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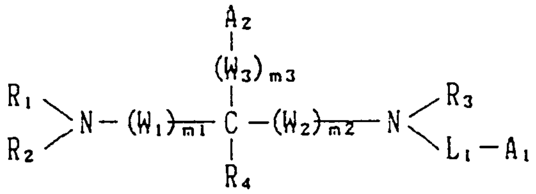
⑤④ Photographic processing composition and method of photographic processing using the same.

⑤⑦ A photographic processing solution for silver halide light-sensitive materials containing a compound of formula (I):



$$\begin{matrix} R_1 \\ R_2 \end{matrix} > N-(W_1)_{m1}-\overset{\overset{A_2}{|}}{\underset{\underset{R_4}{|}}{\overset{(W_3)_{m3}}{\overset{|}{C}}}}-(W_2)_{m2}-N < \begin{matrix} R_3 \\ L_1-A_1 \end{matrix} \qquad (I)$$

wherein R_1 represents an aliphatic group, etc.; R_2, R_3, and R_4 represents a hydrogen atom, etc.; L_1, W_1, W_2 each represents an alkylene group, etc.; and A_1 and A_2 each represents a carboxyl group, etc., or a chelate of this compound with Fe (III), etc. The processing solution can be prevented from deterioration due to incorporated and accumulated metal ions or growth of mold or bacteria. Both the compound (I) and its metal chelate are biodegradable.

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FIELD OF THE INVENTION

This invention relates to an ecologically excellent processing composition for silver halide photographic materials and a method for processing silver halide photographic materials using such a processing composition.

BACKGROUND OF THE INVENTION

In general, silver halide black-and-white (hereinafter abbreviated as B/W) light-sensitive materials are processed in the order of exposure, B/W development, fixing, washing, and the like; silver halide color light-sensitive materials are processed in the order of exposure, color development, desilvering, washing, stabilization, etc.; and silver halide color reversal light-sensitive materials are processed in the order to exposure, B/W development, reversal processing, color development, desilvering, washing, stabilization, etc.

In color development, the exposed light-sensitive silver halide grains are reduced to silver by a color developing agent in a color developer, and the thus produced oxidation product of the color developing agent reacts with a coupler to form a dye. In the subsequent desilvering, the developed silver is oxidized (bleached) to a silver salt by an oxidizing agent (bleaching agent). The silver salt and unreacted silver halide are solubilized by a fixing agent and removed from the photographic material (fixing). Bleaching and fixing are carried out either individually or simultaneously. For the details of these processing steps and compositions used therein, refer to James, The Theory of Photographic Process, 4th Ed., (1977), Research Disclosure No. 17643, pp. 28-29 (Dec., 1978), ibid, No. 18716, p. 651, left to right columns (Nov., 1979), and ibid, No. 307105, pp. 880-881 (Nov., 1989).

In addition to the aforesaid basic processing steps, various auxiliary steps, such as washing, stabilization, hardening, and stopping, are conducted for assuring photographic and physical qualities of a dye image or for maintaining stability of processing.

These processing steps are generally performed in an automatic developing machine. Photographic processing today is conducted in a variety of places from photofinishing laboratories equipped with large-scaled automatic developing machines to camera stores having a small-scaled automatic developing machine which is called "mini-labo". Under such a circumstances, reduction in processing performance has given rise to a problem.

One of the causes of reduction in processing performance resides in incorporation of a metallic ion into a processing solution. It is natural that various metallic ions should enter a processing solution through various routes. For example, water used for preparing a processing solution would be a source of a Ca ion, an Mg ion and, in some cases, an Fe ion; and gelatin used in a light-sensitive material supplies a Ca ion. Cases are met with in which a blix solution splatters to bring an iron chelate compound contained therein into a preceding developing solution. It is also observed that a processing solution containing ions as impregnated into a photographic film is carried over to the next bath.

Influences of the ions undesirably incorporated into a processing solution depend on the ions and the processing solution. More specifically, Ca and Mg ions, if incorporated into a developing solution, react with a carbonate used as a buffering agent to form sediment or sludge, which causes clogging of a filter used in the circulatory system of a developing machine and contamination of films. An Fe ion as in a transition metal salt, if incorporated into a developing solution, causes decomposition of a p-phenylenediamine color developing agent, a B/W developing agent (e.g., hydroquinone or Methol) or a preservative (e.g., hydroxylamine or a sulfite), leading to considerable reduction in photographic performance. Incorporation of transition metal ions, e.g., an Fe ion, into a bleaching solution containing hydrogen peroxide or a persulfate markedly reduces the stability of the solution, resulting in insufficient bleaching. Incorporation of transition metal ions into a fixing solution containing a thiosulfate as usual also reduces the stability of the solution, resulting in formation of turbidity or sludge, which would cause clogging of the filter set in an automatic development machine to reduce the circulating flow of the processing solution. It follows that fixing would be insufficient, and the films may be contaminated. These disorders that might occur in a fixing solution also develop in the subsequent washing step. In particular where the amount of water is cut down and the exchange rate of washing water is so decreased, such problems as decomposition of a thiosulfate (i.e., so-called sulfiding) and precipitation of silver sulfide are extremely apt to arise, often causing fatal stains on the film surface.

A stabilizer prepared from hard water containing large quantity of calcium and magnesium is likely to suffer from growth of bacteria fed on these ions as nutrients, which makes the solution turbid to cause film contamination. Transition metal ions, e.g., an Fe ion, incorporated into the stabilizer remain on films to deteriorate film preservability.

Thus, incorporation of metallic ions into processing solutions causes various disadvantages, and it has been keenly demanded to fine out solutions.

One of the approaches is to use a chelating agent as a sequestering agent, such as aminopolycarboxylic acids, e.g., ethylenediaminetetraacetic acid or diethylenetriaminepentaacetic acid; and organophosphonic acids, e.g., alkylidenediphosphonic acids.

Some of these chelating agents have been put to practical use but do not always satisfy the requirements. For example, ethylenediaminetetraacetic acid is highly effective to scavenge Ca ions but, when added to a developing solution, accelerates decomposition of a developing agent or a preservative for a developing agent in the presence of an Fe ion, resulting in an reduction in image density or an increase in fog. An alkylidenediphosphonic acid does not produce such an adverse effect even in the presence of an Fe ion but, instead, produces solid matter in a processing solution prepared from hard water having a high Ca content, also causing troubles of a developing machine.

To meet the recently increasing social demands for environmental conservation, the rate of replenishment of each processing solution has been decreasing for water saving. With this trend, the retention time of a processing solution in a tank is getting longer, and the above-mentioned problems attributed to accumulating metallic ions are getting acuter. Accordingly, a technique by which processing solutions could be protected against adverse influences of accumulating metallic ions should hold good even for a water saving processing system.

It has also been demanded from the ecological consideration to make the waste liquor from photofinishing laboratories harmless, especially by biodegradation. From this point of view, N-(2-carboxymethoxyphenyl)iminodiacetic acid (West German Patent Publication (OLS) No. 3912551), β-anilinediacetic acid, glycinedipropionic acid (EP-A-430000), and ethylenediamine-N,N'-disuccinic acid (JP-A-4-313752, the term "JP-A" as used herein means an unexamined published Japanese patent application) have been proposed as biodegradable chelating agents. However, these chelating agents do not satisfy both the requirements of biodegradability and photographic processing performance. In addition, when used in a water saving processing system, these chelating agents turned out to allow mold or bacteria to grow, which leads to clogging of a filter and stains of the light-sensitive materials.

In the case of silver halide B/W light-sensitive materials, the materials after B/W development are processed with a processing solution called a reducer containing an oxidizing agent chiefly for gradation control.

The oxidizing agent which is used for bleaching of silver halide color light-sensitive materials or for reduction of silver halide B/W light-sensitive materials generally includes ethylenediaminetetraacetato iron (III) complex salts and 1,3-diaminopropanetetraacetato iron (III) complex salts, but they are hardly biodegraded. Therefore, it has been demanded to develop a biodegradable oxidizing agent as a bleaching agent for color silver halide light-sensitive materials or as a reducing agent for B/W silver halide light-sensitive materials.

Biodegradable bleaching agents so far proposed include N-(2-carboxymethoxyphenyl)iminodiacetato ferrates as disclosed in West German Patent Publication (OLS) No. 3912551, β-alaninediacetato ferrates and glycinedipropionato ferrates as disclosed in EP-A-430000, and ethylenediamine-N,N-disuccinato ferrates as disclosed in JP-A-5-72695. However, a processing solution having bleaching ability containing such a biodegradable bleaching agent is not always effective in desilvering. Besides, it turned out that a bleaching bath containing these biodegradable bleaching agents, when used continuously, gives rise to various problems with time, such as reduction of desilvering properties, development of bleach fog, fogging of unexposed areas in the subsequent color development step due to incorporation of the bleaching bath into the color developing bath, and insufficient prevention of staining with time.

Recently, rapid color processing service with a small-scaled automatic developing machine has been widely spread, and rapid bleachability and stability in fundamental performance of bleaching agent in continuous processing are indispensable.

From the viewpoint of environmental conservation, it has also been demanded to reduce the concentration of a metal chelate compound used as a bleaching agent. However, if used in a reduced concentration, the conventional bleaching agents fail to exhibit sufficient desilvering function from the initial stage of continuous processing.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide a photographic processing composition which does not form sediment or sludge even when metallic ions are incorporated thereinto and a method for processing using the same.

A second object of the present invention is to provide a stable processing composition which undergoes no reduction of the active component or forms no component having photographically adverse influences even when metallic ions are incorporated thereinto and a method for processing using the same.

A third object of the present invention is to provide a processing composition which suppresses reduction in image preservability of a light-sensitive material due to residual metallic ions originated from the processing composition and a method for processing using the same.

A fourth object of the present invention is to provide a processing composition which gives rise to no environmental problem after discharged and a method for processing using the same.

A fifth object of the present invention is to provide a processing composition which hardly suffers from proliferation of mold or bacteria and a method for processing using the same.

A sixth object of the present invention is provide a processing composition which is easy to handle and gives rise to no environmental problem and a method for processing using the same.

A seventh object of the present invention is to provide a processing composition having bleaching ability which exhibits excellent desilvering performance even in a low concentration and a method for processing using the same.

An eighth object of the present invention is provide a processing composition having bleaching ability which is less causative of bleach fog and a method for processing using the same.

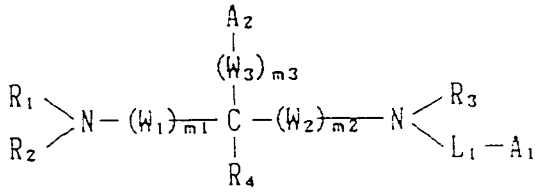
A ninth object of the present invention is to provide a processing composition having bleaching ability which is less causative of stains with time and a method for processing using the same.

A tenth object of the present invention is to provide a processing composition which stably maintains the above-mentioned performance properties even in continuous processing and a method for processing using the same.

An eleventh object of the present invention is to provide a processing composition which is advantageous particularly from the standpoint of biodegradability and environmental conservation and a method for processing using the same.

A twelfth object of the present invention is to provide a processing composition having bleaching ability which, even when incorporated into a preceding developing solution, has little adverse influence on photographic properties and does not interfere with the developing solution in maintaining its function stably, and a method for processing using the same.

The first to fifth objects of the present invention are accomplished by a first embodiment consisting of a photographic processing composition for a silver halide light-sensitive material and a method for processing using the same, in which the processing composition contains at least one of a compound represented by formula (I) or a salt thereof (hereinafter referred to as compound (I)):



$$\begin{array}{c} R_1 \\ R_2 \end{array}\!\!>N-(W_1)_{m1}-\underset{R_4}{\underset{|}{\overset{A_2}{\overset{|}{\overset{(W_3)_{m3}}{\overset{|}{C}}}}}}-(W_2)_{m2}-N<\!\!\begin{array}{l} R_3 \\ L_1-A_1 \end{array} \qquad (I)$$

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0.

The sixth to twelfth objects of the present invention are accomplished by a second embodiment consisting of a photographic processing composition for a silver halide light-sensitive material and a method for processing using the same, in which the processing composition contains at least one of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) and Ce (IV) chelate compounds of compound (I) (inclusive of a salt thereof) (hereinafter referred to as metal chelate compound (I)). The processing solution containing metal chelate compound (I) is particularly useful as a processing solution having bleaching ability.

