult to be oxidized by the bleaching agent and have a buffering effect within the above pH range can be used as a pH buffer in the present invention, in addition to the above organic acids. Examples thereof include organic acids such as acetic acid, glycolic acid, lactic acid, propionic acid, butyric acid, malic acid, chloroacetic acid, levulinic acid, ureidopropionic acid, formic acid, monobromoacetic acid, monochloropropionic acid, pyruvic acid, acrylic acid, isobutyric acid, pivalic acid, aminobutyric acid, valeric acid, isovaleric acid, asparagine, alanine, arginine, ethionine, glycine, glutamine, cysteine, serine, methionine, leucine, histidine, benzoic acid, chlorobenzoic acid, hydroxybenzoic acid, nicotinic acid, cystine, ascorbic acid, and salicylic acid, and organic bases such as pyridine, dimethylpyrazole, 2-methyl-o-oxazoline, aminoacetonitrile, and imidazoles. The plurality of these buffers may be used in combination. Organic acids having a pKa of from 2.0 to 5.5 are preferably used in the present invention and the use of the combination of two or more of these is preferred. These organic acids can be used in the form of an alkali metal salt (e.g., a lithium salt, a sodium salt, a potassium salt) and an ammonium salt. The addition amount of these buffers, other than the compounds represented by formula (III), is, in total, appropriately from 0.001 to 1.5 mol, preferably from 0.001 to 1.0 mol, and particularly preferably from 0.004 to 0.8 mol, per liter of the processing solution having the bleaching ability.

The foregoing acids and alkali agents (e.g., aqueous ammonia, KOH, NaOH, potassium carbonate, sodium carbonate, imidazole, monoethanolamine, diethanolamine) may be used in combination for adjusting the pH of the processing solution having the bleaching ability within the above range. Aqueous ammonia, KOH, NaOH, potassium carbonate and sodium carbonate are preferred of them.

The endeavors have been made to reduce the exhausted nitrogen atoms to the atmosphere with the increasing recognition of the global environmental protection. Accordingly, the processing solution of the present invention preferably does not substantially contain ammonium ion from such a viewpoint.

In addition, in the present invention, "does not substantially contain ammonium ion" means that the concentration of ammonium ion is 0.1 mol/liter or less, preferably 0.08 mol/liter or less, more preferably 0.01 mol/liter or less, and particularly preferably does not contain at all.

Alkali metal ions or alkaline earth metal ions are preferred as the alternative cations to reduce the ammonium ion concentration to the range of the present invention, an alkali metal ion is particularly preferred, above all, a lithium ion, a sodium ion and a potassium ion are preferred, specifically they include potassium nitrate and sodium nitrate, in addition to the sodium salt and the potassium salt of the organic acid ferric complex as a bleaching agent, or the potassium bromide and the sodium bromide as a rehalogenating agent in the processing solution having the bleaching ability.

Potassium hydroxide, sodium hydroxide, potassium carbonate and sodium carbonate are preferably used as an alkali agent for adjusting pH.

In carrying out the processing, it is particularly preferred to subject the processing solution having the bleaching ability of the present invention to aeration to stabilize the photographic performances. Various methods known in the art can be used for aeration including blowing air into the processing solution having the bleaching ability, or absorbing air using an ejector.

In carrying out the air blowing, it is preferred to discharge air into the solution using a diffuser having fine pores. Such a diffuser is widely used in an aeration tank in the activated sludge processing. With regard to the aeration, the item disclosed in Z-121, Using Process C-41, 3rd Edition, pages BL-1 to BL-2, published by Eastman Kodak (1982) can be utilized. In the processing using the processing solution having the bleaching ability of the present invention, vigorous stirring is preferred and the practical example disclosed in JP-A-3-33847, p. 8, right upper column, line 6 to left lower column, line 2 can be utilized as it is.

Bleaching or bleach-fixing process can be carried out at from 30°C to 60°C but the preferred temperature is from 35°C to 50°C.

The time of the bleaching or bleach-fixing process is from 10 seconds to 7 minutes, preferably from 10 seconds to 4 minutes, in the photographic material for photographing, and from 5 seconds to 70 seconds, preferably from 5 seconds to 60 seconds, more preferably from 10 seconds to 45 seconds, in the material for printing. Within these preferred processing conditions, processing with excellent results can be obtained such that rapid processing is feasible without no increment of stain.

Photographic materials processed with the processing solution having the bleaching ability is then fixing or bleach-fixing processed. The fixing solutions or the bleach-fixing solutions disclosed in JP-A-3-33847, page 6, right lower column, line 16 to page 8, left upper column, line 15 are preferably used as such a fixing solution or bleach-fixing solution.

Further, ammonium thiosulfate has been usually used as a fixing agent in the desilvering process, but it may be replaced with other known fixing agents, for example, mesoionic compounds, thioether compounds, thioureas, a large quantity of iodides, or hypo. With respect to these, there are disclosures in JP-A-60-61749, JP-A-60-147735, JP-A-64-21444, JP-A-1-201659, JP-A-1-210951, JP-A-2-44355, and U.S. Patent 4,378,424, for example, ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, guanidine thiosulfate, ammonium thiocyanate, sodium thiocyanate, potassium thiocyanate, dihydroxyethyl thioether, 3,6-dithia-1,8-octanediol, and imidazole can be cited. Thiosulfates and mesoionic compounds are particularly preferred. Ammonium thiosulfate is preferred from the point of rapid fixing ability, but for the purpose of substantially excluding ammonium ion from the processing solution considering the environmental problem, sodium thiosulfate and mesoionic compounds are more preferred. Further, a combined use of two or more fixing agents can ensure more rapid fixing process. For example, it is preferred to use, in addition to ammonium thiosulfate and sodium thiosulfate, ammonium thiocyanate, imidazole, thiourea, thioether, or thiosulfonic acid compounds such as ammonium methanethiosulfonate, in combination, and in such a case, the addition amount of the second fixing agent is from 0.01 to 100 mol% based on ammonium thiosulfate or sodium thiosulfate.

The amount of the fixing agent is from 0.1 to 3.0 mol, preferably from 0.5 to 2.0 mol, per liter of the bleach-fixing solution or fixing solution. The pH of the fixing agent is, although varies depending on the kind of the fixing agent, generally from 3.0 to 9.0, and when thiosulfate is used, from 5.8 to 8.0 is preferred for obtaining stable fixation.

The addition of preservatives to the bleach-fixing solution or the fixing solution can increase the stability of the solution with the lapse of time. Sulfite and/or hydroxylamine, hydrazine, bisulfite addition products of aldehyde (for example, bisulfite addition products of acetaldehyde, particularly preferably bisulfite addition products of aromatic aldehyde disclosed in JP-A-1-298935) are effective as preservatives for the bleach-fixing solution or the fixing solution containing thiosulfate. The use of the sulfinic acid compounds disclosed in JP-A-62-143048 is also preferred. Lower alkylsulfinic acid compounds (having from 1 to 3 carbon atoms) such as ammonium methanesulfinate and benzenesulfinic acid compounds substituted with a sulfo group or a carboxyl group are particularly preferred.

A buffer is preferably added to maintain the pH of the bleach-fixing solution or the fixing solution constant, for example, phosphate, imidazoles such as imidazole, 1-methylimidazole, 2-methylimidazole, and 1-ethylimidazole, triethanolamine, N-allylmorpholine, and N-benzoylpiperazine. Imidazole is most preferably used of these.

Further, it is preferred that after imagewise exposed silver halide color photographic material is processed with the processing solution having the bleaching ability, the material is further processed with the processing solution having the fixing ability containing an aminopolycarboxylic acid and/or an organic phosphonic acid to raise the effect of the present invention.

Examples of such an aminopolycarboxylic acid and organic phosphonic acid include ethylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilotrimethylenephosphonic acid, 2-hydroxy-1,3-diaminopropanetetraacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine-N-(β-hydroxyethyl)-N,N',N'-triacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, iminodiacetic acid, N-(2-carboxyphenyl)iminodiacetic acid, dihydroxyethylglycine, ethyl ether diaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrapropionic acid, glycinedipropionic acid, phenylenediaminetetraacetic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, 1,3-propanediamine-N,N,N',N'-tetramethylenephosphonic acid, serine-N,N-diacetic acid, 2-methylserine-N,N-diacetic acid, 2-hydroxymethylserine-N,N-diacetic acid, hydroxyethyliminodiacetic acid, methyliminodiacetic acid, N-(2-acetamido)iminodiacetic acid, nitrilotripropionic acid, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, 1,4-diaminobutanetetraacetic acid, 2-methyl-1,3-diaminopropanetetraacetic acid, 2-dimethyl-1,3-diaminopropanetetraacetic acid, β-alaninediacetic acid, alanine, tartaric acid, hydrazinediacetic acid, N-hydroxyiminodipropionic acid and alkali metal salts (e.g., lithium salt, sodium salt, potassium salt) and ammonium salts of these compounds.

The addition amount of the above aminopolycarboxylic acid and organic phosphonic acid is preferably from 0.0001 to 0.5 mol/liter, more preferably from 0.01 to 0.1 mol/liter.

The fixing process can be carried out at from 30°C to 60°C, but preferably from 35°C to 50°C.

The time of the fixing process is from 15 seconds to 2 minutes, preferably from 25 seconds to 1 minute and 40 seconds in the photographic material for photographing, and from 8 seconds to 80 seconds, preferably from 10 seconds to 45 seconds in the material for printing.

The desilvering process is usually carried out in combination of the bleaching process, bleach-fixing process, and fixing process. Specifically, the following are cited.

(1) Bleaching — Fixing
(2) Bleaching — Bleach-Fixing
(3) Bleaching — Bleach-Fixing — Fixing
(4) Bleaching — Washing — Fixing
(5) Bleach-Fixing
(6) Fixing — Bleach-Fixing

(1), (2), (3) and (4) are preferred in the photographic material for photographing, and (1), (2) and (3) are more preferred. (5) is preferred in the material for printing.

The present invention can be applied to desilvering process which is carried out after color development process through adjusting, stopping and washing steps, but the preferred process is that in which bleaching process is carried out just after color development.

The processing of the present invention is preferably carried out by an automatic processor. Transportation method in such an automatic processor is disclosed in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. It is preferred to shorten the crossover time between processing tanks in automatic processor for carrying out rapid processing. The automatic processor the crossover time of which is 5 seconds or less is disclosed in JP-A-1-319038.

When continuous processing is carried out by automatic processor according to the method of the present invention, it is preferred to add a replenisher in an amount according to the amount of the processed photographic material, in order to supplement the composition of the processing solution consumed by the processing of the photographic material and to prevent the accumulation of the undesired composition dissolved from the photographic material, in the processing solution. Each process may comprise two or more processing tanks, and in such a case, the countercurrent system in which the replenisher flows from the after bath to the previous bath is preferably used. Particularly, in the washing process or the stabilizing process, a cascade system of from 2 to 4 stages is preferably used.

Lower amount of the replenisher is preferably used unless the variation of the composition of the processing solution adversely affect the photographic performance or the contamination of the processing solution is generated.

Stirring as vigorous as possible is preferred in each processing solution of the present invention to effectively exhibit the effect of the present invention.

Specific examples of the methods of forced stirring include a method in which a jet of the processing solution is impinged on the surface of the emulsion of the photographic material as disclosed in JP-A-62-183460, JP-A-62-183461 and JP-A-3-33847, p. 8, which is adopted in the color negative film processor FP-560B manufactured by Fuji Photo Film Co., Ltd., a method in which the stirring effect is raised using a rotating means as disclosed in JP-A-62-183461, a method in which the photographic material (film) is moved with a wiper blade, which is installed in the solution, in contact with the surface of the emulsion, and the generated turbulent flow at the surface of the emulsion increases the stirring effect, and a method in which the circulating flow rate of the entire processing solution is increased. The method in which a jet of the processing solution is impinged on the surface of the emulsion is most preferred of the above, and it is preferred to adopt this method in all the processing tanks.

The replenishing rate of the color developing replenisher is from 50 ml to 3,000 ml, preferably from 50 ml to 2,200 ml, per m^2 of the photographic material in the color photographic material for photographing, and from 15 ml to 500 ml, preferably from 20 ml to 350 ml, per m^2 of the photographic material in the color photographic material for printing.

The replenishing rate of the bleaching replenisher is from 10 ml to 1,000 ml, preferably from 50 ml to 550 ml, per m^2 of the photographic material in the color photographic material for photographing, and from 15 ml to 500 ml, preferably from 20 ml to 300 ml, per m^2 of the photographic material in the photographic material for printing.

The replenishing rate of the bleach-fixing replenisher is from 200 ml to 3,000 ml, preferably from 250 ml to 1,300 ml, per m^2 of the photographic material in the color photographic material for photographing, and from 20 ml to 300 ml, preferably from 50 ml to 200 ml, per m^2 of the photographic material in the photographic material for printing. The bleach-fixing replenisher may be replenished as one type replenisher, or may be replenished separately as the bleaching solution composition and the fixing solution composition, or may be replenished as the bleach-fixing replenisher by mixing the overflow from the bleaching tank and/or the fixing tank.

The replenishing rate of the fixing replenisher is from 300 ml to 3,000 ml, preferably from 300 ml to 1,200 ml, per m^2 of the photographic material in the color photographic material for photographing, and from 20 ml to 300 ml, preferably from 50 ml to 200 ml, per m^2 of the photographic material in the photographic material for printing.

The replenishing rate of the washing water or stabilizing solution is from 1 to 50 times, preferably from 2 to 30 times, more preferably from 2 to 15 times, of the carryover from the previous bath per unit area.