DETAILED DESCRIPTION OF THE INVENTION

In formula (I), the aliphatic group as represented by R_1, R_2, R_3, and R_4 may be straight, branched or cyclic and may be saturated or unsaturated. The aliphatic group includes an alkyl group, an alkenyl group, an alkynyl group, and a cycloalkyl group, with an alkyl group being preferred. The aliphatic group preferably has 1 to 10 carbon atoms. The alkyl group more preferably has 1 to 4 carbon atoms, with a methyl group and an ethyl group being particularly preferred.

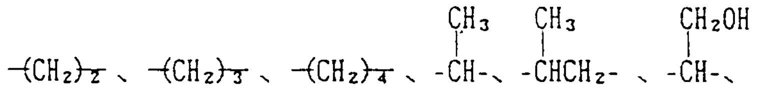
The aliphatic group as R_1, R_2, R_3, and R_4 may be substituted or unsubstituted, preferably substituted. Substituents which may be on the aliphatic groups include an alkyl group (e.g., methyl, ethyl), an alkenyl group (e.g., allyl), an alkynyl group, an alkoxy group (e.g., methoxy, ethoxy), an aryl group (e.g., phenyl or 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, and a hydroxamic acid group. Among them, a sulfo group, a carboxyl group, a hydroxyl group, and a phosphono group are preferred, with a carboxyl group being still preferred.

The aromatic group as represented by R_1, R_2, R_3, and R_4 may be a monocyclic group or a condensed polycyclic group, may be an aromatic hydrocarbon ring or an aromatic heterocyclic ring, and may be substituted or unsubstituted. The aromatic group preferably contains 5 to 15 carbon atoms. The aromatic group is preferably a monocyclic or bicyclic aromatic hydrocarbon group (aryl group) having 6 to 10 carbon atoms, more preferably a substituted or unsubstituted phenyl or naphthyl group, and most preferably a substituted phenyl group. Substituents which may be on the aromatic group are selected from those enumerated as for the aliphatic group R_1.

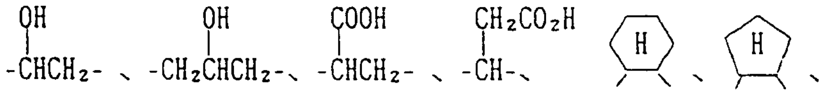
R_4 preferably represents a hydrogen atom.

The alkylene group in L_1, W_1, W_2, and W_3 may be straight, branched or cyclic, and is preferably a straight-chain or branched alkylene group having 1 to 10 carbon atoms, still preferably 1 to 6 carbon atoms. The alkylene group may be substituted or unsubstituted. Substituents therefor are selected from those recited above as for the aliphatic group R_1. Preferred substituents among them are a carboxyl group, a phosphono group, a sulfo group, a hydroxyl group, a substituted or unsubstituted alkyl group having 1 to 3 carbon atoms, and a substituted or unsubstituted aryl group having 6 to 10 carbon atoms (substituents on the alkyl or aryl group including a carboxyl group and a hydroxyl group). Still preferred among them are a carboxyl group, a hydroxyl group, a carboxyl-substituted alkyl group, a hydroxy-substituted alkyl group, an unsubstituted aryl group, a carboxyl-substituted aryl group, and a hydroxy-substituted aryl group.

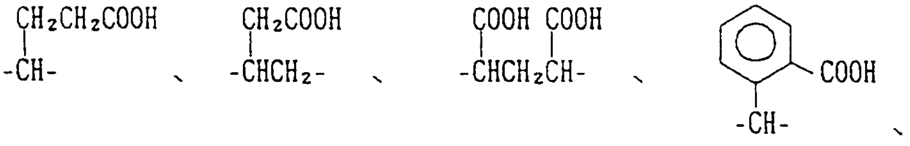
Specific examples of the alkylene group in L_1, W_1, W_2, and W_3 are shown below. $-CH_2-$,



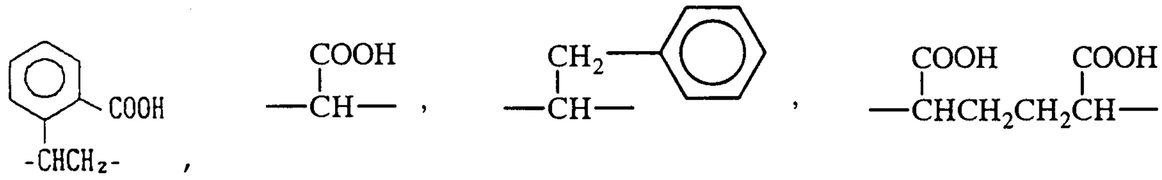
$-(CH_2)_2-$ 、 $-(CH_2)_3-$ 、 $-(CH_2)_4-$ 、 $\overset{CH_3}{-CH-}$ 、 $\overset{CH_3}{-CHCH_2-}$ 、 $\overset{CH_2OH}{-CH-}$ 、



$\overset{OH}{-CHCH_2-}$ 、 $\overset{OH}{-CH_2CHCH_2-}$ 、 $\overset{COOH}{-CHCH_2-}$ 、 $\overset{CH_2CO_2H}{-CH-}$ 、



$\overset{CH_2CH_2COOH}{-CH-}$ 、 $\overset{CH_2COOH}{-CHCH_2-}$ 、 $\overset{COOH\ COOH}{-CHCH_2CH-}$ 、

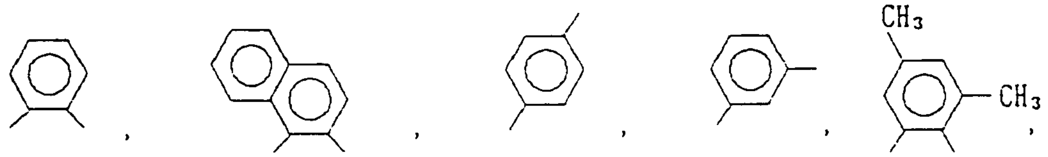


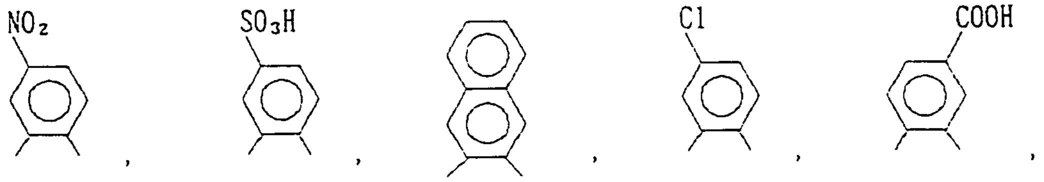
$\overset{COOH}{-CH-}$, $\overset{COOH\qquad COOH}{-CHCH_2CH_2CH-}$

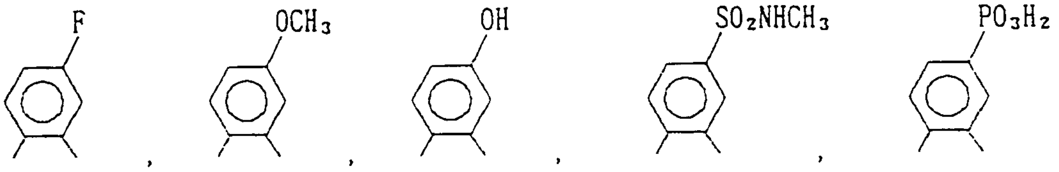
The arylene group in L_1, W_1, and W_2 is preferably a monocyclic or bicyclic aromatic hydrocarbon group which may be substituted or unsubstituted. Substituents therefor are selected from those recited above as for the aliphatic group R_1. The arylene group in L_1, W_1, and W_2 preferably has 6 to 10 carbon atoms, and is still preferably a phenylene group or a naphthylene group, with a phenylene group being particularly preferred.

The alkylene/arylene combination as L_1 includes a substituted or unsubstituted aralkylene group, the substituent of which is selected from those enumerated as for the aliphatic group R_1. The aralkylene group preferably contains 7 to 12 carbon atoms.

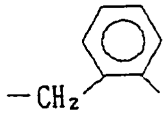
Specific examples of the arylene group in L_1, W_1, and W_2 are shown below.







Examples of the alkylene/arylene combination as L_1 are shown below.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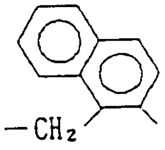
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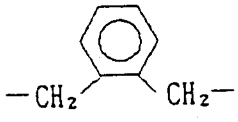
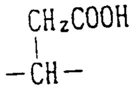
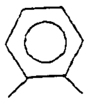


Examples of preferred linking groups as L_1 are shown below.
$-CH_2-$, $-CH_2CH_2-$,



$-\underset{|}{\overset{CH_2COOH}{CH}}-$,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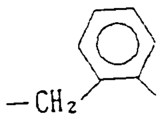
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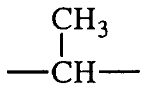
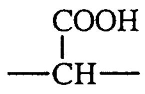
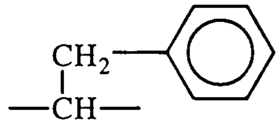


$-\overset{CH_3}{\overset{|}{CH}}-$,



$-\overset{COOH}{\overset{|}{CH}}-$,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L_1 preferably represents an alkylene group.

A_1 preferably represents a carboxyl group, a hydroxyl group or a phosphono group, still preferably a carboxyl group or a hydroxyl group.

A_2 preferably represents a carboxyl group.

W_1 and W_2 each preferably includes linking groups represented by formula (W-1):

$-(W_a-Z_1)_n-(W_b)_k-$ (W-1)

wherein W_a and W_b each represents an alkylene group, an arylene group or an aralkylene group; Z_1 represents -O-, -S-or $-N(R_5)-$; n represents 0, 1, 2 or 3; when n is 2 or 3, (W_a-Z_1)'s may be the same or different; k represents 1, 2 or 3; when k is 2 or 3, W_b's may be the same or different; and R_5 represents a hydrogen atom, an aliphatic group or an aromatic group.

The alkylene, arylene and aralkylene groups as W_a and W_b are the same as explained above for W_1 and W_2.

W_a and W_b each preferably represents an alkylene group, still preferably an alkylene group having 1 to 4 carbon atoms, with a methylene group and an ethylene group being particularly preferred.

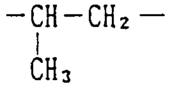
The aliphatic group and the aromatic group as R_5 are as explained above with respect to R_1.

n is preferably 0 or 1, still preferably 0.

k is preferably 1 or 2, still preferably 1.

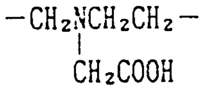
Specific examples of W_1 and W_2, inclusive of those represented by formula (W-1), are shown below.
$-CH_2-$,

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

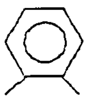


$-\underset{\underset{CH_3}{|}}{CH}-CH_2-$,

$-CH_2OCH_2CH_2-$, $-CH_2OCH_2CH_2OCH_2CH_2-$, $-CH_2SCH_2CH_2-$,



$-CH_2\underset{\displaystyle CH_2COOH}{\underset{|}{N}}CH_2CH_2-$,



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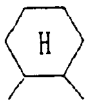

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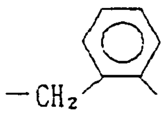

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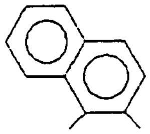

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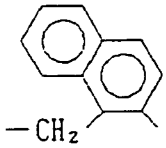

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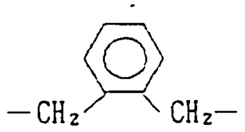

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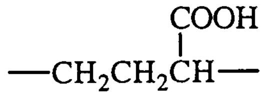
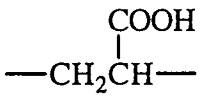
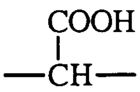


$-CH_2CH_2\overset{\displaystyle COOH}{\overset{|}{CH}}-$,



$-CH_2\overset{\displaystyle COOH}{\overset{|}{CH}}-$,



$-\overset{\displaystyle COOH}{\overset{|}{CH}}-$.

W_3 preferably represents a divalent linking group represented by formula (W-2):

$-(W_c-Z_2)_e-W_d-$ (W-2)

wherein W_c and W_d each represents an alkylene group; Z_2 represents -O-, -S- or $-N(R_6)-$; e represents 0, 1, 2 or 3; when e is 2 or 3, (W_c-Z_2)'s may be the same or different; and R_6 represents a hydrogen atom, an aliphatic group or an aromatic group.

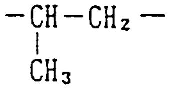
The alkylene group as W_c and W_d are the same as explained above for W_1 and W_2.

W_c and W_d each preferably represents an alkylene group having 1 to 4 carbon atoms, with a methylene group and an ethylene group being still preferred. The aliphatic or aromatic group as R_6 are as explained with respect to those for R_1. e preferably represents 0 or 1, still preferably 0.

Specific examples of W_3, inclusive of those represented by formula (W-2), are shown below.

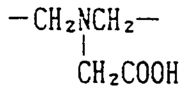
$-CH_2-$,

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



$-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-$,

$-CH_2OCH_2-$, $-CH_2OCH_2CH_2OCH_2-$, $-CH_2SCH_2-$,

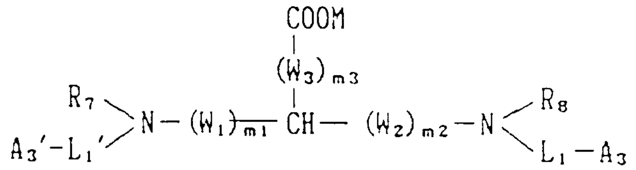


$-CH_2\underset{\displaystyle CH_2COOH}{\underset{|}{N}}CH_2-$.

W_1, W_2, and W_3 each preferably represents an alkylene group, still preferably an alkylene group having 1 to 4 carbon atoms, with a methylene group and an ethylene group being particularly preferred.

m_1, m_2, and m_3 each represents 0 or 1. m_1 and m_3 are each preferably 0, and m_2 is preferably 1.

Of compounds (I), preferred are those represented by formula (II):

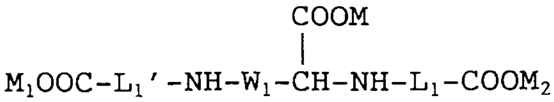


$$\begin{matrix} R_7 \\ A_3'-L_1' \end{matrix}\!\!>N-(W_1)_{m1}-\overset{\displaystyle COOM}{\overset{|}{\underset{}{\overset{(W_3)_{m3}}{\overset{|}{CH}}}}}-(W_2)_{m2}-N\!\!<\!\!\begin{matrix} R_8 \\ L_1-A_3 \end{matrix} \qquad \text{(II)}$$

wherein W_1, W_2, W_3, m_1, m_2, m_3, and L_1 are as defined in formula (I); R_7 and R_8 each independently represents a hydrogen atom or $-L_1''-A_3''$; L_1' and L_1'' each has the same meaning as L_1 defined in formula

(I); L_1, L_1', and L_1'' may be the same or different; A_3, A_3', and A_3'' each represents a carboxyl group or a salt thereof, a phosphono group or a salt thereof, or a combination thereof, the counter cation in the salt being an alkali metal, ammonium, pyridinium, etc.; and M represents a hydrogen atom or a cation (e.g., an alkali metal, ammonium, etc.).

From the viewpoint of biodegradability, still preferred of the compounds of formula (II) are those represented by formula (III):

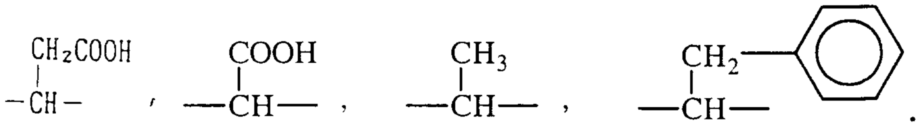


$$M_1OOC\text{-}L_1'\text{-}NH\text{-}W_1\text{-}\underset{}{\overset{\displaystyle COOM}{\overset{|}{C}H}}\text{-}NH\text{-}L_1\text{-}COOM_2 \qquad (III)$$

wherein W_1 and L_1 are as defined in formula (I); L_1' has the same meaning as L_1 in formula (I); L_1 and L_1' may be the same or different; and M, M_1 and M_2, which may be the same or different, have the same meaning as M of formula (II).

Examples of preferred L_1, L_1', and L_1'' are shown below.

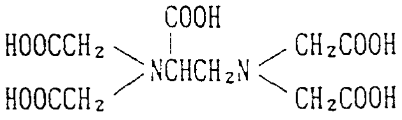
$-CH_2-$, $-CH_2CH_2-$,



It is preferred that L_1 and L_1' do not simultaneously represent a methylene group substituted with a carboxylmethyl group.

Specific examples of compounds (I) are shown below for illustrative purposes only but not for limitation.

1.



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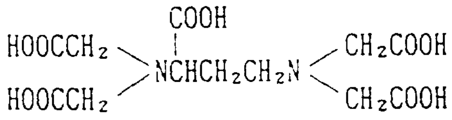

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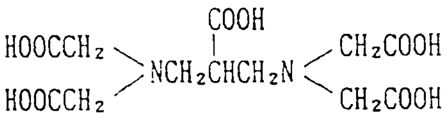

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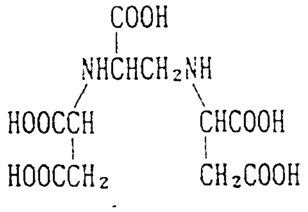

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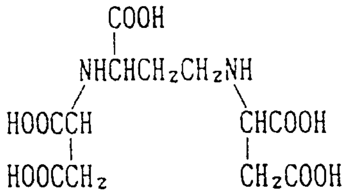

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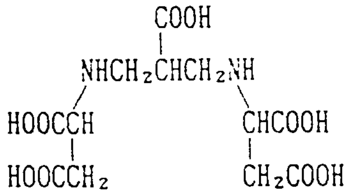

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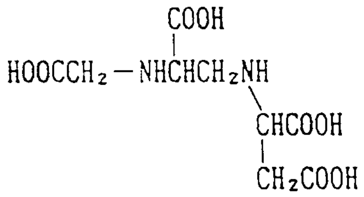
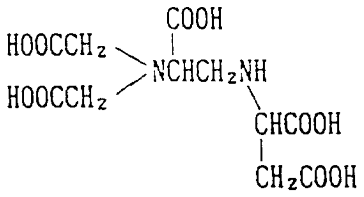


8.

9.



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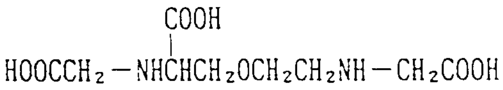
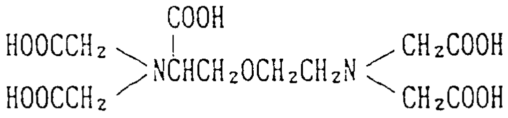


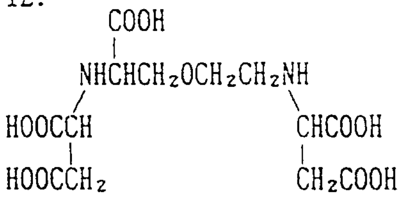
$$\mathrm{HOOCCH_2-NH\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2OCH_2CH_2NH-CH_2COOH}$$

11.



$$\begin{array}{l}\mathrm{HOOCCH_2}\\ \mathrm{HOOCCH_2}\end{array}\!>\mathrm{N\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2OCH_2CH_2N}<\!\begin{array}{l}\mathrm{CH_2COOH}\\ \mathrm{CH_2COOH}\end{array}$$

12.

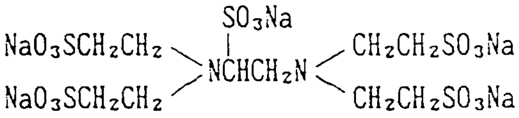


$$\begin{array}{ccc} & \mathrm{COOH} & \\ & | & \\ & \mathrm{NHCHCH_2OCH_2CH_2NH} & \\ / & & \backslash \\ \mathrm{HOOCCH} & & \mathrm{CHCOOH}\\ | & & |\\ \mathrm{HOOCCH_2} & & \mathrm{CH_2COOH}\end{array}$$

13.

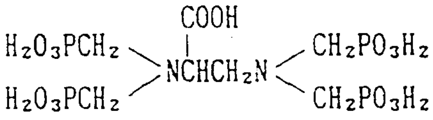
$$\begin{array}{l}\mathrm{NaO_3SCH_2CH_2}\\ \mathrm{NaO_3SCH_2CH_2}\end{array}\!>\mathrm{N\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2N}<\!\begin{array}{l}\mathrm{CH_2CH_2SO_3Na}\\ \mathrm{CH_2CH_2SO_3Na}\end{array}$$

14.



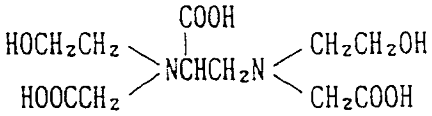
$$\begin{array}{l}\mathrm{NaO_3SCH_2CH_2}\\ \mathrm{NaO_3SCH_2CH_2}\end{array}\!>\mathrm{N\overset{\displaystyle SO_3Na}{\overset{|}{C}}HCH_2N}<\!\begin{array}{l}\mathrm{CH_2CH_2SO_3Na}\\ \mathrm{CH_2CH_2SO_3Na}\end{array}$$

15.



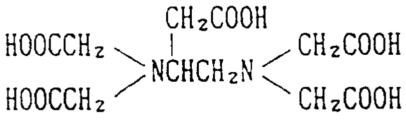
$$\begin{array}{l}\mathrm{H_2O_3PCH_2}\\ \mathrm{H_2O_3PCH_2}\end{array}\!>\mathrm{N\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2N}<\!\begin{array}{l}\mathrm{CH_2PO_3H_2}\\ \mathrm{CH_2PO_3H_2}\end{array}$$

16.



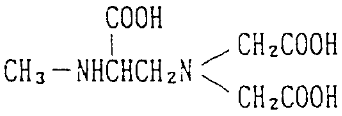
$$\begin{array}{l}\mathrm{HOCH_2CH_2}\\ \mathrm{HOOCCH_2}\end{array}\!>\mathrm{N\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2N}<\!\begin{array}{l}\mathrm{CH_2CH_2OH}\\ \mathrm{CH_2COOH}\end{array}$$

17.



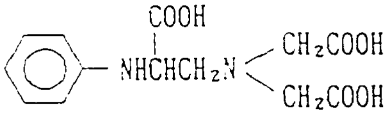
$$\begin{array}{l}\mathrm{HOOCCH_2}\\ \mathrm{HOOCCH_2}\end{array}\!>\mathrm{N\overset{\displaystyle CH_2COOH}{\overset{|}{C}}HCH_2N}<\!\begin{array}{l}\mathrm{CH_2COOH}\\ \mathrm{CH_2COOH}\end{array}$$

18.



$$CH_3-NHCH(COOH)CH_2N(CH_2COOH)_2$$

19.



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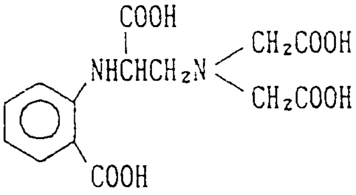

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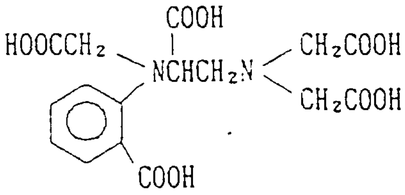

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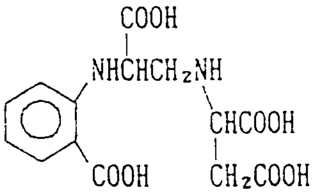

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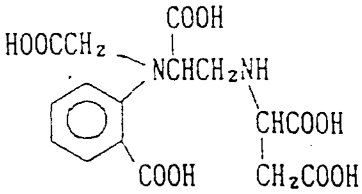

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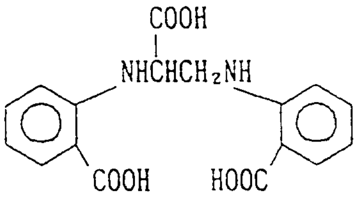

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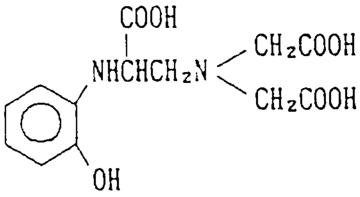

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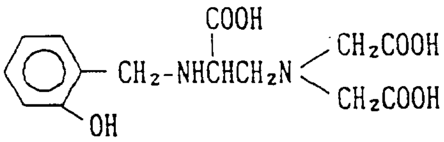

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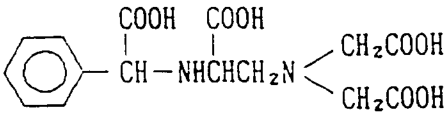

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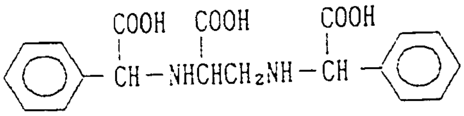

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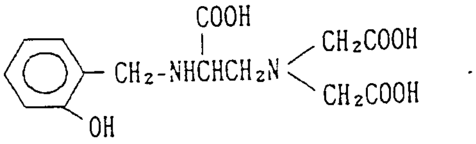