The processing solution having the bleaching ability of the present invention can be reused in the processing by recovering the overflow liquid after use and compensating for the composition by the addition of components. Such a usage is in general called a regeneration and is preferably used in the present invention. With regard to the details of the regeneration, the items disclosed in Fuji Film Processing Manual, Fuji Color Negative Film, CN-16 Process, (revised in August, 1990), pp. 39 and 40 can be applied to.

A kit for preparing the processing solution having the bleaching ability may be either a liquid or a powder, but almost all the raw materials are supplied in powders in a case of exclusive of an ammonium salt, and a hygroscopicity is low, therefore, it is easy to prepare powders.

From the viewpoint of reducing the waste solution, the kit for the above regenerated solution preferably comprises powders which does not need excessive water and can be added directly.

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

In the regeneration method by electrolysis, a regeneration processing is carried out by putting an anode and a cathode in the same bleaching bath, or separating an anode bath from a cathode bath by a diaphragm, as well as a bleaching solution and a developing solution and/or a fixing solution can be regeneration processed at the same time also using a diaphragm. Regeneration of the fixing solution and the bleach-fixing solution are carried out by an electrolytic reduction of the accumulated silver ion. In addition, the removal of the accumulated halogen ion by means of an anion exchange resin is also preferred for maintaining the fixing ability.

An ion exchange or an ultrafiltration is utilized for reducing the amount of the washing water, and an ultrafiltration is particularly preferred.

The imagewise exposed color photographic material of the present invention is generally subjected to color development process before desilvering process. The color developing solutions disclosed in JP-A-3-33847, p. 9, left upper column, line 6 to p. 11, right lower column, line 6, or JP-A-5-197107 can be used in the present invention.

Further, known aromatic primary amine color developing agents are used as the color developing agents in the color developing process and p-phenylenediamine derivatives are preferred examples, and representative examples thereof include 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methylaniline, 4-amino-N-ethyl-N-(3-hydroxypropyl)-3-methylaniline, 4-amino-N-ethyl-N-(4-hydroxybutyl)-3-methyl-aniline, 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-3-methylaniline, 4-amino-N-(3-carbamoylpropyl-N-n-propyl)-3-methylaniline, and 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methoxyaniline, and those disclosed in European Patent Publication (laid open) No. 410,450, JP-A-4-11255 can also be preferably used.

Further, these color developing agents may be sulfate, hydrochloride or sulfite of p-phenylenediamine derivative, or a salt of naphthalenedisulfonate, p-toluenesulfonate, etc. The amount used of the aromatic primary amine developing agent is preferably from 0.0002 mol to 0.2 mol, more preferably from 0.001 to 0.1 mol, per liter of the color developing solution.

The color developing solution generally contains a pH buffer such as carbonate, borate, phosphate or 5-sulfosalicylate of an alkali metal, a development inhibitor or an antifoggant such as a chloride, a bromide, an iodide, benzimidazoles, benzothiazoles, or a mercapto compound. The color developing solution may also contain, if necessary, various preservatives such as hydroxylamine, sulfite, hydrazines, e.g., N,N-biscarboxymethylhydrazine, 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 salt, and amines, a dye forming coupler, a competitive coupler, an auxiliary developing agent such as 1-phenyl-3-pyrazolidone, a tackifier, and various chelating agents typified by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid, and phosphonocarboxylic acid, e.g., ethylenediaminetetraacetic acid, 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 of these acids.

Further, compounds having a biodegradability is preferred as a chelating agent. Examples of such chelating agents are disclosed in JP-A-63-146998, JP-A-63-199295, JP-A-63-267750, JP-A-63-267751, JP-A-2-229146, JP-A-3-186841, German Patent 3,739,610, and EP 468,325.

It is preferred that the processing solutions in the replenisher tank and the processing tank of the color developing solution are shielded with a liquid such as a high boiling point organic solvent to reduce the contact area with air. Liquid paraffin is most preferred as the liquid for shielding and is particularly preferred to be used in a replenisher.

The processing temperature of the color developing solution of the present invention is from 20°C to 55°C and preferably from 30°C to 55°C. The processing time is from 20 seconds to 5 minutes, preferably from 30 seconds to 3 minutes and 20 seconds, and more preferably from 1 minute to 2 minutes and 30 seconds in the photographic material for photographing, and is from 10 seconds to 1 minute and 20 seconds, preferably from 10 seconds to 60 seconds, and more preferably from 10 seconds to 40 seconds in the photographic material for printing.

The processing method of the present invention can be used for color reversal processing. The black-and-white developing solution for use in this process is a black-and-white first developing solution which is usually used in the reversal process of a color photographic material. Various kinds of well known additives which are added to a black-and-white developing solution for a silver halide black-and-white photographic material can be incorporated to the black-and-white first developing solution for a color reversal photographic material.

Representative additives include a developing agent such as 1-phenyl-3-pyrazolidone, metol and hydroquinone, a preservative such as sulfite, an accelerator comprising alkali such as sodium hydroxide, sodium carbonate and potassium carbonate, an inorganic or organic inhibitor such as potassium bromide, 2-methylbenzimidazole, and methylbenzothiazole, a water softener such as polyphosphate, and a development inhibitor such as a trace amount of iodide or a mercapto compound.

The desilvering processed photographic material of the present invention is washing and/or stabilizing processed. The stabilizing solutions disclosed in U.S. Patent 4,786,583 are used in the washing and stabilizing processes. Further, formaldehyde is used as a stabilizing agent in the stabilizing solution, however, N-methylolazolehexamethylenetetramine, bisulfite addition product of formaldehyde, dimethylolurea, azolylmethylamine derivatives are preferred from the safety of the working environment. With respect to these, there are disclosed in JP-A-2-153348, JP-A-4-270344 and EP-504,609A2. Particularly, a combined use of azoles such as 1,2,4-triazole with azolylmethylamine such as 1,4-bis(1,2,4-triazol-1-ylmethyl)piperazine and derivatives thereof is preferred because the high image stability can be obtained thereby and also which generates less vapor pressure of the formaldehyde.

Photographic materials which can be applied to the process of the present invention include a color negative film, a color reversal film, a color paper, a color reversal paper, a direct positive color photographic material, a color negative film for a movie and a color positive film for a movie, and these are disclosed, for example, in JP-A-3-33847, JP-A-3-293662 and JP-A-4-130432. Also, there are no particular limitations on the photographic material of the present invention, such as the support, a coating method, a silver halide emulsion, the kind of the silver halide for use in the surface protective layer (e.g., silver iodobromide, silver iodochlorobromide, silver bromide, silver chlorobromide, silver chloride), the form of the grain (e.g., cubic, tabular, spherical), the grain size, the variation coefficient, the crystal structure (e.g., core/shell structure, multi-phase structure, uniform phase structure), the preparation method (e.g., a single jet method, a double jet method), a binder (e.g., gelatin), a hardening agent, an antifoggant, metal doping agent, a silver halide solvent, a tackifier, an emulsion precipitant, a dimension stabilizer, an adhesion preventive, a stabilizer, a stain inhibitor, a color image stabilizer, a stain inhibitor, a chemical sensitizer, a spectral sensitizer, a sensitivity increasing agent, a supersensitizer, a nucleating agent, a coupler (e.g., a pivaloylacetanilide type or benzoylacetanilide type yellow coupler, a 5-pyrazolone type or pyrazoloazole type magenta coupler, a phenol type or naphthol type cyan coupler, a DIR coupler, a bleaching accelerator releasing coupler, a competitive coupler, a colored coupler), a coupler dispersing method (e.g., a oil-in-water dispersing method using a high boiling point solvent), a plasticizer, an antistatic agent, a lubricant, a coating aid, a surfactant, a brightening agent, a formalin scavenger, a light scattering agent, a matting agent, a light absorbing agent, an ultraviolet absorbing agent, a filter dye, an irradiation dye, a development improver, a delustering agent, a preservative (e.g., 2-phenoxyethanol), and an antimold agent, and disclosures, for example, in Product Licensing, Vol. 92, pp. 107 to 110 (December, 1971), Research Disclosure (hereinafter abbreviated as RD), No. 17643 (December, 1978), RD, No. 18716 (November, 1976), and RD, No. 307105 (November, 1989) can be referred to.

The processing composition of the present invention can be used in every color photographic material but the dry film thickness of the support and all the consitutional layers exclusive of the subbing layer and the backing layer of the color photographic material of the present invention is preferably 18.0 μm or less, more preferably 16.0 μm or less in the color photographic material for photographing, and preferably 10.0 μm or less, more preferably 8.0 μm or less in the printing material, for achieving the objects of the present invention.

When the film thickness is outside the above preferred range, bleaching fog and the stain after processing due to the developing agent remaining after color development increase. The generation of such bleaching fog and the stain is due to the green-sensitive layer, and the magenta color increase is liable to rise compared with cyan or yellow colors.

Further, the lower limit of the film thickness in the regulation is preferably reduced within the range of not greatly impairing the performance of the photographic material. The lower limit of the film thickness of the support and all the consitutional layers exclusive of the subbing layer and the backing layer is 10.0 μm in the color photographic material for photographing, and 6.0 μm in the printing material. In the photographing material, in general, a layer (or layers) is provided between the light-sensitive layer nearest to the support and the subbing layer of the support, the dry film thickness of this layer (or these layers) is preferably 2.0 μm or less. The reduction of the film thickness is either a light-sensitive layer or a light-insensitive layer.

The film swelling factor [(equilibrium swollen film thickness at 25°C in H_2O - total dry film thickness at 25°C, 55% RH) ÷ (total dry film thickness at 25°C, 55% RH) × 100] of the color photographic material of the present invention is preferably from 50 to 200%, more preferably from 70 to 150%. When the swelling factor is outside the above range, the remaining amount of the color developing agent increases, and the photographic performances, the image quality due to desilvering, physical properties of the film such as film strength are adversely affected.

Further, the film swelling rate $T_{1/2}$ of the color photographic material of the present invention is preferably 15 seconds or less, more preferably 9 seconds or less. $T_{1/2}$ is defined as the time to reach ½ of the saturated film thickness, taking 90% of the maximum swollen film thickness obtained after processing at 30°C for 3 minutes and 15 seconds in a color developing solution as the saturated film thickness.

The silver halide to be contained in the photographic emulsion layers of the color photographic material of the present invention may have any silver halide composition, for example, silver chloride, silver bromide, silver chlorobromide, silver iodobromide, silver iodochloride or silver iodochlorobromide.

Silver iodobromide, silver iodochloride or silver iodochlorobromide containing from 0.1 to 30 mol% of silver iodide, particularly silver iodobromide containing from 1 to 25 mol% of silver iodide, is preferably used for the photographic material for photographing or the color reversal photographic material. Silver bromide or silver chlorobromide is preferably used in the direct positive color photographic material, and silver chloride is also preferred for carrying out rapid processing. Silver chloride or silver chlorobromide is preferably used in photographic material for paper, preferably silver chlorobromide containing 80 mol% or more of silver chloride, more preferably 95 mol% or more, and most preferably 98 mol% or more.

Various color couplers can be employed in the color photographic material which are processed by the processing method of the present invention, and specific examples are disclosed in the patents cited in the above RD, No. 17643, VII-C to G, ibid., No. 307105, VII-C to G, and JP-A-62-215272, JP-A-3-33847, JP-A-2-33144, EP-447,969A and EP-482,552A.

Preferred yellow couplers are those disclosed, for example, in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, 4,248,961, JP-B-58-10739, British Patents 1,425,020, 1,476,760, U.S. Patents 3,973,968, 4,314,023, 4,511,649, 5,118,599, EP 249,473A, EP 0,447,969, JP-A-63-23145, JP-A-63-123047, JP-A-1-250944, and JP-A-1-213648, and they can be used in combination as far as the combined use does not impede the effect of the present invention.

Examples of particularly preferred yellow couplers are, for example, the yellow couplers represented by formula (Y) as disclosed in JP-A-2-139544, page 18, left upper column to page 22, left lower column, the acylacetamide based yellow couplers the acyl group of which has characteristics as disclosed in JP-A-5-2248 and European Patent Publication No. 0,447,969, and the yellow couplers represented by formula (Cp-2) as disclosed in JP-5-27389 and EP-0,446,863A2.

5-Pyrazolone based compounds and pyrazoloazole based compounds are preferred as magenta couplers, and more preferred of them are those disclosed in U.S. Patents 4,310,619, 4,351,897, EP 73,636, U.S. Patents 3,061,432, 3,725,067, Research Disclosure, No. 24220 (June, 1984), JP-A-60-33552, Research Disclosure, No. 24230 (June, 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, 4,556,630 and WO 88/04795.

Especially preferred magenta couplers are the pyrazoloazole based magenta couplers represented by formula (I) as disclosed in JP-A-2-139544, page 3, right lower column to page 10, right lower column, and the 5-pyrazolone based magenta couplers represented by formula (M-1) as disclosed in JP-A-2-135944, page 17, left lower column to page 21, left upper column. The most preferred are the foregoing pyrazoloazole based magenta couplers.

Phenol based couplers and naphthol based couplers are representative as cyan couplers, and preferred are those disclosed in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, 4,327,173, German Patent (Laid-Open) Publication No. 3,329,729, EP 0,121,365A, EP 0,249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, 4,296,199, and JP-A-61-42658. In addition to the above, the following couplers can also be used, for example, the pyrazoloazole based couplers disclosed in JP-A-64-553, JP-A-64-554, JP-A-64-555, and JP-A-64-556, the pyrrolotriazole based couplers disclosed in EP-0,488,248A, and EP-0,491,197A, the pyrroloimidazole based couplers disclosed in EP-0,456,226A, the pyrazolopyrimidine based couplers disclosed in JP-A-64-46753, the imidazole based couplers disclosed in U.S. Patent 4,818,672 and JP-A-2-33144, the cyclic active methylene based cyan couplers disclosed in JP-A-64-32260, and the couplers disclosed in JP-A-1-183658, JP-A-2-262655, JP-A-2-85851 and JP-A-3-48243.