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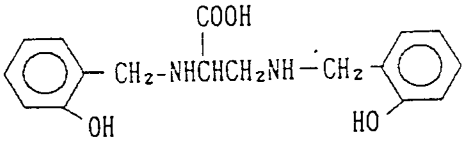

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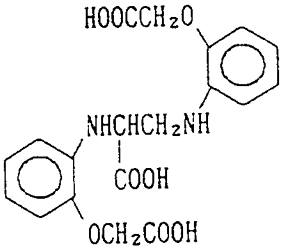

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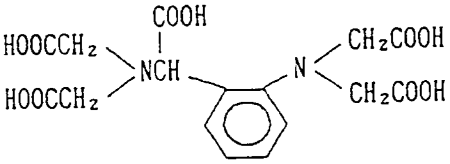

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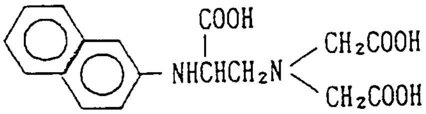

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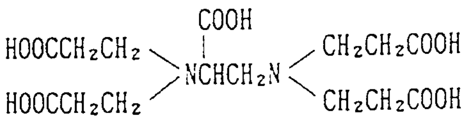

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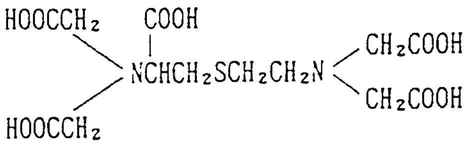

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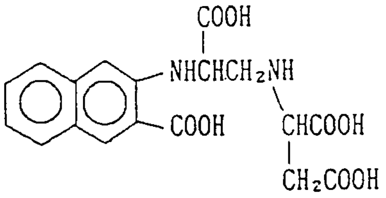

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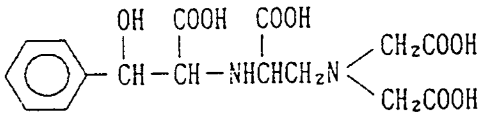

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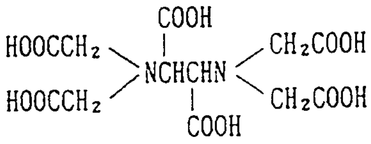

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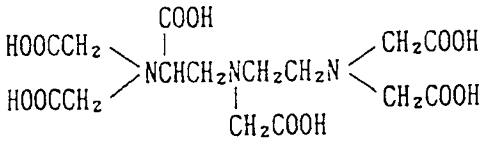

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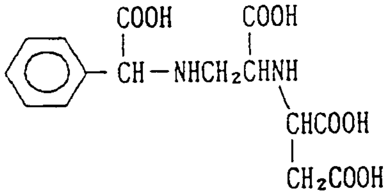

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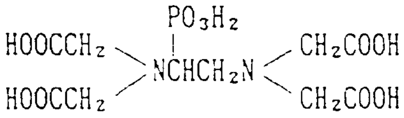

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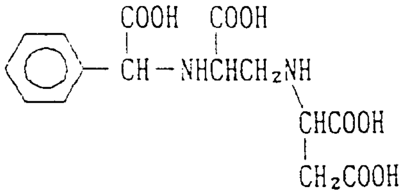

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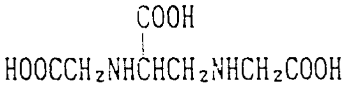
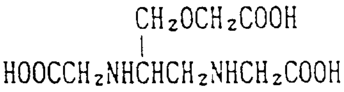


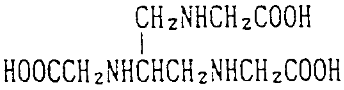
$$HOOCCH_2NH\overset{COOH}{\overset{|}{C}}HCH_2NHCH_2COOH$$

44.



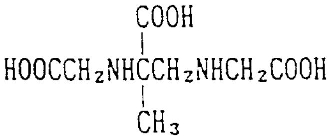
$$HOOCCH_2NH\overset{CH_2OCH_2COOH}{\overset{|}{C}}HCH_2NHCH_2COOH$$

45.



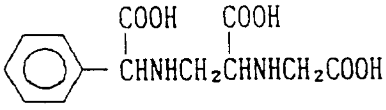
$$HOOCCH_2NH\overset{CH_2NHCH_2COOH}{\overset{|}{C}}HCH_2NHCH_2COOH$$

46.

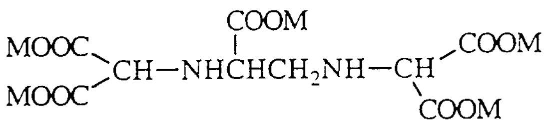


$$HOOCCH_2NH\underset{CH_3}{\underset{|}{\overset{COOH}{\overset{|}{C}}}}CH_2NHCH_2COOH$$

47.

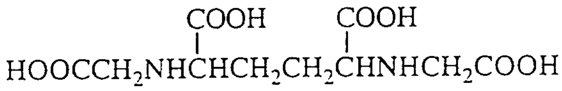


48.



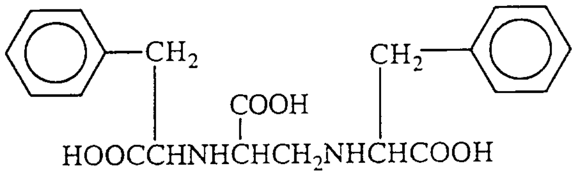
M=Na

49.



$$\mathrm{HOOCCH_2NH\overset{COOH}{\overset{|}{C}}HCH_2CH_2\overset{COOH}{\overset{|}{C}}HNHCH_2COOH}$$

50.



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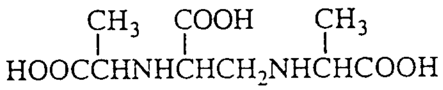
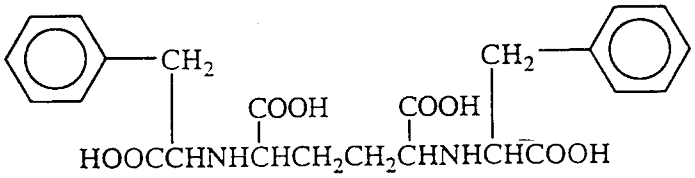
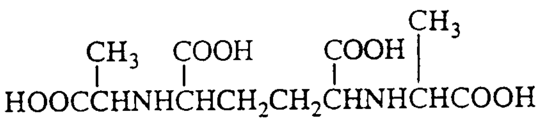


$$\mathrm{HOOC\overset{CH_3}{\overset{|}{C}}HNH\overset{COOH}{\overset{|}{C}}HCH_2NH\overset{CH_3}{\overset{|}{C}}HCOOH}$$

52.



53.

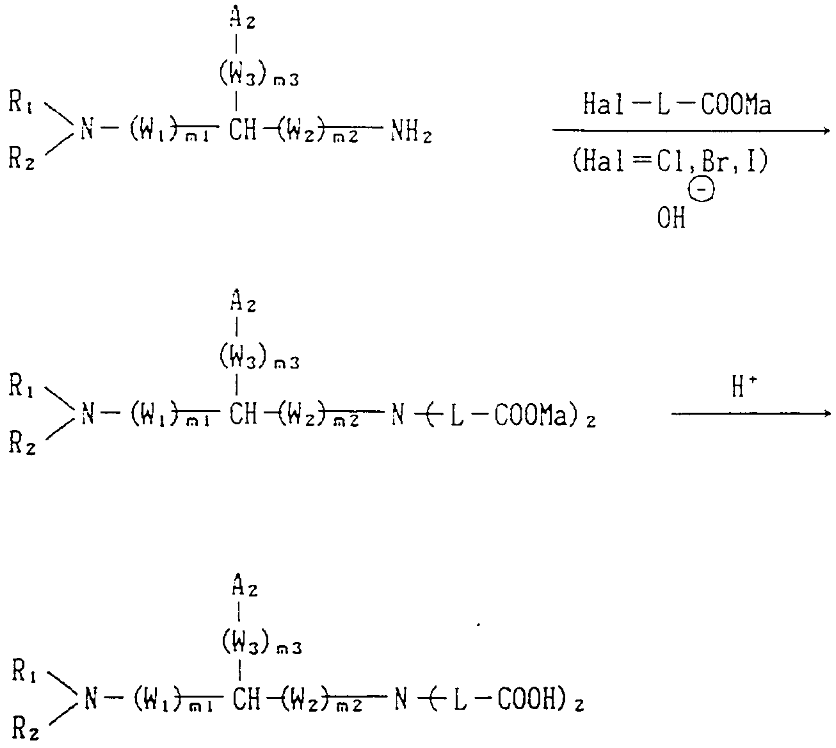


$$\mathrm{HOOC\overset{CH_3}{\overset{|}{C}}HNH\overset{COOH}{\overset{|}{C}}HCH_2CH_2\overset{COOH}{\overset{|}{C}}HNH\overset{CH_3}{\overset{|}{C}}HCOOH}$$

The compound represented by formula (I) may be a salt formed with an organic or inorganic cation, such as an ammonium salt (e.g., an ammonium salt, a tetraethylammonium salt), an alkali metal salt (e.g., a lithium salt, a sodium salt, a potassium salt), or an acid salt (e.g., a hydrochloride, a sulfate, an oxalate).

Compound (I) can be synthesized by reacting a diamine compound with a halogen-substituted alkylcarboxylic acid or a salt thereof (process A) or with a β-substituted acrylic acid or a salt thereof (process B) as shown in the following reaction schemes:

Process A:

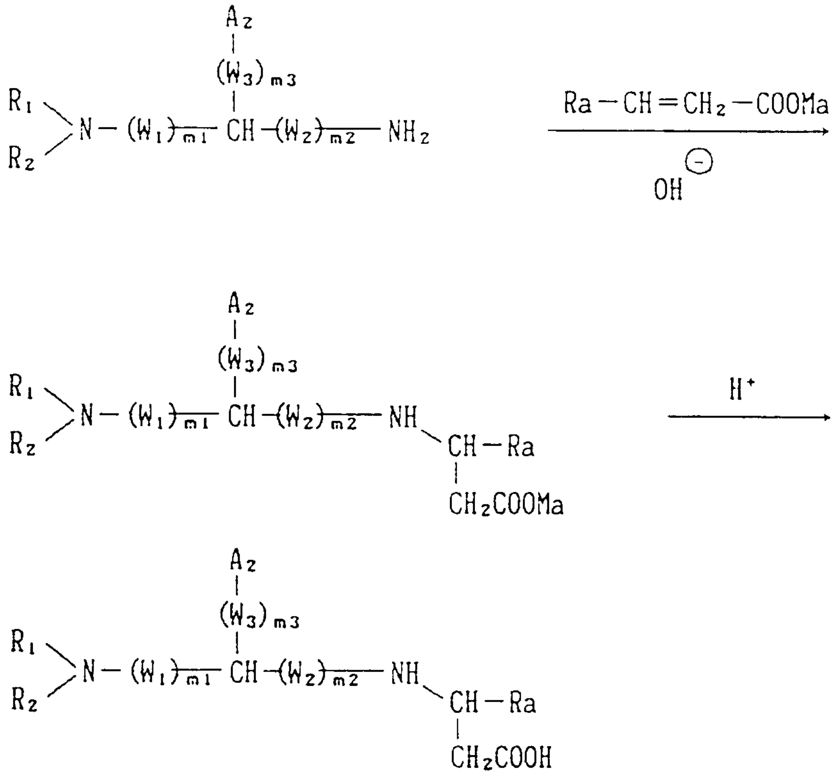


$$\begin{matrix} & & A_2 & & \\ & & | & & \\ & & (W_3)_{m3} & & \\ & & | & & \\ R_1R_2N- & (W_1)_{m1} & CH & (W_2)_{m2} & NH_2 \end{matrix} \xrightarrow[\substack{(Hal = Cl, Br, I) \\ \ominus \\ OH}]{Hal-L-COOMa}$$

$$\begin{matrix} & & A_2 & & \\ & & | & & \\ & & (W_3)_{m3} & & \\ & & | & & \\ R_1R_2N- & (W_1)_{m1} & CH & (W_2)_{m2} & N(L-COOMa)_2 \end{matrix} \xrightarrow{H^+}$$

$$\begin{matrix} & & A_2 & & \\ & & | & & \\ & & (W_3)_{m3} & & \\ & & | & & \\ R_1R_2N- & (W_1)_{m1} & CH & (W_2)_{m2} & N(L-COOH)_2 \end{matrix}$$

Process (B):



In the above formulae, W_1, W_2, W_3, R_1, R_2, m_1, m_2, m_3, and A_2 have the same meanings as those in formula (I); L has the same meaning as L_1 in formula (I); plural L's may be the same or different; Ma represents a hydrogen atom or a cation; and R_a has the same meaning as R_1 in formula (I).