Typical examples of polymerized dye forming couplers are disclosed in U.S. Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, 4,576,910, British Patent 2,102,137 and EP 341,188A, etc.

The couplers disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,570 and German Patent Publication No. 3,234,533 are preferred as couplers the colored dyes of which have an appropriate diffusibility.

Compounds which release photographically useful residual groups upon coupling can also preferably be used in the present invention. The preferred DIR couplers which release development inhibitors are disclosed, for example, in the patents cited in the foregoing Research Disclosure, No. 17643, item VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, U.S. Patents 4,248,962 and 4,782,012.

The couplers disclosed in British Patents 2,097,140, 2,131,188, JP-A-59-157638, and JP-A-59-170840 are preferred as couplers which imagewise release nucleating agents or development accelerators at the time of development.

Other couplers which can be used in the color photographic element of the present invention include the competitive couplers disclosed in U.S. Patent 4,130,427, the multiequivalent couplers disclosed in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, the DIR redox compound releasing couplers, DIR coupler releasing couplers, DIR coupler releasing redox compounds or DIR redox releasing redox compounds disclosed in JP-A-60-185950 and JP-A-62-24252, the couplers which release dyes which restore colors after separation disclosed in EP 173,302A, the bleaching accelerator releasing couplers disclosed in Research Disclosure, No. 11449, ibid., No. 24241 and JP-A-61-201247, the ligand releasing couplers disclosed in U.S. Patent 4,555,477, the leuco dye releasing couplers disclosed in JP-A-63-75747, and the couplers which release fluorescent dyes disclosed in U.S. Patent 4,774,181.

The supports which can be preferably used in the present invention are disclosed, for example, in RD, No. 17643, p. 28 and ibid., No. 18716, p. 647, right column to p. 648, left column.

Further, the present invention can also be used as a reducing solution for modifying the silver image comprising dot image and/or line original obtained by development processing the exposed silver halide photographic material for photomechanical process.

The supports which can be preferably used in the present invention include, in addition to those disclosed, for example in RD, No. 17643, p. 28, ibid., No. 18716, p. 647, right column to p. 648, left column, and ibid., No. 307105, p.

879, the supports disclosed in Kokai Giho 94-6023 (Open Technique), Hatsumei Kyokai, p. 2, left column, line 18 to p. 18, left column, line 2, and polyethylene 2,6-naphthalate is particularly preferred of them.

Specifically, there is no particular limitation on the materials of the support of the photographic material for use in the present invention, and various plastic films can preferably be used, for example, cellulose derivatives (e.g., diacetyl, triacetyl, propionyl, butanoyl, acetylpropionylacetate), polyamide, the polycarbonate disclosed in U.S. Patent 3,023,101, the polyester disclosed in JP-B-48-40414 (e.g., polyethylene terephthalate, poly-1,4-cyclohexanedimethylene terephthalate, polyethylene naphthalate), polystyrene, polypropylene, polyethylene, polysulfone, polyacrylate, and polyether imide, and particularly preferred are triacetyl cellulose and polyethylene terephthalate.

These films may have a polar group (epoxy, $-CO_2M$, -OH, $-NR_2$, $-NR_3X$, $-SO_3M$, $-OSO_3M$, $-PO_3M_2$, $-OP_3M_2$, wherein M represents a hydrogen atom, an alkali metal or ammonia, R represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms, and X represents an anion).

Particularly preferred supports are polyethylene terephthalate, polyethylene naphthalate, polyacrylate, and copolymers comprising these as raw materials and polymer blend of them.

These supports are preferably subjected to heat setting treatment after being biaxially stretched before use, and they may be heat relaxed, if necessary. Further, these supports are preferred to be previously subjected to heat treatment at a temperature lower than Tg to reduce the curling habit. For example, the Tg of polyethylene terephthalate is about 120°C, therefore, it is preferred for carrying out the heat treatment at 119°C or less for 0.2 to 48 hours, more preferably at 115°C for 24 hours, in the case of polyethylene terephthalate. It is effective and preferred for the shortening of the heat treatment time to raise the temperature once higher than the Tg and then lower the temperature gradually near the Tg. In the case of polyethylene naphthalate, the heat treatment time can be extremely shortened by maintaining the temperature once between 130°C or more and 200°C or less, then lowering to 125°C, and after then further lowering the temperature to 100°C over 40 minutes.

When the thus heat treated support is measured by a differential scanning calorimeter, an endothermic peak appears near Tg, and the larger the endothermic peak is, it means the film is difficult to curl. The heat treatment is carried out as to provide preferably 100 mcal/g or more, more preferably 200 mcal/g.

The thickness of the support of the present invention is preferably from 60 µm to 300 µm, more preferably from 70 µ to 200 µm.

When the thickness is 60 µm or less, the gutter-like curl is conspicuous due to the contraction stress of the emulsion layer during drying, and the flatness is apt to reduce, on the other hand, if it is 300 µm or more, it is difficult to handle, although the film strength is increased.

A plasticizer may be added to these support for imparting softness. Triphenylphosphate, biphenyldiphenylphosphate, dimethylethylphosphate are preferred as inclusion in a plasticizerfor for cellulose ester.

The surface activation treatment is conducted to get photographic layers (e.g., a light-sensitive silver emulsion layer, an interlayer, a filter layer, a layer having electric conductivity) to strongly adhere to the support, such as a chemical treatment, a mechanical treatment, a corona discharge treatment, a flame treatment, an ultraviolet treatment, a high frequency treatment, a glow discharge treatment, an active plasma treatment, a laser treatment, a mixed acid treatment, and an ozone treatment, and then the photographic emulsion may be directly coated to thereby obtain adherence, alternatively, after the surface treatment, or without the surface treatment, a subbing layer is provided on the support and the photographic emulsion layer may be coated thereon. The treatment is desired to be conducted under high temperature (e.g., preferably from 100°C to 200°C for several seconds to several minutes), from this point, a corona discharge treatment, a flame treatment, an ultraviolet treatment, and a glow discharge treatment are particularly preferred of these treatments.

A gelatin solution dispersed in methylene chloride/ketone/alcohol mixed organic solvent is single layer coated and the subbing layer is provided on cellulose derivative.

Chromium salt (e.g., chrome alum), aldehydes (formaldehyde, glutaraldehyde), isocyanates, active halogen compounds (2,4-dichloro-6-hydroxy-s-triazine), epichlorohydrin resins, and vinylsulfoalkyl based hardening agents can be cited as gelatin hardening agents. Various additives can be added to these subbing layer coating solution, if necessary, for example, a surfactant, an antistatic agent, an antihalation agent, a coloring dye, a pigment, a coating aid, and an antifoggant. An etching agent such as resorcinol, chloral hydrate, or chlorophenol can be incorporated in the subbing layer coating solution.

A photographic material in which a magnetic recording layer is provided on the opposite side of the support on which the silver halide emulsion layer is coated is preferred as the silver halide color photographic material for use in the present invention.

Ferromagnetic fine powders which can be used in the magnetic recording layer of the present invention include ferromagnetic iron oxide fine powders, Co-doped ferromagnetic iron oxide fine powders, ferromagnetic chromium dioxide fine powders, ferromagnetic metal powders, ferromagnetic alloy powders and barium ferrite.

As one example of the ferromagnetic alloy powders, there can be cited ferromagnetic alloy powders in which a metal part accounts for 75 wt% or more, 80 wt% or more of the metal part comprises at least one ferromagnetic metal or alloy (Fe, Co, Ni, Fe-Co, Fe-Ni, Co-Ni, Co-Fe-Ni), and 20 wt% or less of the metal part is accounted for by other component

(Al, Si, S, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Mo, Rh, Pd, Ag, Sn, Sb, B, Ba, Ta, W, Re, Au, Hg, Pb, P, La, Ce, Pr, Nb, Te, Bi). The above ferromagnetic metal part may contain a small amount of water, hydroxide or oxide.

The preparation methods of these ferromagnetic powders are well known and the ferromagnetic powders for use in the present invention can be prepared according to known methods.

Any form and size of the ferromagnetic powder can be used and selected from the wide range. With respect to the form, any of an acicular, a rice grain-like, a spherical, a cubic, or a tabular form may be used, but an acicular form and a tabular form are preferred from the electromagnetic conversion characteristics. A crystal size and a specific surface are not particularly limited, but is preferably a crystal size of 400 A or less, S_{BET} of 20 m^2/g or more, particularly preferably 30 m^2/g or more. The pH of the ferromagnetic powders and the surface treatment are not limited (the surface may be treated with a material containing an element such as titanium, silicon and aluminum, or may be treated with an organic compound such as an adsorptive compound having a nitrogen-containing heterocyclic ring, e.g., carboxylic acid, sulfonic acid, sulfate, phosphonic acid, phosphate, or benzotriazole). The preferred pH range is from 5 to 10. The ferromagnetic iron oxide fine powders can be used without limitation on the ratio of iron(II) to iron(III). These magnetic recording layers are disclosed in JP-A-47-32812 and JP-A-53-109604.

The addition amount of the ferromagnetic fine powders per m^2 of the transparent support is from 4×10^{-4} g to 3 g, preferably from 10^{-3} g to 1 g, more preferably from 4×10^{-3} g to 4×10^{-1} g.

Known thermoplastic resins, thermosetting resins, radiation setting resins, reactive type resins and the mixtures thereof conventionally used as a binder for magnetic recording medium can be used as a binder for the magnetic recording layer of the present invention.

Tg of the above resins is from -40°C to 150°C, weight average molecular weight if from 10,000 to 300,000, preferably from 10,000 to 100,000.

Examples of the above thermoplastic resins include vinyl based copolymers such as a vinyl chloride/vinyl acetate copolymer, a vinyl chloride/vinyl acetate/vinyl alcohol/maleic acid (and/or) acrylic acid copolymer, a vinyl chloride/vinylidene chloride copolymer, a vinyl chloride/acrylonitrile copolymer, and an ethylene/vinyl acetate copolymer, cellulose derivatives such as nitrocellulsoe, cellulose acetate propionate, cellulose acetate butyrate resin, rubber based resins such as acrylate resin, polyvinyl acetal resin, polyvinyl butyral resin, polyesterpolyurethane resin, polyether-polyurethane resin, polycarbonate-polyurethane resin, polyester resin, polyether resin, polyamide resin, amino resin, styrene-butadiene resin, butadiene-acrylonitrile resin, silicone based resins, and fluorine based resins.

Vinyl chloride resins are high in dispersibility of ferromagnetic fine powders and is preferred.

The above thermoplastic resin to which a group having a carbon-carbon unsaturation bonding is connected as a radiation setting founctional group is used as a radiation setting resins. Preferred functional groups are an acryloyl group and a methacryloyl group.

A polar group (an epoxy group, $-CO_2M$, -OH, $-NR_2$, $-NR_3X$, $-SO_3M$, $-OSO_3M$, $-PO_3M_2$, $-OP_3M_2$, wherein M represents a hydrogen atom, an alkali metal or ammonia, when there are present a plurality of M in one group they may be different, R represents a hydrogen atom or an alkyl group, and X represents an anion) may be incorporated into the molecules of the above described binders.

The above enumerated high molecular binders are used alone or in the mixture of two or more kinds, and curing treatment can be carried out by adding well known isocyanate based crosslinking agents and/or radiation setting type vinyl based monomers.

A hydrophilic binder can be used in the magnetic recording layer of the present invention.

Hydrophilic binders for use in the present invention are disclosed in RD, No. 17643, p. 26 and RD, No. 18716, p. 651, such as a water-soluble polymer, a cellulose ester, a latex polymer, and a water-soluble polymer ester. Examples of water-soluble polymers include gelatin, gelatin derivative, casein, agar, sodium alginate, starch, polyvinyl alcohol, a polyacrylic acid copolymer, and a maleic anhydride copolymer. Examples of cellulose esters include carboxymethyl cellulose and hydroxyethyl cellulose. Examples of latex polymers include a vinyl chloride-containing copolymer, a vinylidene chloride-containing copolymer, an acrylic acid ester-containing copolymer, a vinyl acetate-containing copolymer, and a butadiene-containing copolymer. Most preferred binder is gelatin.

Gelatin is classified into alkali-processed (lime-processed) gelatin which is immersed in an alkali bath before extraction of gelatin during preparation process, acid-processed gelatin which is immersed in an acid bath, double immersion gelatin which is subjected to both processes, and enzyme-processed gelatin, and any of them can be used. Gelatin is partially replaced with colloidal albumin, casein, cellulose derivatives such as carboxymethyl cellulose, hydroxyethyl cellulose, agar, sugar derivatives such as sodium alginate, starch derivatives and dextran, synthetic hydrophilic colloid such as polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid copolymers, polyacrylamide or derivatives thereof, partially hydrolyzed product, and gelatin derivatives.

It is preferred to harden the magnetic recording layer containing gelatin, and examples of hardening agents which can be used for the magnetic recording layer include, for example, aldehyde based compounds such as formaldehyde and glutaraldehyde, ketone compounds such as diacetyl and cyclopentanedione, bis(2-chloroethylurea), 2-hydroxy-4,6-dichloro-1,3,5-triazine, and the compounds having a reactive halogen as disclosed in U.S. Patent 3,288,775, 2,732,303, British Patents 974,723, and 1,167,207, divinylsulfone, 5-acetyl-1,3-diacryloylhexahydro-1,3,5-triazine, and the compounds having a reactive olefin as disclosed in U.S. Patents 3,635,718, 3,232,763, and British Patent 994,869, N-hydroxymethylphthalimide, and the N-methylol compounds as disclosed in U.S. Patents 2,732,316 and 2,586,168, the isocyanates as disclosed in U.S. Patent 3,103,437, the aziridine compounds as disclosed in U.S. Patent 3,017,280 and 2,983,611, the acid derivatives as disclosed in U.S. Patents 2,725,294 and 2,725,295, the epoxy compounds as disclosed in U.S. Patent 3,091,537, and halogen carboxyaldehydes such as mucochloric acid. Examples of inorganic hardening agents include chrome alum, zirconium sulfate, the carboxyl group activating type hardening agents as disclosed in JP-B-56-12853, JP-B-58-32699, Belgian Patent 825,726, JP-A-60-225148, JP-A-51-126125, JP-B-58-50699, JP-A-52-54427 and U.S. Patent 3,321,313.

The amount used of the hardening agent is usually from 0.01 to 30 wt%, preferably from 0.05 to 20 wt%, based on the dry gelatin.

The thickness of the magnetic recording layer is from 0.1 µm to 10 µm, preferably from 0.2 µm to 5 µm, and more preferably from 0.5 µm to 3 µm.

The magnetic recording layer of the present invention is substantially transparent and is preferably provided on almost entire surface of the back surface. The magnetic recording layer can be provided by coating, printing or adhesion on the back surface of the transparent support. Further, it is also preferred to prepare a transparent support having the magnetic recording layer by flow stretching together a polymer solution of magnetized grain dispersion and a polymer solution for preparing the transparent support. In this case, the compositions of two polymers are preferably the same.

The magnetic recording layer may be imparted with performances such as lubrication improvement, curling control, antistatic, and adhesion prevention, or may be provided with other layer having these performances. Further, a protective layer adjacent to the magnetic recording layer may be prepared to improve scratch resistance, if necessary.

The S/N ratio of the magnetic signal can be improved by increasing the smoothness of the back surface of the transparent support having the magnetic recording layer by calendering processing. In such a case, a light-sensitive layer is preferably coated on the transparent support after calendering process.

The light-sensitive layer of the present invention is preferred to have a layer having electric conductivity and the electric resistance of the electric conductivity is preferably $10^{12}\Omega$/cm (25°C, 10% RH) or less before and after development process. When the photographic material of the present invention is not provided with a layer having the electric conductivity, the electric resistance is from 10^{15} to $10^{16}\Omega$/cm (25°C, 10% RH) or so.

Materials preferably used as electric conductive materials are crystalline metal oxide grains, and those containing oxygen deficiency, those containing a little amount of different atoms which form a donor against the metal oxide used are preferred as, in general, they have high electric conductivity, and particularly the latter is preferred as they do not give fog to the silver halide emulsion. Preferred examples of the metal oxides include ZnO, TiO_2, SnO_2, Al_2O_3, In_2O_3, SiO_2, MgO, BaO, MoO_3, V_2O_5, or composite oxides of them, particularly ZnO, TiO_2 and SnO_2 are preferred. As examples of the metal oxides containing different atoms, for example, addition of Al or In to ZnO, Sb, Nb and halogen element to SnO_2, Nb and Ta to TiO_2 are effective. The addition amount of these different atoms is preferably from 0.01 mol% to 30 mol%, particularly preferably from 0.1 mol% to 10 mol%. Further, silicone compounds may be added during grain formation for improving fine grain dispersion and transparency.

These metal oxide fine grains have electric conductivity and the volume resistivity is $10^7\Omega$/cm or less, particularly $10^5\Omega$/cm or less. The lower limit of the volume resistivity is preferably $10^{-4}\Omega$/cm or so.

These oxides are disclosed in JP-A-56-143431, JP-A-56-120519 and JP-A-58-62647.

Further, as disclosed in JP-B-59-6235, electric conductive materials prepared by sticking the above metal oxides on other crystalline metal oxide grains or fibrous materials (e.g., titanium oxide) may be used.

The grain size which can be used is preferably 1 µm or less, but when it is 0.5 µm or less, the stability after dispersion is good and easy to use. Further, when electric conductive grains of sizes of 0.3 µm or less are used to reduce light scattering as far as possible, it becomes feasible to prepare a transparent photographic material.

When the electric conductive material is acicular or fibrous, preferably the length is 30 µm or less and the diameter is 1 µm or less, particularly preferably the length is 10 µm or less and the diameter is 0.3 µm or less, and the length/diameter ratio is 3 or more.

These metal oxide having electric conductivity may be coated without a binder, and in such a case it is preferred to further coat a binder thereon.

The metal oxide is further preferably coated with a binder.

The binder is not particularly limited and the binder for use in the above magnetic layer can be used. For example, water-soluble binders such as gelatin, dextran, polyacrylamide, starch, and polyvinyl alcohol may be used, or synthetic polymer binders such as poly(meth)acrylate, polyvinyl acetate, polyurethane, polyvinyl chloride, polyvinylidene chloride, styrene/butadiene copolymer, polystyrene, polyester, polyethylene, polyethylene oxide, polypropylene, and polycarbonate may be used in organic solvent, further, these polymer binders may be used in the form of dispersion in water.

Spherical and fibrous metal oxides may be used in admixture.

The addition amount of the metal oxide in the present invention is preferably from 0.0005 to 1 g/m^2, more preferably from 0.0009 to 0.5 g/m^2, and particularly preferably from 0.0012 to 0.3 g/m^2.

A heat resisting agent, a weather resisting agent, an inorganic grain, a water-soluble resin, and an emulsion may be added to the layer comprising metal oxide for the purpose of matting and film quality improvement within the range not hindering the effect of the present invention.

For example, inorganic fine grains may be added from the metal oxide into the layer. Examples of inorganic fine grains added are silica, colloidal silica, alumina, alumina sol, caolin, talc, mica, and calcium carbonate. The average grain size of the fine grains is preferably from 0.01 to 10 µm, more preferably from 0.01 to 5 µm, and the amount is preferably from 0.05 to 10 parts, particularly preferably from 0.1 to 5 parts in weight ratio to the solid part in the coating solution.

The layers to which the electric conductive metal oxides are added are not particularly limited, and there can be cited, for example, a protective layer, an interlayer, an emulsion layer, an UV layer, an antihalation layer, a subbing layer, a backing layer, and a backing protective layer. The preferred are a protective layer, an interlayer, an anti-halation layer, a subbing layer, a backing layer, and a backing protective layer, and the more preferred are a subbing layer, a backing layer, an interlayer, and an antihalation layer.

Specifically, the addition of the electric conductive material to the backing layer (particularly, a first backing layer nearest to the support) is most preferred.

Those disclosed in JP-A-4-62543, p. 6, right upper column, line 17 to p. 10, right upper column, line 17, and Kokai Giho 94-6023 (Open Technique), Hatsumei Kyokai, p. 18, left column, line 3 to p. 83, right column, line 10 are preferably used for the photographic material of the present invention.

With respect to the package (patrone) for encasing the photographic material of the present invention, any known package may be used, but those having the forms disclosed in U.S. Patent 4,834,306, Fig. 1 to Fig. 3, U.S. Patent 4,846,418, Fig. 1 to Fig. 3, and U.S. Patent 5,296,887, Fig. 1 to Fig. 7 are particularly preferred.

Every film format can be applied to the present invention such as type 135 according to Japanese Industrial Standards, JIS K-7519 (1982), those disclosed in JP-A-4-123047, JP-A-4-123059, JP-A-4-123051, JP-A-4-125560, JP-A-4-156450 and JP-A-4-287040, as well as any known formats.

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

EXAMPLE 1

Multilayer color photographic material Sample 101 was prepared as follows.

1) Support

The support which was used in the present invention was prepared as follows.

100 weight parts of commercially available polyethylene-2,6-naphthalate polymer and 2 weight parts of Tinuvin P. 326 (product of Geigy), as an ultraviolet absoring agent, were dried in a usual method, then, melted at 300°C, subsequently, extruded through a T-type die, and stretched 3.0 times in a lengthwise direction at 140°C and then 3.0 times in a width direction at 130°C, and further fixed for 6 seconds at 250°C and the PEN film having the thickness of 90 µm was obtained.

Further, a part of it was spooled around a stainless steel spool having a diameter of 20 cm and provided a heat history at 110°C for 48 hours.

2) Coating of a subbing layer

A subbing layer having the following composition was coated on each side of the above support after both surfaces of the support were subjected to corona discharge, UV discharge, further, glow discharge and flame discharge treatments. The subbing layer was provided on the side which was heated at a higher temperature at the time of stretching. The corona discharge treatment was carried out using solid state corona processor model 6KVA available from Pillar Co., Ltd. which can treat the support of 30 cm wide at a rate of 20 m/min. At that time, the treatment of 0.375 KV·A·min/m^2 was conducted to the support from the reading of the electric current and voltage. The discharge frequency at the treatment time was 9.6 KHz, gap clearance between the electrode and the induction roll was 1.6 mm. UV discharge treatment was conducted by heating at 75°C. Further, glow discharge treatment was conducted by a cylindrical electrode at 3,000 w and irradiated for 30 sec.

Gelatin	3 g
Distilled Water	25 cc
Sodium-α-sulfodi-2-ethylhexylsuccinate	0.05g
Formaldehyde	0.02g
Salicylic Acid	0.1 g
Diacetyl Cellulose	0.5 g
p-Chlorophenol	0.5 g
Resorcin	0.5 g
Cresol	0.5 g
$(CH_2{=}CHSO_2CH_2CH_2NHCO)_2CH_2$	0.2 g
Trimethylolpropane Triazine	0.2 g
Trimethylolpropanetristoluenediisocyanate	0.2 g
Methanol	15 cc
Acetone	85 cc
Formaldehyde	0.01g
Acetic Acid	0.01g
Concentrated Hydrochloric Acid	0.01g

3) Coating of a backing layer

An antistatic layer, a magnetic recording layer and a sliding layer having the following compositions were coated on one side of the above support as a backing layer after being coated with a subbing layer.

3-1) Coating of an antistatic layer

3-1-1) Preparation of electrically conductive fine grain dispersion solution (a composition dispersion solution of stannic oxide-antimony oxide) 230 weight parts of stannic chloride hydrate and

23 weight parts of antimony trichloride were dissolved in 3,000 weight parts of ethanol and homogeneous solution was obtained. An aqueous sodium hydroxide solution (1N) was dropwise added to the above solution until the pH of the solution reached 3, thereby the coprecipitate of colloidal stannic oxide and antimony oxide was obtained. The thus-obtained coprecipitate was allowed to stand at 50°C for 24 hours and obtained reddish brown colloidal precipitate.

The reddish brown colloidal precipitate was isolated by a centrifugal separator. Water was added to the precipitate and washed by centrifugation to remove excessive ion. The excessive ion was removed by repeating this operation three times.

200 weight parts of the colloidal precipitate from which the excessive ion was removed was again dispersed in 1,500 weight parts of water, atomized in a kiln heated to 650°C, thereby a bluish fine grain powder of a composite of stannic oxide-antimony oxide having an average grain size of 0.005 μm was obtained. The specific resistance of this fine grain powder was 5 Ω·cm.

The pH of the mixed solution comprising 40 weight parts of the above fine grain powder and 60 weight parts of water was adjusted to 7.0. This mixed solution was dispersed coarsely by a disperser, then dispersed using a horizontal sand mill (Dyno Mill, manufactured by WILLYA. BACHOFENAG) until the residence time reached 30 minutes, thus the objective product was prepared. The average grain size of the second agglomerate was about 0.04 μm. 3-1-2) Coating of an electrically conductive layer

The following formulation was coated on the support so as to the dry film thickness reached 0.2 µm and dried at 115°C for 60 seconds.

Electrically Conductive Fine Grain Dispersion Solution prepared in 3-1-1)	20 weight parts
Gelatin	2 weight parts
Water	27 weight parts
Methanol	60 weight parts
p-Chlorophenol	0.5 weight parts
Resorcin	2 weight parts
Polyoxyethylenenonylphenyl Ether	0.01 weight parts

The resistance of the obtained electrically conductive film was $10^{8.0}$ (100 V) and this showed excellent antistatic property.

3-1) Coating of a magnetic recording layer

220 g of water and 150 g of silane coupling agent of poly(polymerization degree: 16)oxyethylenetrimethoxysilane were added to 1,100 g of magnetic substance Co-adherend γ-Fe_2O_3 (acicular, major axis: 0.14 µm, minor axis: 0.03 µm, specific surface area: 41 m^2/g, saturation magnetization: 89 emu/g, the surface was surface treated with 2 wt%, respectively, based on Fe_2O_3, of aluminum oxide and silicon oxide, coercive force: 930 Oe, Fe^{+2}/Fe^{+3} is 6/94) and kneaded in an open kneader for 3 hours. This coarsely dispersed viscous solution was dried at 70°C a whole day and night and the water was removed, and heat treated at 110°C for 1 hour to prepare the surface treated magnetic grains.

Further, this product was again kneaded in the open kneader according to the following formulation.

The Above Surface Treated Magnetic Grain	1,000 g
Diacetyl Cellulose	17 g
Methyl Ethyl Ketone	100 g
Cyclohexanone	100 g

Further, this product was finely dispersed by a sand mill (1/4 G) at 200 rpm for 4 hours according to the following formulation.

The Above Kneaded Product	100 g
Diacetyl Cellulose	60 g
Methyl Ethyl Ketone	300 g
Cyclohexanone	300 g

Further, acetyl cellulose and $C_2H_5C(CH_2OCONH\text{-}C_6H_3(CH_3)NCO)_3$ as a hardening agent were added in an amount of 20 wt% based on the binder. This was diluted with equal amounts of methyl ethyl ketone and cyclohexanone so that the obtained solution provided the viscosity of 80 cp. The solution was coated on the above electrically conductive layer using a bar coater, the film thickness was 1.2 µm. Coating was carried out so that the coating amount of the magnetic substance was 0.6 g/m^2. Silica grains (0.3 µm) as a matting agent and aluminum oxide (0.5 µm) as an abrasive were added each in an amount of 10 mg/m^2. Drying was conducted at 115°C for 6 min (the roller and transporting apparatus of the drying zone were 115°C).