These reactions can be carried out with reference to the processes described in Zh. Neorg. Khim., Vol. 25, No. 6, pp. 1692-1694 (1980) and Bull. Soc. Chim. France, No. 11, pp. 2778-2782 (1964).

Typical examples of the synthesis of compounds (I) are described in Synthesis Examples. All the percents are by weight unless otherwise noted.

SYNTHESIS EXAMPLE 1

Synthesis of Compound 1

In 50 ml of water was dissolved 28.0 g (0.28 mol) of sodium chloroacetate. While stirring the solution at room temperature, 5.6 g (0.04 mol) of D,L-2,3-diaminopropionic acid hydrochloride was added thereto. Then, 32.0 g (0.32 mol) of a 40% aqueous solution of sodium hydroxide was slowly added thereto dropwise at 50 °C so as to keep the mixture at pH between 9 and 10. After the addition, the mixture was stirred at that temperature for 2 hours. The reaction mixture was concentrated under reduced pressure to 50 ml, and concentrated hydrochloric acid was added thereto to adjust to pH 1.2, whereupon a white solid precipitated. The solid was collected by filtration an dried under reduced pressure to obtain 3.72 g (0.01 mol; yield: 25%) of Compound 1 as a dihydrate. Melting point: 129-130 °C (decomposition).

SYNTHESIS EXAMPLE 2

Synthesis of Compound 4

In 80 ml of water was dissolved 38.4 g (0.240 mol) of disodium maleate. While stirring the solution at room temperature, 5.6 g (0.04 mol) of D,L-2,3-diaminopropionic acid hydrochloride was added thereto.

Then, 8 g (0.08 mol) of a 40% aqueous solution of sodium hydroxide was added thereto, followed by stirring at 90 ° C for 24 hours. The reaction mixture was concentrated under reduced pressure to 50 ml, and concentrated hydrochloric acid was added thereto to adjust to pH 3.0. The precipitate of excess maleic acid was removed, and the solution was adjusted to pH 1.2, followed by allowing to stand at 4 ° C for 1 week, whereupon a white solid precipitated. The solid was collected by filtration an dried under reduced pressure to obtain 2.96 g (0.009 mol; yield: 22%) of Compound 4. Melting point: 185-190 ° C.

SYNTHESIS EXAMPLE 3

Synthesis of Compound 48

The title compound was synthesized according to the process described in Zurnal Obschchei Khimii, Vol. 52, No. 3, pp. 658-662 (1992) as follows.

In a three-necked flask were charged 5 g (0.036 mol) of D,L-2,3-diaminopropionic acid hydrochloride (a product of Tokyo Kasei K.K.) and 50 ml of water, and 19.5 g (0.107 mol) of bromomalonic acid (synthesized by referring to Berichte der Deutschen Chemischen Gesellschaft, Vol. 35, p. 1813 (1902)) was added thereto while stirring under cooling with ice. A 20% sodium hydroxide aqueous solution was added thereto with stirring under ice-cooling until the pH reached about 9 to 10. The mixture was heated at 40 ° C while stirring on a warm water bath, and a 20% sodium hydroxide aqueous solution was further added thereto dropwise so as to keep the pH of the reaction system between 9 and 10. After 8 hours' heating with stirring, the reaction mixture was allowed to cool to room temperature, and 500 ml of methanol was added. The thus precipitated solid was collected by filtration, thoroughly washed with methanol, and dried under reduced pressure in the presence of diphosphorus pentoxide to obtain 12.3 g (0.029 mol; yield: 82.7%) of Compound 48.

SYNTHESIS EXAMPLE 4

Synthesis of Compound 43

In a three-necked flask were charged 1.62 g (3.87 mmol) of Compound 48 synthesized in Synthesis Example 3, 15 ml of water, and 20 ml of 36% hydrochloric acid, and the mixture was heated under reflux for 2 hours while stirring. The reaction mixture was distilled under reduced pressure, and water was added to the residue. Distillation under reduced pressure and water addition were repeated three times to remove the excess hydrochloric acid as much as possible.

Finally, 5 ml of a 20% sodium hydroxide aqueous solution was added to the residue, followed by heating under reflux for 2 hours to open the lactam ring formed by the above acid treatment. To the reaction mixture was added 36% hydrochloric acid with stirring under ice-cooling to adjust to pH about 8, at which the precipitate formed was separated by filtration. To the filtrate was further added 36% hydrochloric acid with stirring and ice-cooling to adjust to pH of about 1.5, at which the precipitate formed was collected by filtration, thoroughly washed with water and acetone, and dried under reduced pressure over diphosphorus pentoxide to obtain 420 mg (1.83 mmol; yield: 47.3%) of Compound 43 hemihydrate as a white solid. Melting point: 191-192 ° C (decomposition).

SYNTHESIS EXAMPLE 5

Synthesis of Compound 49

1) Preparation of diethyl meso-2,5-diphthalimidoadipate:

In 50 ml of dimethylformamide were added 15.0 g (0.042 mol) of diethyl meso-2,5-dibromoadipate (a product of Aldrich) and 17.3 g (0.093 mol) of potassium phthalimide, and the mixture was heated at 90 ° C for 40 minutes while stirring. After cooling the reaction mixture to room temperature, 60 ml of chloroform and 240 ml of water were added thereto for liquid-liquid separation by means of a separatory funnel. The chloroform layer was separated. The aqueous layer was extracted with two 20 ml portions of chloroform, and the extract was combined with the above separated chloroform layer. The combined chloroform layer was washed successively with 40 ml of an ice-cooled 0.1M sodium hydroxide aqueous solution, 40 ml of water, two 40 ml portions of 0.05N hydrochloric acid, and two 40 ml portions of water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. To the concentrate was added 60 ml of ethyl ether, followed by stirring, whereupon crystals were precipitated, which were collected by filtration, washed with ethyl ether, and dried to obtain 14.1 g (0.029 mol; yield: 68.2%) of diethyl meso-2,5-diphthalimidoadipate as an intermediate product.

2) Preparation of meso-2,5-diaminoadipic acid:

To 150 ml of methanol were added 14.0 g (0.028 mol) of diethyl meso-2,5-diphthalimidoadipate obtained above and 2.9 g (0.057 mol) of hydrazine monohydrate, and the mixture was heat-refluxed with stirring for 1 hour. After cooling the reaction mixture to room temperature, 70 ml of water was added, and methanol was removed under reduced pressure. To the residue was added 70 ml of concentrated hydrochloric acid, and the suspension was heated under reflux with stirring for 1 hour. The reaction mixture was cooled to 0°C, and the thus formed crystals of phthalhydrazide were separated by filtration. The filtrate was concentrated under reduced pressure to remove hydrochloric acid as much as possible, and 50 ml of water was added thereto. Any insoluble matter was separated by filtration, and the filtrate was adjusted to pH 5 with a 5N sodium hydroxide aqueous solution and allowed to stand at 0°C. The thus formed white crystals were collected and dried to obtain 4.2 g (0.023 mol; yield: 79.9%) of meso-2,5-diaminoadipic acid hemihydrate as an intermediate product.

3) Preparation of Compound 49:

Ten milliliters of water were added 2.0 g (10.8 mmol) of meso-2,5-diaminoadipic acid hemihydrate prepared above, and 5.9 g (32.40 mol) of bromomalonic acid (synthesized by referring to Berichte der Deutschen Chemischen Gesellschaft, Vol. 35, p. 1813 (1902)) was added thereto while stirring under cooling with ice so that the inner temperature might not exceed 10°C. Then, a 5N sodium hydroxide aqueous solution was added thereto with stirring under ice-cooling so that the inner temperature might not exceed 10°C until the pH reached about 9 to 10. The mixture was heated at 40°C while stirring on a warm water bath, and a 5N sodium hydroxide aqueous solution was further added thereto dropwise so as to keep the pH of the reaction system between 9 and 10. After 8 hours' heating with stirring, the reaction mixture was allowed to cool to room temperature, and 200 ml of methanol was added. The thus formed glutinous matter was thoroughly washed with methanol, and 50 ml of water was added, followed by removal of methanol by evaporation under reduced pressure. To the residue was added 10 ml of 36% hydrochloric acid, followed by concentration at 60°C under reduced pressure, and water was again added to the residue, followed by removal of hydrochloric acid under reduced pressure. These procedures were repeated three times to drive out the excess hydrochloric acid as much as possible. Finally, the residue was adjusted to pH 1.8 with a 5N sodium hydroxide aqueous solution while stirring under ice-cooling, and the mixture was allowed to stand at 0°C. The white crystals thus formed were collected and dried to obtain 0.65 g (2.2 mmol; yield: 20.4%) of Compound 49. Melting point: 196-197°C.

The first embodiment of the present invention will be described below in detail.

Compound (I) is applicable to all the processing compositions used for processing silver halide B/W or color light-sensitive materials. For example, it is applicable to a B/W developer for general use, a lith infectious developer, a fixer, washing water (or a washing solution), etc. for B/W light-sensitive materials; and a color developer, a bleaching bath, a fixer, a blix bath, a compensating bath, a stop bath, a hardener, washing water (or a washing solution), a stabilizer, a rinsing solution, a fogging solution, a toning solution, etc. for color light-sensitive materials.

The amount of compound (I) to be added to these processing compositions usually ranges from 10 mg to 50 g per liter, while being subject to variation according to the processing composition as hereinafter described in more detail.

The amount to be added to a B/W developer or a color developer is preferably from 0.5 to 10 g/ℓ, still preferably from 0.5 to 5 g/ℓ. Addition of compound (I) to a B/W or color developer is effective to prevent formation of sediment or sludge and to prevent decomposition of a developing agent or a preservative thereby to suppress variations of photographic characteristics, such as sensitivity and gradation.

The amount to be added to a bleaching solution is preferably from 0.1 to 20 g/ℓ, still preferably from 0.1 to 5 g/ℓ. Addition of compound (I) to a bleaching solution is effective to improve the stability of the bath and to prevent insufficient bleach.

The amount to be added to a fixer or a blix bath is preferably from 1 to 40 g/ℓ, still preferably from 1 to 20 g/ℓ. Use of compound (I) in a fixer or a blix bath is effective to improve the stability of the bath, to prevent formation of turbidity or sludge, and to prevent staining of non-image areas after processing.

The amount to be added to a washing solution or a stabilizer is preferably from 50 mg to 1 g/ℓ, still preferably from 50 to 300 mg/ℓ. Use of compound (I) in these processing solutions is effective in prevention of turbidity, retention of dye image preservability, and prevention of staining of non-image areas after processing.

In the above-described applications, compounds (I) may be used either individually or in combination of two or more thereof. Compounds (I) may also be used in combination with various known chelating agents as far as the effects of compounds (I) are not impaired.

Examples of useful chelating agents with which compounds (I) may be combined include aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, transcyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, iminodiacetic acid, methyliminodiacetic acid, carbamoylmethyliminodiacetic acid, hydroxyethyliminodiacetic acid, and ethylenediamine-N-(β-hydroxyethyl)-N,N',N'-triacetic acid; organophosphonic acids, such as 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid; and a hydrolyzate of a maleic anhydride polymer as disclosed in EP-A-345172.

Processing solutions to which compound (I) can be added according to the first embodiment of the present invention are explained below in detail.

A B/W developer preferably contains a hydroquinone developing agent, e.g., hydroquinone, bromohydroquinone, methylhydroquinone, or 2,5-dichlorohydroquinone, and, as an auxiliary developing agent, a p-aminophenol developing agent, e.g., N-methyl-p-aminophenol, or a 3-pyrazolidone developing agent, e.g., 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone. Suitable preservatives for a B/W developer includes sulfite compounds, such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium metabisulfite, formaldehyde-sodium bisulfite.

A B/W developer preferably has a pH between 9 and 13. Alkalis to be used for pH adjustment include sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. The developer may further contain pH buffering agents, such as boric acid, borax, silicates, sodium tertiary phosphate, and potassium tertiary phosphate. It may furthermore contain a development inhibitor, such as potassium bromide or potassium iodide; an organic solvent, such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol, or methanol; and an antifoggant, such as an indazole derivative, a benzimidazole derivative or a benzotriazole derivative. Other additives which may be incorporated into a B/W developer if desired include development accelerators, such as those described in Research Disclosure, Vol. 176, No. 17643, Item XXI (Dec., 1978); amine compounds described in U.S. Patent 4,269,929, JP-A-61-267759, and JP-A-2-208652; toning agents; surface active agents; hardening agents; silver stain inhibitors, such as those described in JP-A-56-24347; and amino compounds, such as alkanolamines, as described in EP-A-136582, British Patent 958678, U.S. Patent 3,232,761, and JP-A-56-106244, which are used for the purpose of development acceleration or contrast increase.

A fixer for B/W light-sensitive materials is an aqueous solution at pH 4.2 to 7.0 containing a thiosulfate, e.g., sodium thiosulfate or ammonium thiosulfate, as a fixing agent. It is preferable to use a meso-ionic compound described in JP-A-57-150842 in addition to a thiosulfate. The fixer may further contain a hardening agent, e.g., a water-soluble aluminum salt; tartaric acid, citric acid, gluconic acid or derivatives thereof; a preservative, e.g., a sulfite or a bisulfite; a pH buffering agent, e.g., acetic acid or boric acid; and a pH adjusting agent, e.g., sulfuric acid.

A color developer is an aqueous alkali solution at pH 9 to 12 containing an aromatic primary amine color developing agent as a main ingredient. Useful color developing agents include aminophenol compounds and p-phenylenediamine compounds, with the latter being preferred. Typical examples of the p-phenylenediamine developing agents are 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 4-amino-N-ethyl-N-γ-hydroxypropylaniline, 4-amino-N-ethyl-N-δ-hydroxybutylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline, and a sulfate, a hydrochloride or a p-toluenesulfonate of these compounds. A color developer usually contains a pH buffering agent, such as an alkali metal carbonate (e.g., potassium carbonate), a borate or a phosphate; and a development inhibitor or an antifoggant, such as a chloride (e.g., potassium chloride), a bromide (e.g., potassium bromide), an iodide (e.g., potassium iodide), a benzimidazole compound, a benzotriazole compound, a benzothiazole compound or a mercapto compound. If desired, a color developer may contain a preservative, such as hydroxylamines (e.g., hydroxylamine, diethylhydroxylamine, bis(sulfonatoethyl)hydroxylamine) and sulfites (e.g., sodium sulfite, sodium bisulfite); an organic solvent, such as ethylene glycol or diethylene glycol; a development accelerator, such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, and amine compounds; a dye-forming coupler; a completing coupler; an auxiliary developing agent, such as 1-phenyl-3-pyrazolidone; a nucleating agent, such as sodium borohydride or a hydrazine compound; a tackifier; a brightening agent, such as a 4,4'-diamino-2,2'-disulfostilbene compound; and various surface active agents, such as an alkylsulfonic acid, an arylsulfonic acid, an aliphatic carboxylic acid, or an aromatic carboxylic acid.

A bleaching agent to be used in a bleaching bath or a blix bath includes compounds of polyvalent metals, e.g., iron (III); peracids; quinones; and iron salts. Typical bleaching agents include iron chloride; ferricyanides, bichromates, organic complex salts of iron (III) (e.g., metal complex salts of aminopolycarboxylic acids, e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and 1,3-diaminopropanetetraacetic acid); and persulfates. A bleaching bath or a blix bath containing an aminopolycarboxylic acid iron (III) complex salt is used at a pH between 3.5 and 8.

A bleaching bath or a blix bath may contain known additives, such as a re-halogenating agent, such as ammonium bromide, sodium bromide, potassium bromide or ammonium chloride; a pH buffering agent, such as ammonium nitrate; and a metal corrosion inhibitor, such as ammonium sulfate.

In addition to the above-mentioned components, a bleaching bath or a blix bath preferably contains an organic acid for prevention of bleach stain. Organic acids suitable for this purpose are compounds having an acid dissociation constant (pKa) of from 2 to 5.5, such as acetic acid, glycolic acid, and propionic acid.

A fixing agent which can be used in a fixer or a blix bath for color light-sensitive materials include thiosulfates, thiocyanates, thioether compounds, thioureas, meso-ionic compounds, and iodides used in quantity. Thiosulfates are generally used, and ammonium thiosulfate is most widely applicable. A combination of a thiosulfate and a thiocyanate, a thioether compound or thiourea is also preferred.

A fixer or blix bath may contain preservatives, such as sulfites, bisulfites, carbonyl-bisulfurous acid adducts, and the sulfinic acid compounds described in EP-A-294769; various brightening agents; defoaming agents; surface active agents; polyvinyl pyrrolidone; methanol; buffering agents, such as imidazole; and bleach accelerators, such as compounds having a mercapto group or a disulfide group as described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630.

A washing solution or a stabilizer may contain bactericides, such as inorganic phosphorous acid, isothiazolone compounds, thiabendazole compounds, and chlorinated bactericides (e.g., sodium dichloroisocyanurate); metal salts, such as a magnesium salt, an aluminum salt, and a bismuth salt; surface active agents; and hardening agents. A washing solution and/or a stabilizer may further contain various antibacterial or antifungal agents for prevention of formation of fur or generation of mold on a processed light-sensitive material. Such antibacterial or antifungal agents include thiazolylbenzimidazole compounds described in JP-A-57-157244 and JP-A-58-105145, isothiazolone compounds described in JP-A-54-27424 and JP-A-57-8542, chlorophenol compounds, such as trichlorophenol, bromophenol compounds, organotin compounds, organozinc compounds, thiocyanic or isothiocyanic acid compounds, acid amide compounds, diazine or triazine compounds, thiourea compounds, benzotriazole alkylguanidine compounds, quaternary ammonium salts, such as benzalkonium chloride, antibiotics, such as penicillin, and antifungal agents described in J. Antibact. Antifung. Agents, Vol. 1, No. 5, pp. 207-223 (1983). These antibacterial or antifungal agents may be used individually or in combination thereof. Additionally, various bactericides described in JP-A-48-83820 are also useful.

In a stabilizer, while formaldehyde is generally used as a dye stabilizer, it is preferable for working safety to use N-methylol-azole, hexamethylenetetramine, a formaldehyde-bisulfurous acid adduct, dimethylolurea, an azolylmethylamine derivative, etc. The details of these dye stabilizers are described in JP-A-2-153348, JP-A-4-270344, and EP-A-504609. In particular, a combination of an azole compound, such as 1,2,4-triazole, and an azolylmethylamine derivative, such as 1,4-bis(1,2,4-triazol-1-ylmethyl)piperazine, is preferred for its high dye image stabilizing activity and safety (low formaldehyde vapor pressure). A stabilizer may further contain buffering agents for pH adjustment, such as boric acid and sodium hydroxide; sulfiding inhibitors, such as alkanolamines; brightening agents; and so on.

The light-sensitive materials which may be processed according to the first embodiment of the present invention include ordinary B/W silver halide light-sensitive materials (for general photographing, X-ray photography or for printing), ordinary multi-layer silver halide color light-sensitive materials (e.g., color negative films, color reversal films, color positive films, color negative films for movies, color paper, reversal color paper, and direct positive color paper), infrared-sensitive material for laser scanners, and diffusion transfer light-sensitive materials (for silver diffusion transfer or color diffusion transfer).

These light-sensitive materials may have a wide variety of layer structures, either single-sided or double-sided, according to the end use, including, for example, a plurality of silver halide emulsion layers sensitive to red, green or blue, a subbing layer, an antihalation layer, filter layers, intermediate layers, a surface protective layer, and the like.

The light-sensitive materials are not particularly limited in kind of a support; method of coating; kind of silver halides to be used in silver halide emulsion layers or a surface protective layer (e.g., silver iodobromide, silver iodochlorobromide, silver bromide, silver chlorobromide and silver chloride), grain shape thereof (e.g., cube, plate, sphere), grain size thereof, coefficient of variation of grain size, crystal structure thereof (e.g., core/shell structure, multi-phase structure, or homogeneous phase structure), or method of preparation thereof (e.g., single jet process or double jet process); kind of binders (e.g., gelatin), hardening agents, antifoggants, metal dopants, silver halide solvents, thickeners, emulsion precipitants, dimensional stabilizers, antiblocking agents, stabilizers, stain inhibitors, dye image stabilizers, stain preventing agents, chemical sensitizers, spectral sensitizers, sensitivity improving agents, supersensitizers, nucleating agents, couplers (e.g., pivaloylacetanilide type yellow couplers, benzoylacetanilide type yellow couples, 5-pyrazolone type magenta couplers, pyrazoloazole type magenta couplers, phenol type cyan couplers, naphthol type cyan couplers, DIR couplers, bleach accelerator-releasing couplers, competing couplers, colored couplers); method of dispersing couplers (e.g., oil-in-water dispersion using high-boiling organic solvents); kind of additives, such as plasticizers, antistatic agents, lubricants, coating aids, surface active agents, whitening agents, formalin scavengers, light scattering agents, matting agents, light absorbents, UV absorbents, filter dyes, irradiation dyes, development improving agents, antiglazing agents, antiseptics (e.g., 2-phenoxyethanol), antifungal agents, and the like. For the details, reference can be made, e.g., in Product Licensing, Vol. 92, pp. 107-110 (Dec., 1971), Research Disclosure Nos. 17643 (Dec., 1978), 18716 (Nov., 1979), and 307105 (Nov., 1989), JP-A-4-34548 (p. 15, lower left col., l. 1 to p. 20, lower right col., l. 3), JP-A-4-184432 (p. 7, right col., l. 32 to p. 9, right col., l. 26), and JP-A-4-274237 (p. 6, right col., l. 30 to p. 9, right col., l. 49).

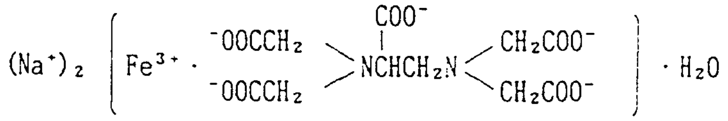
The second embodiment according to the present invention will then be explained below in more detail.

The metal salt constituting metal chelate compound (I) according to the second embodiment is selected from salts of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III), and Ce (IV). Preferred of them are Fe (III) salts, Mn (III) salts, and Co (IV) salts, with Fe (III) salts being still preferred.

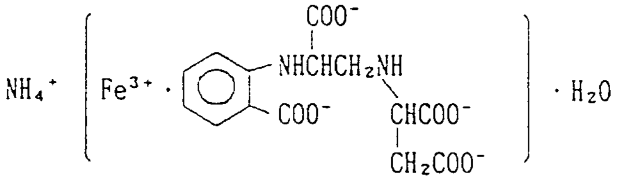
Metal chelate compound (I) of the present invention is not particularly restricted as long as they are complexes formed between compound (I) and the aforesaid metal salt. For example, the complex may be formed in a solution in situ between compound (I) and the metal salt, such as a sodium, ammonium, potassium or lithium salt of ferric sulfate, ferric chloride, ferric nitrate, or ferric phosphate, in a solution. Compound (I) is used in an molar ratio of 1.0 or higher, usually from 1 to 30, to the metallic ion. Where the resulting metal chelate compound has low stability, it is recommended to use compound (I) at a high molar ratio to metallic ion within the above range. As a matter of course, a metal chelate compound separately prepared and isolated may be used.

Specific but non-limiting examples of metal chelate compounds (I) are shown below for illustrative purposes only but not for limitation.