The increment of the color density of D^B of the magnetic recording layer was about 0.1 when blue filter was used at status M of X-light. Saturation magnetization moment of the magnetic recording layer was 4.2 emu/m^2, coercive force was 923 Oe, and squarish ratio was 65%.

3-1) Preparation of a sliding layer

A sliding layer was prepared by coating the following composition so that the solid part of the coating amount became the following amounts, and dried at 110°C for 5 min to prepare a sliding layer.

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

Compound a/Compound b (6/9) were dissolved in the solution of xylene and propylene glycol monomethyl ether (volume ratio: 1/1) of the same amount heated at 105°C, this solution was poured into 10 times of propylene glycol monomethyl ether (25°C) and finely dispersed. This was further diluted with 5 times of acetone, dispersed again using a high pressure homogenizer and the obtained dispersion (average grain size: 0.01 µm) was added to the coating solution.

The obtained sliding layer showed excellent performances of, dynamic friction coefficient: 0.06 (a stainless steel hard ball of 5 mmϕ, load: 100 g, speed: 6 cm/min), static friction coefficient: 0.07 (clip method). The sliding property with the surface of the emulsion shown below provided dynamic friction coefficient of 0.12.

4) Coating of a light-sensitive layer

Layers having the following composition were superposed on the opposite side of the above obtained backing layer and a color negative photographic film was prepared.

Composition of Light-Sensitive Layer

The main components for use in each layer are classified as follows:

ExC:	Cyan Coupler
ExM:	Magenta Coupler
ExY:	Yellow Coupler
ExS:	Sensitizing Dye
UV:	Ultraviolet Absorber
HBS:	High Boiling Point Organic Solvent
H:	Hardening Agent for Gelatin

The numeral corresponding to each component indicates the coated amount in unit of g/m^2, and the coated amount of silver halide is shown as the calculated weight of silver. Further, in the case of a sensitizing dye, the coated amount is indicated in unit of mol per mol of silver halide in the same layer.

Sample 101

First Layer: Antihalation Layer

Black Colloidal Silver	0.18 as silver
Gelatin	1.40
ExM-1	0.18
ExF-1	2.0×10^{-3}
HBS-1	0.20

Second Layer: Interlayer

Silver Iodobromide Emulsion G	0.065 as silver
2,5-Di-t-pentadecylhydroquinone	0.18
ExC-2	0.020
UV-1	0.060
UV-2	0.080
UV-3	0.10
HBS-1	0.10
HBS-2	0.020
Gelatin	1.04

Third Layer: Low Sensitive Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion A	0.25 as silver
Silver Iodobromide Emulsion B	0.25 as silver
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-7	0.0050
ExC-8	0.010
Cpd-2	0.025
HBS-1	0.10
Gelatin	0.87

Fourth Layer: Middle Sensitive Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion D	0.70 as silver
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	0.025
ExC-7	0.0010
ExC-8	0.0070
Cpd-2	0.023
HBS-1	0.10
Gelatin	0.75

Fifth Layer: High Sensitive Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion E	1.40 as silver
ExS-1	2.4×10^{-4}
ExS-2	1.0×10^{-4}
ExS-3	3.4×10^{-4}
ExC-1	0.12
ExC-3	0.045
ExC-6	0.020
ExC-8	0.025
Cpd-2	0.050
HBS-1	0.22
HBS-2	0.10
Gelatin	1.20

Sixth Layer: Interlayer

Cpd-1	0.10
HBS-1	0.50
Gelatin	1.10

Seventh Layer: Low Sensitive Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion C	0.35 as silver
ExS-4	3.0×10^{-5}
ExS-5	2.1×10^{-4}
ExS-6	8.0×10^{-4}
ExM-1	0.010
ExM-2	0.33
ExM-3	0.086
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.72

Eighth Layer: Middle Sensitive Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion D	0.80 as silver
ExS-4	3.2×10^{-5}
ExS-5	2.2×10^{-4}
ExS-6	8.4×10^{-4}
ExM-2	0.13
ExM-3	0.030
ExY-1	0.018
HBS-1	0.16
HBS-3	8.0×10^{-3}
Gelatin	0.89

Ninth Layer: High Sensitive Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion E	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	0.030
ExM-4	0.040
ExM-5	0.019
Cpd-3	0.040
HBS-1	0.25
HBS-2	0.10
Gelatin	1.40

Tenth Layer: Yellow Filter Layer

Yellow Colloidal Silver	0.030 as silver
Cpd-1	0.16
HBS-1	0.60
Gelatin	0.60

Eleventh Layer: Low Sensitive Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion C	0.18 as silver
ExS-7	8.6×10^{-4}
ExY-1	0.020
ExY-2	0.22
ExY-3	0.50
ExY-4	0.020
HBS-1	0.28
Gelatin	1.08

Twelfth Layer: Middle Sensitive Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion D	0.40 as silver
ExS-7	7.4×10^{-4}
ExC-7	7.0×10^{-3}
ExY-2	0.050
ExY-3	0.10
HBS-1	0.050
Gelatin	0.78

Thirteenth Layer: High Sensitive Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion F	0.10 as silver
ExS-7	4.0×10^{-4}
ExY-2	0.10
ExY-3	0.10
HBS-1	0.070
Gelatin	0.86

Fourteenth Layer: First Protective Layer

Silver Iodobromide Emulsion G	0.20 as silver
UV-4	0.11
UV-5	0.17
HBS-1	5.0×10^{-2}
Gelatin	1.00

Fifteenth Layer: Second Protective Layer

H-1	0.40
B-1 (diameter: 1.7 µm)	5.0×10^{-2}
B-2 (diameter: 1.7 µm)	0.10
B-3	0.10
S-1	0.20
Gelatin	1.20

Further, W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salts, lead salts, gold salts, platinum salts, iridium salts and rhodium salts were appropriately included in each layer to improve preservability, processing properties, pressure resistance, fungicidal and biocidal properties, antistatic properties and coating properties.

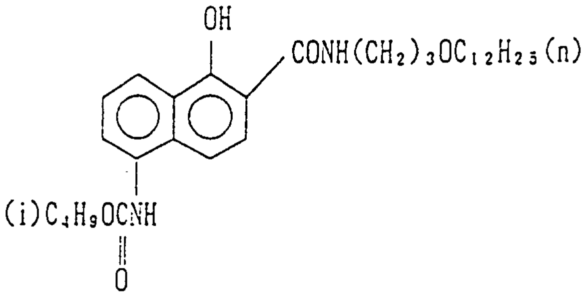
TABLE 1

Emulsion	Average AgI Content (%)	Average Grain Size (µm)	Variation Coefficient of the Grain Size (%)	Diameter/ Thickness Ratio	Silver Amount Ratio [core/middle/shell] (AgI content)	Grain Structure and Form
A	4.0	0.45	27	1	[1/3] (13/1)	double structure, octahedral grain
B	8.9	0.70	14	1	[3/7] (25/2)	double structure, octahedral grain
C	2.0	0.55	25	7	—	uniform structure, tabular grain
D	9.0	0.65	25	6	[12/59/29] (0/11/8)	triple structure, tabular grain
E	9.0	0.85	23	5	[8/59/33] (0/11/8)	triple structure, tabular grain
F	14.5	1.25	25	3	[37/63] (34/3)	double structure, tabular grain
G	1.0	0.07	15	1	—	uniform structure, fine grain

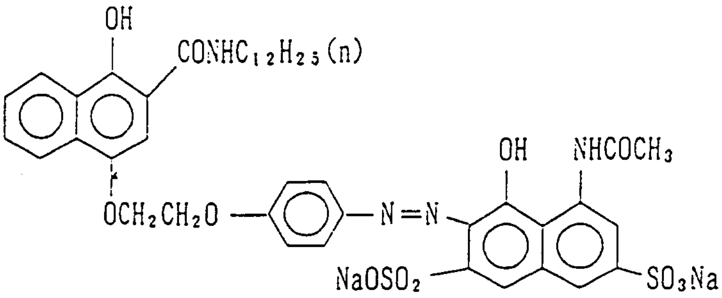
In Table 1,

(1) Emulsions A to F were subjected to reduction sensitization during preparation of the grains with thiourea dioxide and thiosulfonic acid according to the examples of JP-A-2-191938.
(2) Emulsions A to F were subjected to gold sensitization, sulfur sensitization and selenium sensitization in the presence of the spectral sensitizers indicated in each light-sensitive layer and sodium thiocyanate according the the examples of JP-A-3-237450.
(3) Low molecular weight gelatin was used in the preparation of tabular grains according to the examples of JP-A-1-158426.
(4) There were observed, using a high pressure electron microscope, such dislocation lines as disclosed in JP-A-3-237450 in tabular grains and regular crystal grains having a grain structure.

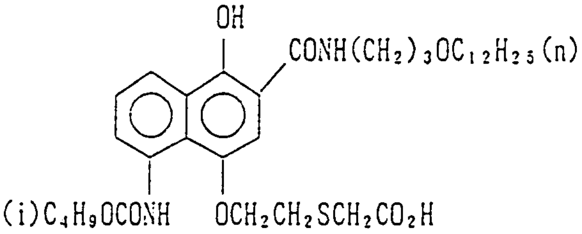
ExC-1



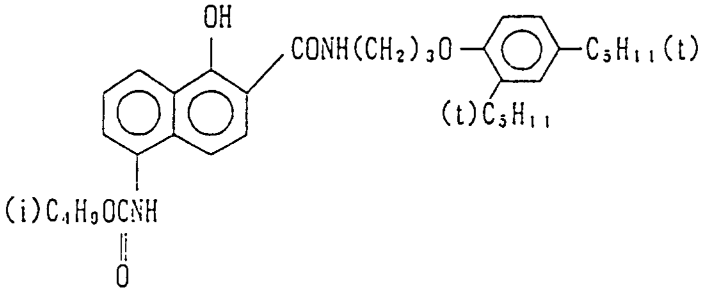
ExC-2



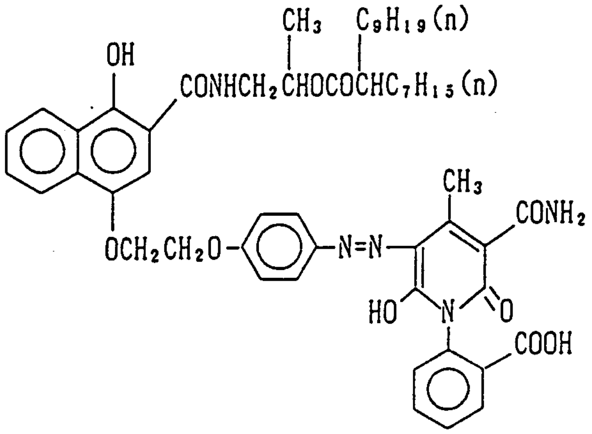
ExC-3



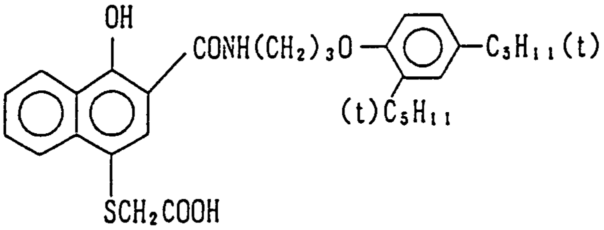
ExC-4



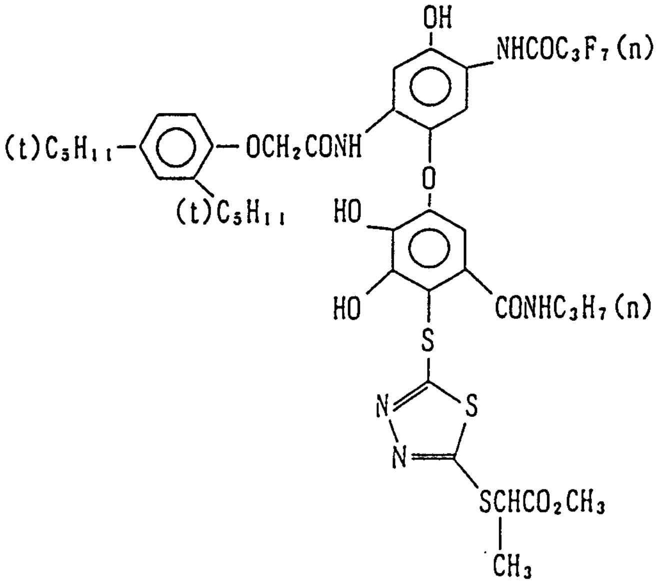
ExC－5



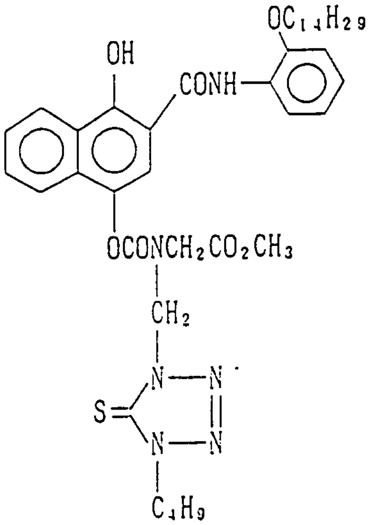
ExC－6



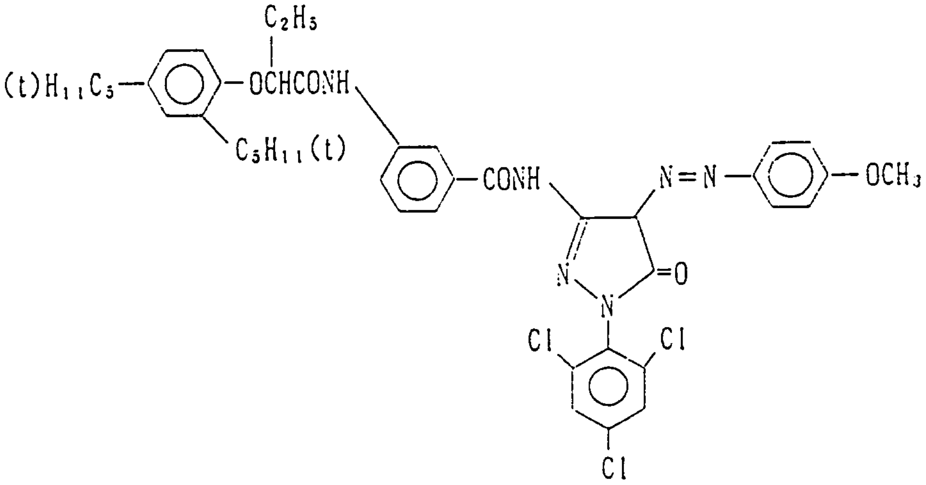
ExC－7



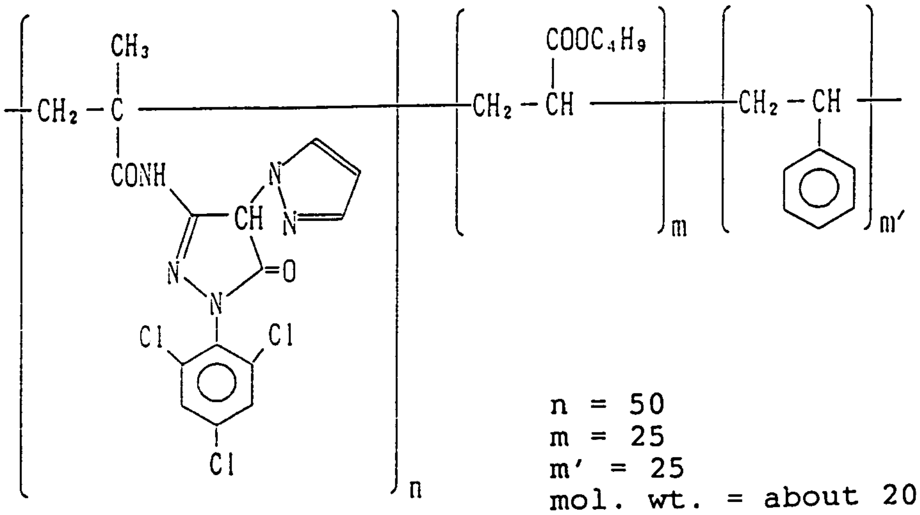
ExC－8


OC14H29
OH
CONH
OCONCH2CO2CH3
CH2
N
N
S
N
N
C4H9

ExM－1

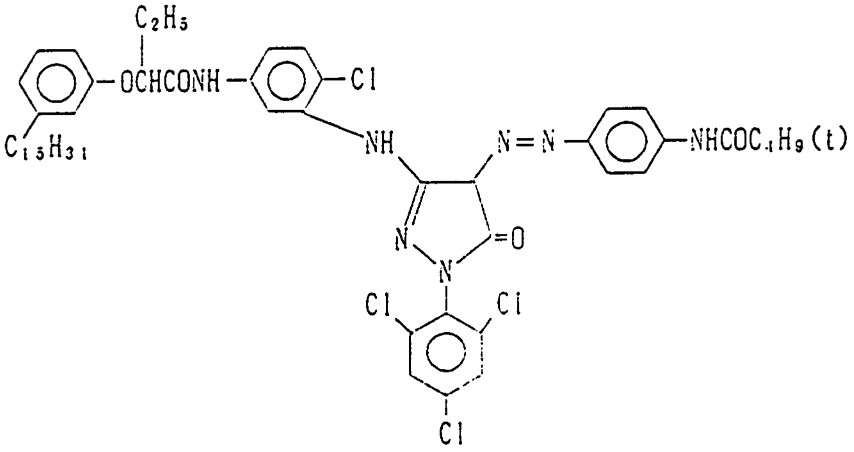

C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N=N
OCH3
N
N
=O
Cl
Cl
Cl

ExM-2

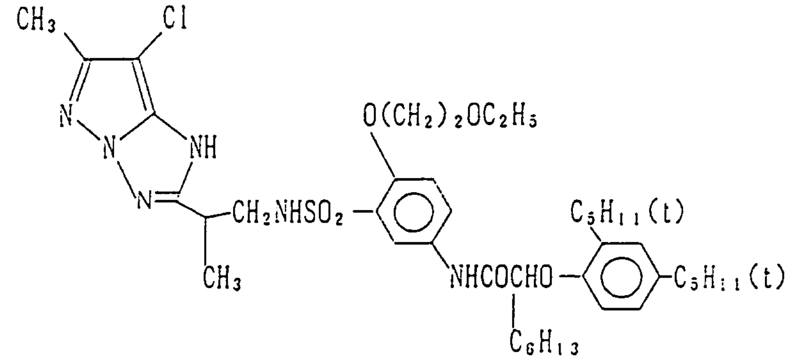


n = 50
m = 25
m' = 25
mol. wt. = about 20,000

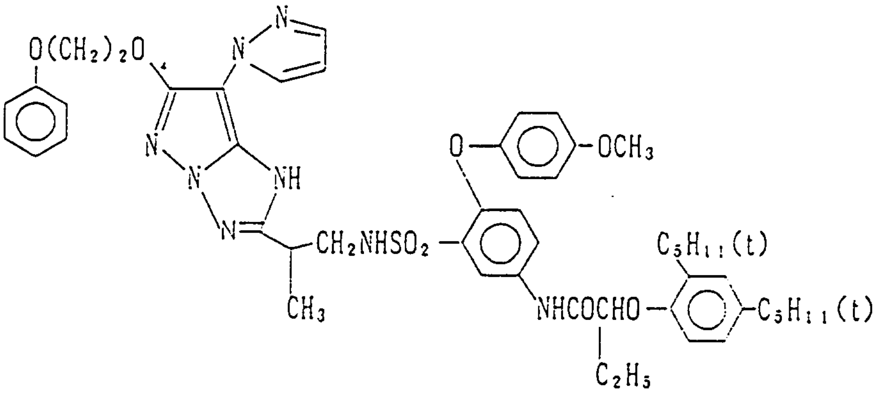
ExM-3



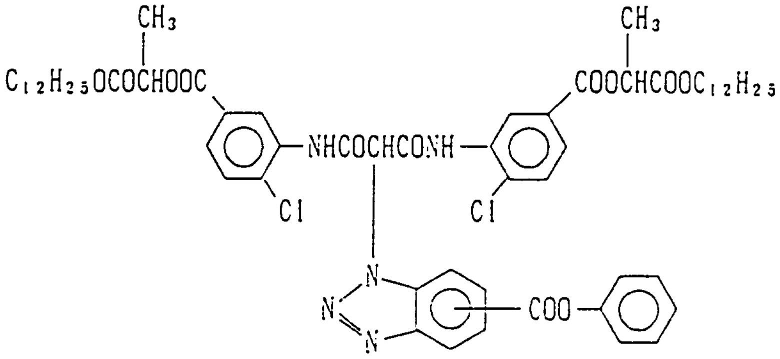
ExM－4



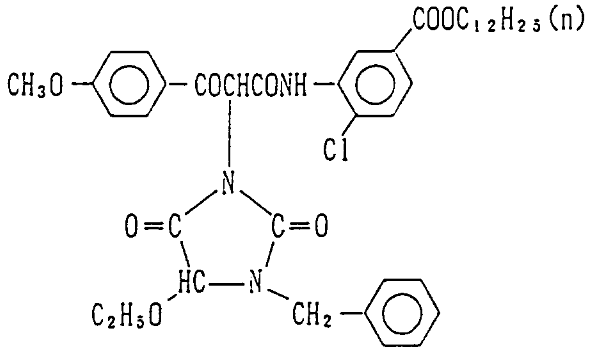
ExM－5



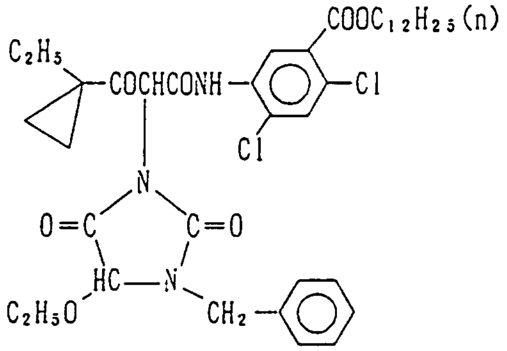
ExY－1



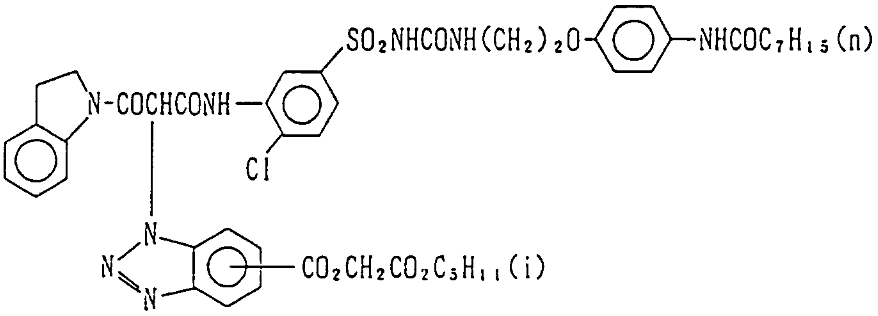
ExY－2



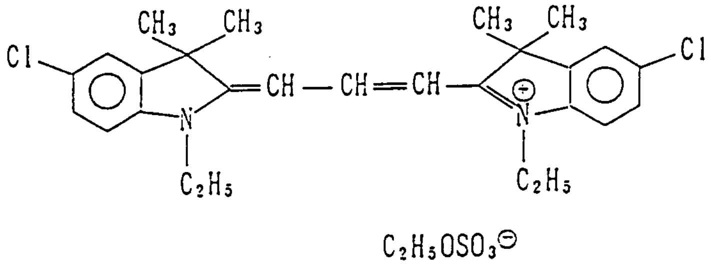
ExY－3



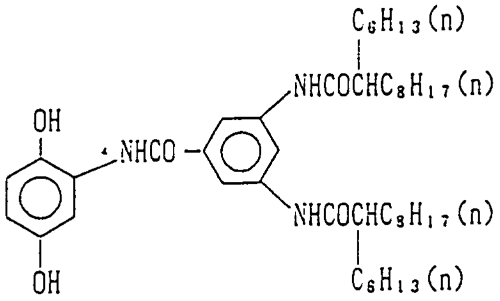
ExY－4



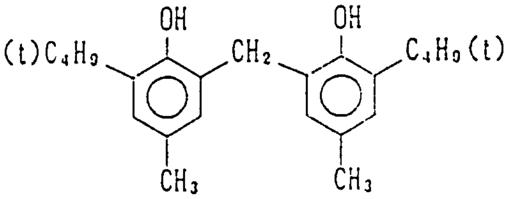
ExF−1



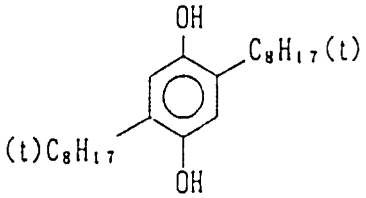
Cpd−1



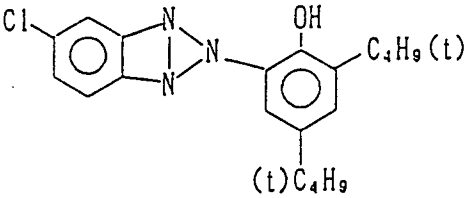
Cpd−2



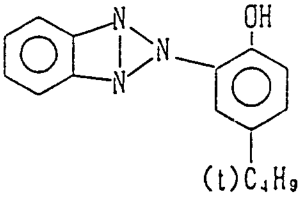
Cpd−3



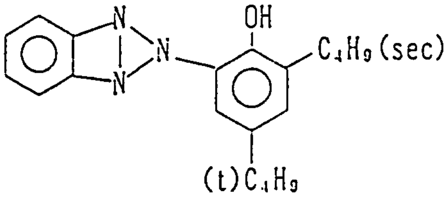
UV－1



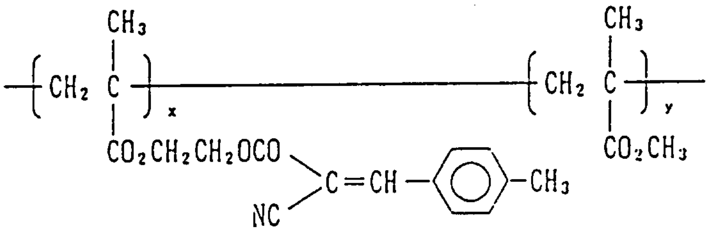
UV－2



UV－3

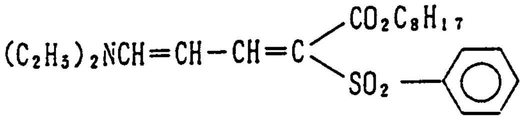


UV－4



x : y =70 : 30 (wt%)