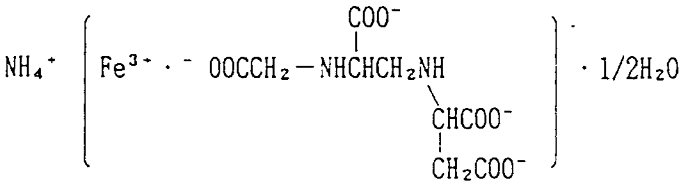
K－1



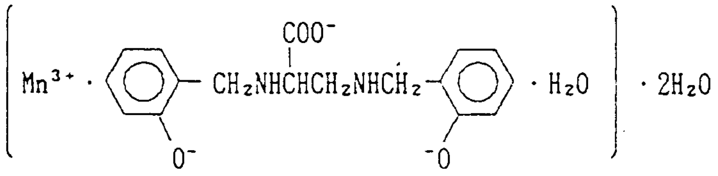
K－2



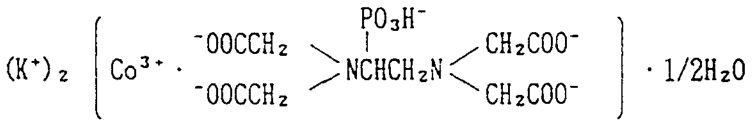
K－3



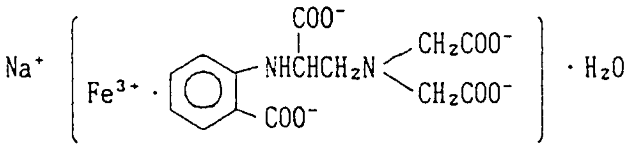
K－4



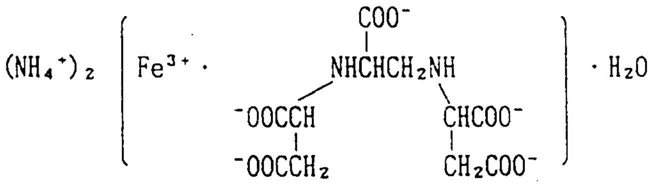
K－5



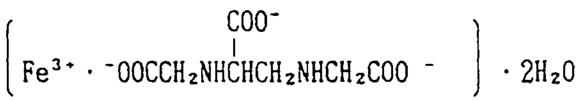
K－6



K－7



K－8



$$\left[Fe^{3+} \cdot {}^{-}OOCCH_2NH\overset{COO^-}{\overset{|}{C}}HCH_2NHCH_2COO^- \right] \cdot 2H_2O$$

Metal chelate compound (I) acts as an oxidizing agent for a silver halide light-sensitive material, i.e., as a bleaching agent for a color light-sensitive material or as a reducer for a B/W light-sensitive material for photomechanical processing. It performs an especially excellent function as a bleaching agent for a color light-sensitive material.

For use as a bleaching agent, an imagewise exposed and then color developed silver halide color light-sensitive material is processed with a processing composition containing metal chelate compound (I) as a bleaching agent.

That is, the second embodiment of the present invention is characterized by a novel oxidizing agent to be added to a processing solution, particularly a bleaching agent to be used in a processing solution having bleaching ability for a color light-sensitive material. With respect to other elements or materials, a wide choice can be made appropriately among those commonly employed.

While metal chelate compound (I) may be used in any processing solution, such as a fixer or an intermediate bath between color development and desilvering, as well as a processing solution having bleaching ability, it is particularly effective as a bleaching agent of a processing solution having bleaching ability used for color light-sensitive materials, i.e., a bleaching bath or a blix bath, when used in a concentration of from 0.005 to 1 mol per liter.

In what follows, the second embodiment of the present invention will be explained chiefly with reference to a processing composition having bleaching ability as a preferred embodiment.

As mentioned above, an effective amount of metal chelate compound (I) as a bleaching agent is 0.005 to 1 mol, preferably 0.01 to 0.5 mol, still preferably 0.05 to 0.5 mol, per liter of a processing composition having bleaching ability. It should be mentioned here that metal chelate compound (I) exhibits excellent performance even when used as such a low concentration of from 0.005 to 0.2 mol, preferably 0.01 to 0.2 mol, still preferably 0.05 to 0.18 mol, per liter.

For use as a bleaching agent in a processing solution having bleaching ability, metal chelate compound (I) may be used in combination with other known bleaching agents as long as the effects of metal chelate compound (I) are not impaired. Such other bleaching agents are preferably used in a concentration up to 0.01 mol, still preferably up to 0.005 mol, per liter. Examples of the other useful bleaching agents include Fe (III), Co (III) or Mn (III) chelate compounds obtained by using the following chelating agents other than compounds (I), persulfates (e.g., peroxodisulfates), hydrogen peroxide, and hydrobromides. The chelating agents for the above Fe (III), Co (III) or Mn (III) chelate compounds are 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, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, 1,3-propylenediamine-N,N,N',N'-tetramethylenephosphonic acid, nitrilodiacetic-monopropionic acid, nitrilomonoacetic-dipropionic acid, 2-hydroxy-3-aminopropionic-N,N-diacetic acid, serine-N,N-diacetic acid, 2-methyl-serine-N,N-diacetic acid, 2-hydroxymethyl-serine-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, citric acid, and salts of these acids with an alkali metal (e.g., lithium, sodium or potassium) or ammonium. Additionally, bleaching agents described in the following publications are also useful: 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, EP-A-430000, and West German Patent Publication (OLS) No. 3912551.

The processing solution having bleaching ability which contains metal chelate compound (I) preferably contains a halide, such as a chloride, a bromide or an iodide, as a rehalogenating agent for acceleration of silver oxidation. An organic ligand capable of forming a sparingly soluble silver salt may be added in place of the halide. The halide is added in the form of a salt with an alkali metal, ammonium, guanidine or an amine, for example, sodium bromide, ammonium bromide, potassium chloride, guanidine hydrochloride or potassium bromide. The rehalogenating agent is suitably used in a processing solution having bleaching ability at a concentration of not more than 2 mol per liter. More specifically, a suitable concentration of the rehalogenating agent in a bleaching bath is from 0.01 to 2.0 mol/ℓ, preferably from 0.1 to 1.7 mol/ℓ, still preferably from 0.1 to 0.6 mol/ℓ; and that in a blix bath is from 0.001 to 2.0 mol/ℓ, preferably from 0.001 to 1.0 mol/ℓ, still preferably from 0.001 to 0.5 mol/ℓ.

If desired, the processing solution having bleaching ability according to the second embodiment may contain compound (I) per se as has been described with reference to the first embodiment of the present invention. In particular, where metal chelate compound (I) used has poor stability, it is preferable to add compound (I) in an amount of up to about 30 mols per mole of metal chelate compound (I).

If desired, the bleaching bath or blix bath may further contain bleaching accelerators, corrosion inhibitors (preventive of corrosion of a processing tank), buffering agents for pH adjustment, brightening agents, defoaming agents, and the like.

Useful bleaching accelerators include compounds having a mercapto group or a disulfide group as described 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); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in U.S. Patent 3,706,561; iodides described in JP-A-58-16235; polyethylene oxides described in German Patent 2,748,430; polyamine compounds described in JP-B-45-8836 (the term "JP-B" as used herein means an "examined published Japanese patent application"); and imidazole compounds described in JP-A-49-40493. The mercapto compounds of British Patent 1,138,842 are especially recommended.

Suitable corrosion inhibitors include nitrates, such as ammonium nitrate, sodium nitrate, and potassium nitrate. The corrosion inhibitor is used in an amount usually of from 0.01 to 2.0 mol/ℓ, preferably from 0.05 to 0.5 mol/ℓ.

The bleaching bath or blix bath has a pH between 2.0 and 8.0, preferably between 3.0 and 7.5. In some detail, a bleaching or blix bath which is to be used for processing a light-sensitive material for photographing immediately after color development has a pH of 7.0 or lower, preferably 6.4 or lower, in order to suppress bleach fog. In this case, an especially preferred pH of the bleaching bath is from 3.0 to 5.0. With respect to a lower limit of the pH, metal chelate compound (I) tends to become instable at pH of 2.0 or lower. Accordingly, a preferred pH range is from 2.0 to 6.4. A pH range between 3 and 7 is preferred for light-sensitive materials for printing.

Any buffering agent can be used for the pH adjustment as long as it is insusceptible to oxidation with a bleaching agent and capable of buffering within the above pH range. Suitable buffering agents 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, oxalic acid, malonic acid, succinic acid, tartaric acid, maleic acid, fumaric acid, oxalo-acids, glutaric acid, adipic acid, aspartic acid, glutaminic acid, cystine, ascorbic acid, phthalic acid, terephthalic acid, picolinic acid, and salicylic acid; and organic bases, such as pyridine, dimethylpyrazole, 2-methyl-o-oxazoline, aminoacetonitrile, and imidazole. These buffering agents may be used in combination of two or more thereof. Preferred of them are organic acids having a pKa of 2.0 to 5.5, with acetic acid, glycolic acid, malonic acid, succinic acid, maleic acid, fumaric acid, picolinic acid, glutaric acid, adipic acid, and a combination of two or more thereof being especially preferred. These organic acids may be used in the form of an alkali metal salt (e.g., lithium salt, sodium salt or potassium salt) or an ammonium salt. The total amount of the buffering agents is suitably 0.1 to 3.0 mol/liter of the processing solution having bleaching ability, preferably 0.1 to 2.0 mol/ℓ, still preferably 0.2 to 1.8 mol/ℓ, most preferably 0.4 to 1.5 mol/ℓ.

pH adjustment of the processing solution having bleaching ability may also be effected by using an alkali in combination with the above-mentioned acid. Useful alkalis are aqueous ammonia, KOH, NaOH, potassium carbonate, sodium carbonate, imidazole, monoethanolamine, and diethylamine, with aqueous ammonia, KOH, NaOH, potassium carbonate, and sodium carbonate being preferred.

With the growing recognition of the need of environmental protection, efforts have been exerted to reduce a nitrogen level discharged into the air. From this viewpoint, it is desired that the processing composition of the present invention should contain substantially no ammonium ion. The term "substantially no ammonium ion" as used in the present invention means an ammonium ion concentration of not higher than 0.1 mol/ℓ, preferably not higher than 0.08 mol/ℓ, still preferably not higher than 0.01 mol/ℓ, and most preferably zero.

In order to reduce the ammonium ion concentration to the above level, it is effective to replace an ammonium ion with other cation species, preferably an alkali metal ion or an alkaline earth metal ion, still preferably an alkali metal ion, particularly a lithium ion, a sodium ion or a potassium ion. More specifically, reduction of ammonium ion concentration can be achieved by, for example, using a sodium or potassium salt of an organic acid iron (III) complex as a bleaching agent, using potassium bromide, sodium bromide, potassium nitrate or sodium nitrate as a rehalogenating agent in the processing solution having bleaching ability, or using potassium hydroxide, sodium hydroxide, potassium carbonate or sodium carbonate as an alkali for pH adjustment.

Aeration of the processing solution having bleaching ability is effective for stable maintenance of its photographic performance. Aeration can be carried out by any means known in the art. For example, air is blown into the processing composition or an ejector is used for air absorption.

Blowing of air is preferably conducted through such an air diffuser having fine pores as is widely used in air agitation tanks for an activated sludge process. For the details of aeration, the description of Z-121, Using Process C-41, 3rd Ed., BL-1 to 2, Eastman Kodak Co. (1982) can be referred to. The processing using the processing solution having bleaching ability according to the present invention is preferably carried out with forced agitation. Forced agitation can be effected in the manner described in JP-A-3-33847, p. 8, upper right col., l. 6 to lower left col., l. 2.

Bleaching or blix is carried out at a temperature ranging from 30 to 60 ° C, preferably from 35 to 50 ° C.

The bleaching and/or blix time is from 10 seconds to 7 minutes, preferably from 10 seconds to 4 minutes, for light-sensitive materials for photographing; and from 5 to 70 seconds, preferably 5 to 60 seconds, still preferably 10 to 45 seconds, for light-sensitive materials for printing. With these processing conditions satisfied, bleaching or blix can be achieved rapidly without involving increase of stain.

A light-sensitive material processed with a processing solution having bleaching ability is then subjected to fixing or bleach-fixing (blix). The fixer or blix bath used for preference is described in JP-A-3-33847, p. 6, lower right col., l. 16 to p. 8, upper left col., l. 15.

While ammonium thiosulfate is generally used as a fixing agent in the desilvering step, other known fixing agents, such as meso-ionic compounds, thioether compounds, thioureas, iodides (used in quantities), and Hypo, may be used in place of ammonium thiosulfate. The details for these fixing agents are described 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. Specific examples of useful fixing agents are ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, guanidine thiosulfate, ammonium thiocyanate, sodium thiocyanate, potassium thiocyanate, dihydroxyethyl thioether, 3,6-dithia-1,8-octanediol, and imidazole. Preferred of them are thiosulfates and meso-ionic compounds. Although ammonium thiosulfate is excellent in rapidness in fixing, sodium thiosulfate and meso-ionic compounds are preferred considering that an ammonium ion should be excluded from processing solutions for the sake of environmental protection. Rapid fixing would be achieved by using two or more fixing agents in combination, for example, a combination of ammonium thiosulfate or sodium thiosulfate with ammonium thiocyanate, imidazole, thiourea or a thioether compound. In this case, the latter fixing agent is preferably used in an amount of 0.01 to 100 mol% based on the former fixing agent (ammonium thiosulfate or sodium thiosulfate).

The fixing agents are used in a total concentration of 0.1 to 3.0 mol/liter of the blix bath or fixer, preferably 0.5 to 2.0 mol/ℓ. The pH of the fixer, though dependent on the kind of the fixing agent, is generally from 3.0 to 9.0. In using a thiosulfate, a pH between 5.8 and 8.0 is preferred for stable fixing performance.