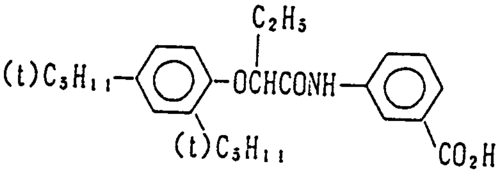
UV-5



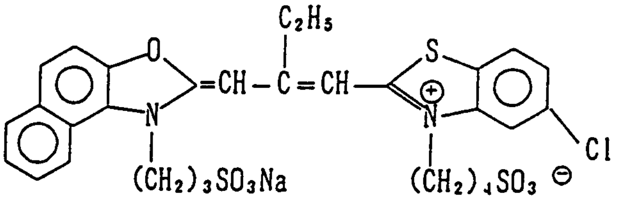
HBS-1 Tricresyl Phosphate

HBS-2 Di-n-butyl Phthalate

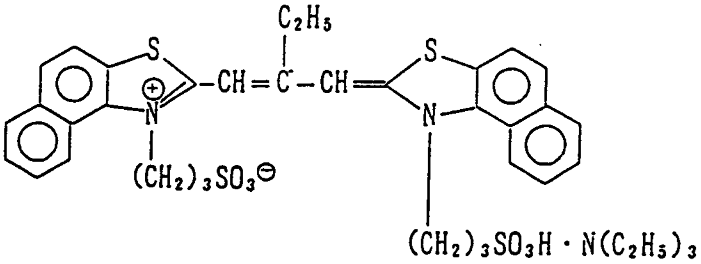
HBS-3



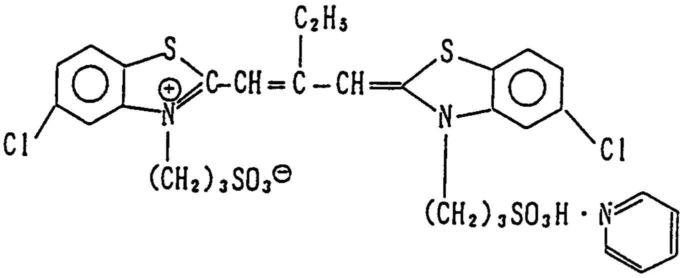
ExS－1



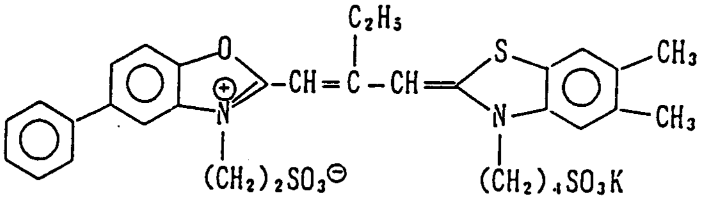
ExS－2



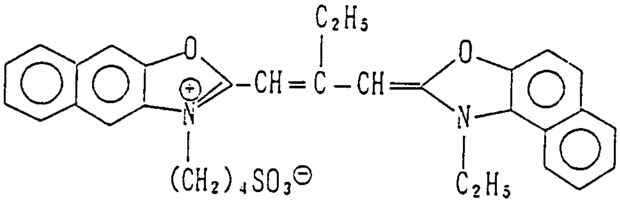
ExS－3



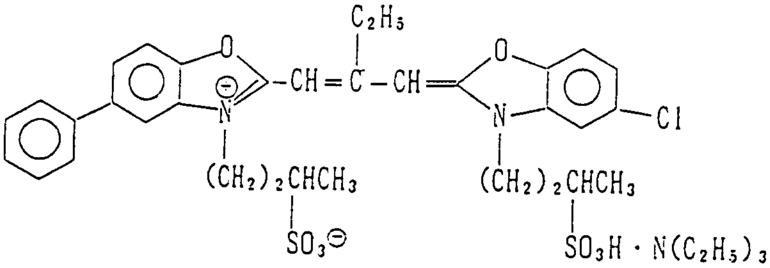
ExS－4



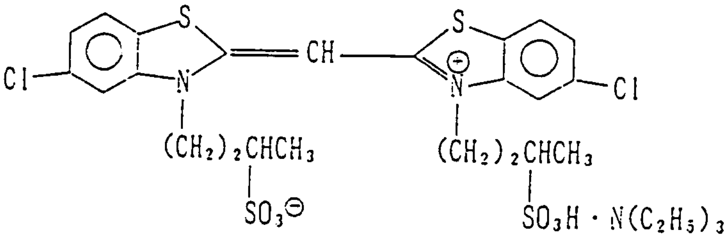
ExS-5



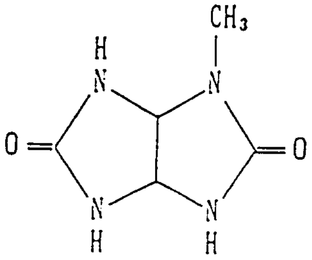
ExS-6



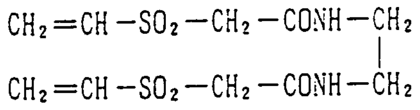
ExS-7



S-1

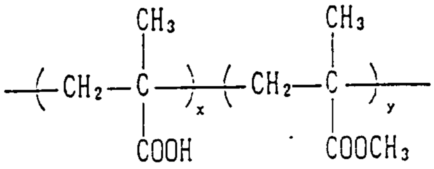


H − 1



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

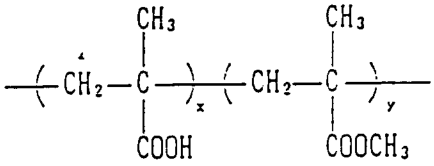
B − 1



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

x/y=10/90

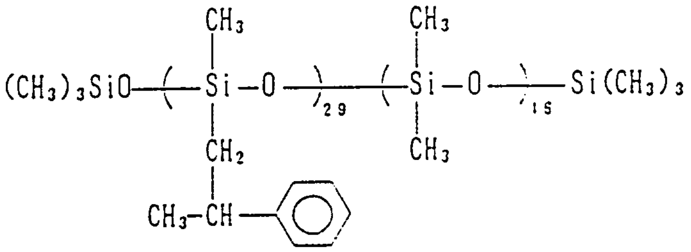
B − 2



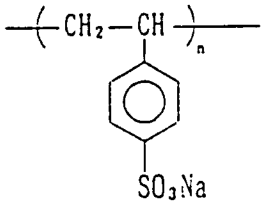
$$-\!\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y\!-$$

x/y=40/60

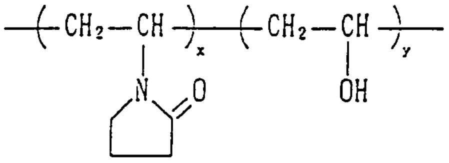
B − 3



B − 4

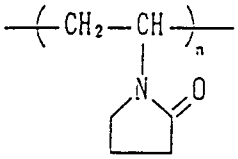


B－5



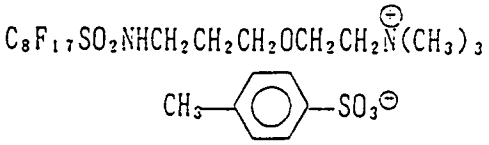
x/y=70/30

B－6

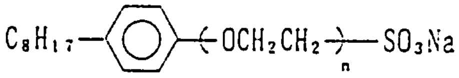


(mol. wt. about 10,000)

W－1

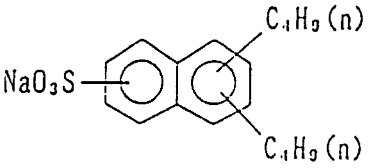


W－2

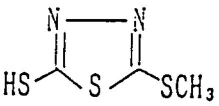


n＝2 ～ 4

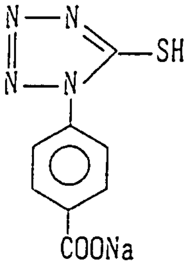
W－3



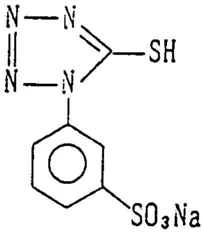
F－1



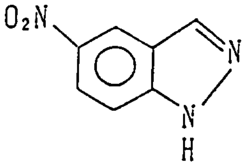
F－2



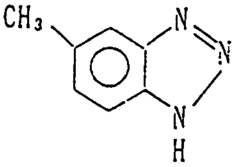
F－3



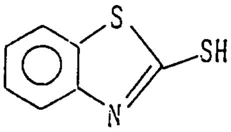
F－4



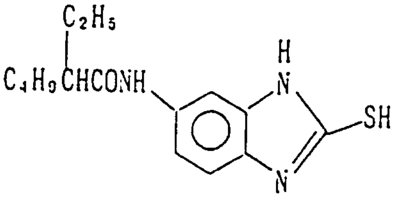
F－5



F－6



F－7



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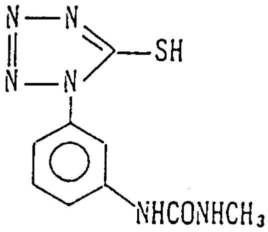

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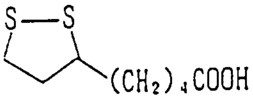
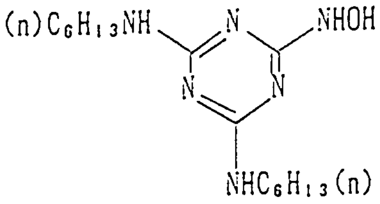
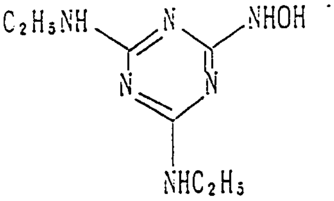


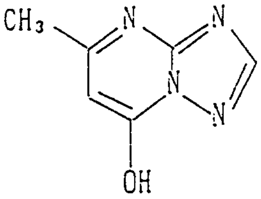
F－１０



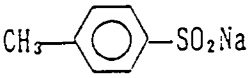
F－１１



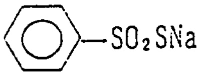
F－１２



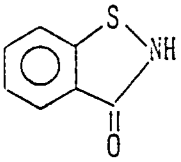
F－１３



F－１４



F－１５



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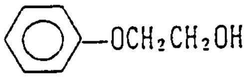
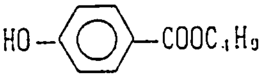


F－１７



Multilayer color photographic Sample 101 was subjected to continuous wedge exposure, then processed using an automatic processor according to the following process.

Processing Step				
Step	Processing Time	Processing Temperature (°C)	Replenishment Rate* (ml)	Tank Capacity (liter)
Color Development	3 min 10 sec	38.0	20	20
Bleaching	1 min 00 sec	38.0	25	40
Washing (1)	15 sec	24	countercurrent system from (2) to (1)	10
Washing (2)	15 sec	24	15	10
Fixing	3 min 00 sec	38	15	30
Washing (3)	30 sec	24	countercurrent system from (4) to (3)	10
Washing (4)	30 sec	24	1,200	10
Stabilization	30 sec	38	20	10
Drying	4 min 20 sec	55		

* Replenishment rate per 1 meter of 35 mm wide photographic material

The composition of each processing solution is described below.

Color Developing Solution		
	Tank Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic Acid	1.0	1.3
Disodium Catechol-3,5-disulfonate	0.3	0.4
Disodium N,N-Bis(2-sulfonatoethyl)hydroxylamine	2.0	2.5
Sodium Sulfite	4.0	4.9
Potassium Carbonate	30.0	39.3
Potassium Bromide	1.4	0.25
Potassium Iodide	1.5 mg	—
Hydroxylamine Sulfate	2.4	3.2
4-[N-Ethyl-N-(β-hydroxyethyl)-amino]-2-methylaniline Sulfate	4.5	6.2
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	10.05	10.15

Bleaching Solution		
	Tank Solution (g)	Replenisher (g)
Chelating Compound (shown in Table A)	0.06 mol	0.072 mol
Ferric Nitrate Nonahydrate	0.05 mol	0.06 mol
Sodium Persulfate	shown in Table A	1.2 mol times of tank soln.
Compound Represented by Formula (III) (shown in Table A)	shown in Table A	1.2 mol times of tank soln.
Organic Base (shown in Table A)	shown in Table A	1.2 mol times of tank soln.
Imidazole	1.0	1.2
Sodium Chloride	20	24
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with sodium hydroxide and nitric acid)	4.5	4.0

Fixing Solution A		
	Tank Solution (g)	Replenisher (g)
Sodium Sulfite	20.0	22.0
Sodiumthiosulfate	180	200
Imidazole	10	12
Acetic Acid (90%)	3.3	4.0
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	6.7	6.8

Stabilizing Solution A (replenisher equals tank solution) (unit: g)	
Sodium p-Toluenesulfinate	0.03
Polyoxyethylene-p-monononylphenyl Ether (average polymerization degree: 10)	0.2
Disodium Ethylenediaminetetraacetate	0.05
1,2,4-Triazole	1.3
1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75
Water to make	1.0 ℓ
pH	8.5

The above-processed multilayer color photographic Sample 101 was examined for the remaining silver amount of the part of the maximum color density using fluorescent X-ray analysis. The results obtained are shown in Table A.

In addition, Dmin measured through green light (G light) of the processed Sample 101 was read.

Processing was conducted in the same manner except that CN-16X N2X bleaching solution for color negative films was used as standard processing and bleaching was conducted at 38°C for 3 minutes.

Dmin value of each sample was indicated as ΔDmin taking that of the sample of standard process as standard. (ΔDmin = Dmin of each sample - Dmin of the standard sample)

Sample 101 was exposed to 100 Lux at 4,800°K for 1/100 sec and bleaching processed with each bleaching agent (bleaching time was 10 min for desilvering completely). The cyan density and magenta density of the obtained sample was measured.

These values were indicated by the difference between each sample and the sample of standard process same as in the above Dmin values (ΔD_R and ΔD_G).

The results obtained are also shown in Table A.

TABLE A

Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount ($\mu g/cm^2$)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_R	Reduction of Magenta Density ΔD_G	Remarks
101	–	0.12	III-1 (0.03)	acetic acid (0.5)	8.5	0.22	-0.25	-0.45	Comparison
102	–	0.12	III-1 (0.03)	4-sulfophthalic acid (0.5)	9.7	0.25	-0.19	-0.25	"
103	I-1	–	–	acetic acid (0.5)	80.2	0.08	-0.06	0.00	"
104	–	0.12	–	acetic acid (0.5)	102.2	0.16	-0.03	-0.02	"
105	–	0.12	III-1 (0.03)	succinic acid (0.5)	9.7	0.24	-0.10	-0.26	"

TABLE A (cont'd)

Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount (μg/cm^2)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_R	Reduction of Magenta Density ΔD_G	Remarks
106	Comparative Compound A	0.12	—	acetic acid (0.5)	12.1	0.20	-0.19	-0.35	Comparison
107	"	0.12	III-1 (0.03)	acetic acid (0.5)	10.9	0.21	-0.18	-0.40	"
108	"	0.12	—	succinic acid (0.5)	13.5	0.20	-0.18	-0.40	"
109	"	0.12	III-1 (0.03)	succinic acid (0.5)	12.6	0.22	-0.16	-0.25	"
110	Comparative Compound B	0.12	III-1 (0.03)	succinic acid (0.5)	12.9	0.21	-0.16	-0.27	"

TABLE A (cont'd)

Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount (μg/cm^2)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_R	Reduction of Magenta Density ΔD_G	Remarks
111	Comparative Compound C	0.12	III-1 (0.03)	succinic acid (0.5)	11.1	0.24	-0.17	-0.30	Comparison
112	I-1	0.12	—	acetic acid (0.5)	7.2	0.11	-0.14	-0.17	Invention
113	I-1	0.12	III-1 (0.03)	acetic acid (0.5)	4.1	0.09	0.00	-0.15	"
114	I-1	0.12	—	succinic acid (0.5)	7.3	0.09	-0.13	-0.01	"
115	I-1	0.12	III-1 (0.03)	succinic acid (0.5)	4.0	0.07	0.00	-0.01	"
116	I-2	0.12	III-1 (0.03)	succinic acid (0.5)	4.2	0.07	0.00	-0.01	"

TABLE A (cont'd)

Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount (µg/cm^2)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_G	Reduction of Magenta Density ΔD_G	Remarks
117	I-7	0.12	III-1 (0.03)	succinic acid (0.5)	4.6	0.07	0.00	-0.01	Invention
118	I-11	0.12	III-1 (0.03)	succinic acid (0.5)	4.9	0.07	0.00	-0.01	"
119	I-20	0.12	III-1 (0.03)	succinic acid (0.5)	5.1	0.07	0.00	-0.01	"
120	I-1	0.12	III-68 (0.03)	succinic acid (0.5)	4.2	0.07	0.00	-0.01	"
121	II-1	0.12	III-1 (0.03)	succinic acid (0.5)	4.1	0.07	0.00	-0.01	"
122	II-15	0.12	III-1 (0.03)	succinic acid (0.5)	4.0	0.07	0.00	-0.01	"

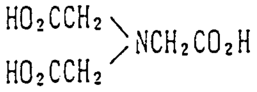
TABLE A (cont'd)

Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount ($\mu g/cm^2$)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_G	Reduction of Magenta Density ΔD_G	Remarks
123	II-19	0.12	III-1 (0.03)	succinic acid (0.5)	4.0	0.07	0.00	-0.01	Invention
124	II-48	0.12	III-1 (0.03)	succinic acid (0.5)	4.9	0.07	0.00	-0.01	"
125	I-1	0.12	III-2 (0.03)	succinic acid (0.5)	4.0	0.07	0.00	0.00	"
126	I-1	0.12	III-11 (0.03)	succinic acid (0.5)	4.0	0.07	-0.02	-0.01	"
127	I-1	0.12	III-4 (0.03)	succinic acid (0.5)	4.0	0.07	0.00	-0.01	"
128	I-1	0.12	III-1 (0.03)	glutaric acid (0.5)	4.0	0.07	0.00	-0.01	"

TABLE A (cont'd)

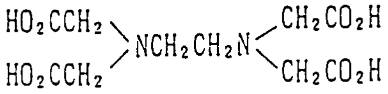
Process No.	Chelating Compound	$Na_2S_2O_8$ (mol)	Compound of Formula (III) (mol)	Organic Acid in Bleaching Solution (mol)	Remaining Amount of Silver Amount ($\mu g/cm^2$)	Increase of Stain ΔDmin	Reduction of Cyan Density ΔD_G	Reduction of Magenta Density ΔD_G	Remarks
129	I-1	0.06	III-1 (0.03)	maleic acid (0.5)	4.0	0.07	0.00	-0.01	Invention
130	I-1	0.04	III-1 (0.03)	succinic acid (0.5)	14.0	0.06	0.00	-0.01	"
131	I-1	0.60	III-1 (0.03)	succinic acid (0.5)	4.1	0.13	0.00	-0.01	"

Comparative Compound A



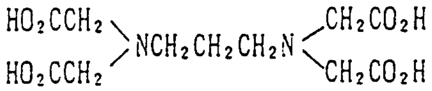
$$\left.\begin{matrix}\mathrm{HO_2CCH_2}\\\mathrm{HO_2CCH_2}\end{matrix}\right>\mathrm{NCH_2CO_2H}$$

Comparative Compound B



$$\left.\begin{matrix}\mathrm{HO_2CCH_2}\\\mathrm{HO_2CCH_2}\end{matrix}\right>\mathrm{NCH_2CH_2N}\left<\begin{matrix}\mathrm{CH_2CO_2H}\\\mathrm{CH_2CO_2H}\end{matrix}\right.$$

Comparative Compound C



$$\left.\begin{matrix}\mathrm{HO_2CCH_2}\\\mathrm{HO_2CCH_2}\end{matrix}\right>\mathrm{NCH_2CH_2CH_2N}\left<\begin{matrix}\mathrm{CH_2CO_2H}\\\mathrm{CH_2CO_2H}\end{matrix}\right.$$

It can be seen from the results in Table A that desilvering performance was incompatible with the reduction of stain in comparative samples but, according to the present invention, good results were obtained both in desilvering performance and the reduction of stain.

Further, the reduction of cyan density can be prevented by adding the compound represented by formula (III), and the reduction of magenta density can be prevented by adding the carboxylic acid of the present invention.

In addition, in Process No. 115, when processing was carried out similarly except that 0.05 mol/liter of ethylenediamine-N,N'-disuccinic acid was added to the fixing solution, ΔDmin decreased by 0.03. From this fact, the incorporation of aminopolycarboxylic acids to the fixing solution affects the improvement of the effect of the present invention.

EXAMPLE 2

Multilayer Color Photographic Paper A disclosed in Example 1 of JP-A-5-341469 was cut to a width of 127 mm and imagewise exposed using an automatic printer, then continuous processing was carried out using a roll type automatic developing processor until the color developing replenisher reached 2 times of the tank volume.

Processing Step				
Step	Processing Time (sec)	Processing Temperature (°C)	Replenishment Rate* (ml)	Tank Capacity (liter)
Color Development	45	38.5	73	8
Washing	25	24.0	400	8
Bleaching	45	38.0	60	8**
Washing	45	24.0	400	8
Fixing	45	38.0	60	8
Washing (1)	30	24.0	***	8
Washing (2)	30	24.0	***	8
Washing (3)	30	24.0	400	8
* Replenishment rate per m^2 of the photographic material				
** The bleaching tank was installed with an aeration device and aeration was carried out at a rate of 1 liter per minute.				
*** Washing (3) → (2) → (1) is a countercurrent system cascaded to the direction of the arrow.				

The composition of each processing solution is described below.

Color Developing Solution		
	Tank Solution (g)	Replenisher (g)
Water	800 ml	800 ml
Ethylenediaminetetraacetic Acid	3.0	3.0
Disodium 4,5-Dihydroxybenzene-1,3-disulfonate	0.5	0.5
Triethanolamine	12.0	12.0
Potassium Chloride	6.5	-
Potassium Bromide	0.045	0.020
Potassium Carbonate	27.0	27.0
Diaminostilbene Based Fluorescent Brightening Agent (Uvitex CK, Ciba Geigy) Sodium Sulfite	0.7 0.1	2.0 0.1
Disodium N,N-Bis(sulfonatoethyl)hydroxylamine	5.0	10.0
N-Ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline· 3/2 Sulfate·Monohydrate	5.0	11.5
Water to make	1.0 ℓ	1.0 ℓ
pH (25°C, adjusted with potassium hydroxide and sulfuric acid)	10.07	11.35

Bleaching Solution		
	Tank Solution (g)	Replenisher (g)
Water	700 ml	700 ml
Compound I-1	10.0	20.0
2,6-Pyridinedicarboxylic Acid	5.0	10.0
Acetic Acid	5.3	10.6
Gelatin	0.5	1.0
Imidazole	0.5	1.0
Ferric Nitrate (nonahydrate)	5.5	11.0
Sodium Persulfate	15.0	30.0
Sodium Bromide	7.6	16.2
pH was adjusted with sodium hydroxide	4.6	3.7
Water to make	1.0 ℓ	1.0 ℓ

Fixing Solution		
	Tank Solution (g)	Replenisher (g)
Water	700 ml	700 ml
Ethylenediamine-N,N'-disuccinic Acid	15	30.0
Sodium Thiosulfate	80	160.0
Sodium Sulfite	0.5	1.0
pH was adjusted with acetic acid	6.5	6.5
Water to make	1.0 ℓ	1.0 ℓ

Desilvering performance and the reduction of stain were excellent in the above processing.

EXAMPLE 3

The biodegradability test was conducted with Compounds I-1, II-1, II-2, II-3, II-5, II-7, II-9, II-10, II-14, II-15, II-17, II-20, III-1, III-4, III-11 and III-15 according to 302B modified Zahn-Wellens Method defined in the OECD chemical test guideline. Each of these compounds showed good biodegradability (70% or more was decomposed for 20 days). From this results, it can be seen the compounds of the present invention were preferred from the global environmental protection.

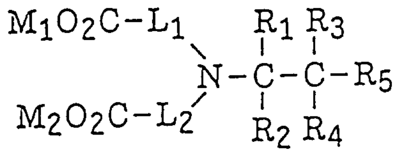
The compounds of the present invention are excellent in biodegradability and desired from the standpoint of the environmental protection, and stain generation after processing is less and excellent in desilvering.

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

Claims

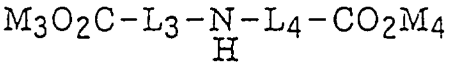
1. A method for processing a silver halide color photographic material which comprises processing an imagewise exposed silver halide color photographic material with a processing solution having bleaching ability after color

development, wherein said processing solution having bleaching ability contains at least one ferric complex salt of the compound represented by the following formula (I) or (II) and persulfate:



(I)

wherein R_1, R_2, R_3, R_4 and R_5 each represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, a carboxyl group, a phosphono group, a hydroxy group or a sulfo group, provided that at least one of R_1, R_2, R_3, R_4 and R_5 represents a carboxyl group, a phosphono group, an aliphatic group substituted with a sulfo group or a carboxyl group, an aryl group substituted with a sulfo group or a carboxyl group or a heterocyclic group substituted with a sulfo group or a carboxyl group; L_1 and L_2 each represents a divalent aliphatic group, a divalent aromatic group or a divalent linking group containing these groups; and M_1 and M_2 each represents a hydrogen atom or a cation;

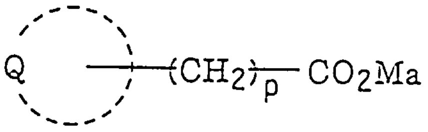


$$M_3O_2C-L_3-\underset{H}{N}-L_4-CO_2M_4 \qquad \text{(II)}$$

wherein L_3 and L_4 each represents a divalent aliphatic group, a divalent aromatic group or a divalent group containing these groups; and M_3 and M_4 each represents a hydrogen atom or a cation.

2. A method for processing a silver halide color photographic material as claimed in claim 1, wherein said processing solution having bleaching ability contains at least one heterocyclic compound having a carboxyl group or the salt thereof in the molecule.

3. A method for processing a silver halide color photographic material as claimed in claim 2, wherein said heterocyclic compound containing a carboxyl group or the salt thereof in the molecule is represented by the following formula (III):



(III)

wherein Q represents a non-metal atomic group necessary for forming a heterocyclic ring; p represents 0 or 1; and Ma represents a hydrogen atom or a cation.

4. A method for processing a silver halide color photographic material as claimed in claim 1, wherein said processing solution having the bleaching ability contains at least one hydrocarbon organic acid having two or more carboxyl groups.

5. A method for processing a silver halide color photograpahic material as claimed in claim 1, wherein said processing solution having bleaching ability contains additionally at least one hydrocarbon organic acid having two or more carboxyl group.

6. A method for processing a silver halide color photographic material as claimed in claim 1, wherein the ferric complex salt of the compound represented by formula (I) or (II) is used in an amount of from 0.001 to 1 mol per liter of the processing solution.

7. A method for processing a silver halide color photographic material as claimed in claim 1, the persulfate is used in an amount of from 0.001 to 2.0 mol per liter of the processing solution.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95111340.6

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)
D,A	EP - A - 0 602 600 (EASTMAN KODAK COMPANY) * Claims; page 4, lines 28-32 * --	1-7	G 03 C 7/407
A	EP - A - 0 520 457 (FUJI PHOTO FILM CO., LTD.) * Claims; page 27, lines 29-49 * --	1-7	
A	EP - A - 0 588 289 (FUJI PHOTO FILM CO., LTD.) * Claims; page 23, lines 9-44 * --	1-7	
D,A	EP - A - 0 430 000 (AGFA-GEVAERT AG) * Page 2, lines 13-42 * ----	1,4,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
			G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-11-1995	SCHÄFER

CATEGORY OF CITED DOCUMENTS

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

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