The blix bath or fixer may contain preservatives to improve stability with time. Effective preservatives for a blix bath or fixer containing a thiosulfate are a sulfite and/or hydroxylamine, hydrazine or an aldehyde-bisulfite adduct (e.g., an acetaldehyde-bisulfite adduct, especially the aromatic aldehyde-bisulfite adduct described in JP-A-1-298935). The sulfinic acid compounds described in JP-A-62-143048 are also suitable.

The blix bath or fixer may also contain buffering agents for maintaining the pH constant. Suitable buffering agents include phosphates, imidazole compounds (e.g., imidazole, 1-methylimidazole, 2-methylimidazole, and 1-ethylimidazole), triethanolamine, N-allylmorpholine, and N-benzoylpiperazine.

Further, the fixer can contain various chelating agents for scavenging iron ions carried over from a preceding bleaching bath to thereby improve the liquid stability. Suitable chelating agents include 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, dihydroxyethylglycine, ethyl ether diaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrapropionic 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-methyl-serine-N,N-diacetic acid, 2-hydroxymethyl-serine-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, alanine, tartaric acid, hydrazinodiacetic acid, N-hydroxyiminodipropionic acid, and an alkali metal salt (e.g., lithium salt, sodium salt or potassium salt) or an ammonium salt of these compounds.

These chelating agents are preferably added in a total amount of 0.01 to 0.5 mol/ℓ, preferably 0.03 to 0.2 mol/ℓ.

Fixing is carried out at a temperature ranging from 30 to 60 ° C, preferably from 35 to 50 ° C.

The fixing time is from 15 seconds to 2 minutes, preferably 25 to 100 seconds for light-sensitive materials for photographing; and from 8 to 80 seconds, preferably from 10 to 45 seconds for light-sensitive materials for printing.

Desilvering is generally effected through any of the following combinations of bleach, blix, and fixing:

1) Bleach-fixing
2) Bleach-blix
3) Bleach-blix-fixing
4) Bleach-washing-fixing
5) Blix
6) Fixing-blix

Combinations (1) to (4), particularly (1) to (3), are suitable to light-sensitive materials for photographing; and procedure (5) is suitable to light-sensitive materials for printing.

The second embodiment of the present invention is also applicable to a processing system in which desilvering is preceded by compensation, stopping, washing, and the like.

The photographic processing is preferably performed by means of an automatic developing machine. A method for carrying a light-sensitive material in an automatic developing machine is described in JP-A-60-191257, JP-A-60-191258, and JP-A-60-191259. For rapid processing, it is preferable to reduce the cross-over time between two processing tanks. An automatic developing machine having a cross-over time of 5 seconds or shorter is described in JP-A-1-319038.

In carrying out photographic processing in a continuous manner by the use of an automatic developing machine, a processing solution is preferably replenished with a replenisher in proportion to the amount of the processed light-sensitive material thereby to compensate for the loss of the components of the processing solution and to suppress accumulation of an undesired component dissolved out of the light-sensitive material in the processing solution. One processing step may be conducted in two or more tanks. This being the case, a replenisher is preferably fed from the final bath to the prebath in a counter current system. In particular, a washing step or a stabilizing step is preferably carried out in a cascade flow system comprising 2 to 4 stages.

The amount of each replenisher to be fed to the respective running processing solution should be reduced unless the change in composition of the respective running processing solution adversely affects photographic properties or causes contamination of the following processing solution.

In order to obtain the full effects of the present invention, each processing solution is preferably used under forced agitation.

Forced agitation can be effected by the methods described in JP-A-62-183460, JP-A-62-183461, and JP-A-3-33847 (page 8); for example, a method in which a jet stream of a processing solution is made to strike against the emulsion layer side of a light-sensitive material (the method adopted in a color negative film processor FP-560B, manufactured by Fuji Photo Film Co., Ltd.); a method of using a rotary means to increase the agitation effect (the method of JP-A-62-183461); a method in which a turbulent flow is caused on the emulsion layer side of a moving light-sensitive material by means of a wiper blade set in a processing tank in such a manner that the blade contact with the emulsion layer; and a method comprising increasing the circulating flow of the whole processing solution. The method of using a jet stream of a processing solution is the best of all, and it is recommended to adopt this system in every processing tank.

The rate of replenishment for a color developer is 50 to 3000 ml, preferably 50 to 2200 ml, per m^2 of a color light-sensitive material for photographing; or 15 to 500 ml, preferably 20 to 350 ml, per m^2 of a color light-sensitive material for printing.

The rate of replenishment for a bleaching bath is 10 to 1000 ml, preferably 50 to 550 ml, per m^2 of a color light-sensitive material for photographing; or 15 to 500 ml, preferably 20 to 300 ml, per m^2 of a light-sensitive material for printing.

The rate of replenishment for a blix bath is 200 to 3000 ml, preferably 250 to 1300 ml, per m^2 of a color light-sensitive material for photographing; or 20 to 300 ml, preferably 50 to 200 ml, per m^2 of a light-sensitive material for printing. A blix bath may be replenished with one liquid type replenisher, or the replenisher may be divided into a bleaching composition and a fixing composition. The overflow from a bleaching bath and/or a fixing bath may be used as a component of a blix replenisher.

The rate of replenishment for a fixer is 300 to 3000 ml, preferably 300 to 1200 ml, per m^2 of a color light-sensitive material for photographing; or 20 to 300 ml, preferably 50 to 200 ml, per m^2 of a light-sensitive material for printing.

The amount of a replenisher for a washing solution or a stabilizer is 1 to 50 times, preferably 2 to 30 times, still preferably 2 to 15 times, the amount of the liquid carried over from the precedent bath per unit area of a light-sensitive material.

An overflow of a processing solution having bleaching ability may be reused after correction of the composition, called regeneration. The processing solution having bleaching ability according to the second embodiment of the present invention is suited to effect such regeneration. For the details of regeneration, refer to Fuji Film Processing Manual, Fuji color Negative Film, CN-16 Processing, pp. 39-40 (rev. Aug., 1990), published by Fuji Photo Film Co., Ltd.

The kit for preparing a processing solution having bleaching ability containing metal chelate compound (I) may be either a liquid type or a powder type. Where no ammonium salt is used, a powdered kit is easier to prepare because almost all the materials are supplied in a powdered form and are hardly hygroscopic. The kit for regeneration is preferably a powder type; for such can be added as it is without using water in favor of reduction of waste liquid.

A processing solution having bleaching ability can be regenerated by aeration as previously described and also by the methods described in Nippon Shashin Gakkai (ed.), Shashinkogaku no Kiso, "Gin-en Shashinhen", Coronasha (1979), such as electrolytic regeneration, and regeneration with bromic acid, chlorous acid, bromine, a bromine precursor, a persulfate, hydrogen peroxide, hydrogen peroxide generated by utilizing a catalyst, bromous acid, ozone, etc.

Electrolytic regeneration of a bleaching bath can be conducted by putting a cathode and an anode in a bleaching bath with or without a diaphragm. A bleaching bath, a developer and/or a fixer may be regenerated simultaneously by electrolytic regeneration using a diaphragm.

Regeneration of a fixer or a blix bath can be conducted by electrolytically reducing the accumulated silver ion. It is effective for maintenance of fixing ability to remove the accumulated halogen ion by using an anion-exchange resin.

In order to minimize the amount of washing water, the spend washing water is regenerated by ion exchange treatment or, for preference, ultrafiltration.

An imagewise exposed color light-sensitive material is subjected to color development prior to desilvering. A color developer to be used in the present invention is described in JP-A-3-33847, p. 9, upper left col., l. 6 to p. 11, lower right col., l. 6 and JP-A-5-197107.

A color developing agent to be in the color development step includes known aromatic primary amine color developing agents, preferably p-phenylenediamine derivatives. Typical examples of the p-phenylenediamine developing agents are 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-methylaniline, 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-3-methylaniline, 4-amino-N-(3-carbamoylpropyl-N-n-propyl)-3-methylaniline, 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methoxyaniline, and the compounds described in EP-A-410450 and JP-A-4-11255. The p-phenylenediamine derivative may be a salt, such as a sulfate, a hydrochloride, a sulfite, a naphthalenedisulfonate, and a p-toluenesulfonate. The aromatic primary amine developing agent is used in a concentration of 0.0002 to 0.2 mol, preferably 0.001 to 0.1 mol, per liter of a color developer.

The color development is carried out at 20 to 55 °C, preferably 30 to 55 °C. The developing time is from 20 seconds to 5 minutes, preferably 30 seconds to 3 minutes and 20 seconds, still preferably 1 to 2.5 minute, for a light-sensitive material for photographing, or for 10 seconds to 1 minute and 20 seconds, preferably 10 to 60 seconds, still preferably 10 to 40 seconds, for a light-sensitive material for printing.

The processing method of the second embodiment is also applicable to a color reversal process. A B/W developer to be used for color reversal development is a so-called first B/W developer which is generally employed for reversal development of a color light-sensitive material. The first B/W developer for color reversal development may contain various additives known for a B/W developer for a B/W silver halide light-sensitive material.

Typical additives for the first developer include developing agents, such as 1-phenyl-3-pyrazolidone, methol, and hydroquinone; preservatives, such as sulfites; alkaline accelerators, such as sodium hydroxide, sodium carbonate, and potassium carbonate; organic or inorganic restrainers, such as potassium bromide, 2-methylbenzimidazole, and methylbenzothiazole; water softeners, such as polyphosphates; and development inhibitors, such as a trace amount of an iodide or a mercapto compound.

The desilvered light-sensitive material is then subjected to washing with water and/or stabilizing. A stabilizer to be used is described in U.S. Patent 4,786,583. In a stabilizer, while formaldehyde is generally used as a dye stabilizer, it is preferable for working safety to use N-methylol-azole-hexamethylenetetramine, a formaldehyde-bisulfurous acid adduct, dimethylolurea, an azolylmethylamine derivative, etc. The details of these dye stabilizers are described in JP-A-2-153348, JP-A-4-270344, and EP-A-504609. In particular, a combination of an azole compound, such as 1,2,4-triazole, and azolylmethylamine or its derivative, such as 1,4-bis(1,2,4-triazol-1-ylmethyl)piperazine, is preferred for its high dye image stabilizing activity and safety (low formaldehyde vapor pressure).

Light-sensitive materials to which the processing method according to the second embodiment of the present invention is applicable include color negative films, color reversal films, color paper, color reversal paper, direct positive color light-sensitive materials, color negative films for movies, and color positive films for movies. Examples of these light-sensitive materials are described in JP-A-3-33847, JP-A-3-293662, and JP-A-4-130432.

The light-sensitive materials are not particularly limited in kind of a support; method of coating; kind of silver halides to be used in silver halide emulsion layers or a surface protective layer (e.g., silver iodobromide, silver iodochlorobromide, silver bromide, silver chlorobromide and silver chloride), grain shape thereof (e.g., cube, plate, sphere), grain size thereof, coefficient of variation of grain size, crystal structure thereof (e.g., core/shell structure, multi-phase structure, or homogeneous phase structure), or method of preparation thereof (e.g., single jet process or double jet process); kind of binders (e.g., gelatin), hardening agents, antifoggants, metal dopants, silver halide solvents, thickeners, emulsion precipitants, dimensional stabilizers, antiblocking agents, stabilizers, stain inhibitors, dye image stabilizers, stain preventing agents, chemical sensitizers, spectral sensitizers, sensitivity improving agents, supersensitizers, nucleating agents, couplers (e.g., pivaloylacetanilide type yellow couplers, benzoylacetanilide type yellow couples, 5-pyrazolone type magenta couplers, pyrazoloazole type magenta couplers, phenol type cyan couplers, naphthol type cyan couplers, DIR couplers, bleach accelerator-releasing couplers, competing couplers, colored couplers); method of dispersing couplers (e.g., oil-in-water dispersion using high-boiling organic solvents); kind of additives, such as plasticizers, antistatic agents, lubricants, coating aids, surface active agents, whitening agents, formalin scavengers, light scattering agents, matting agents, light absorbents, UV absorbents, filter dyes, irradiation dyes, development improving agents, antiglazing agents, antiseptics (e.g., 2-phenoxyethanol), antifungal agents, and the like. For the details, reference can be made, e.g., in Product Licensing, Vol. 92, pp. 107-110 (Dec., 1971) and Research Disclosure Nos. 17643 (Dec., 1978), 18716 (Nov., 1979), and 307105 (Nov., 1989).

While the processing compositions according to the present invention can be used for any kind of color light-sensitive materials, it is preferable for accomplishing the objects of the second embodiment that a total dry thickness except the thickness of a support and a subbing layer and a backing layer for the support is not more than 20.0 μm, still preferably not more than 18.0 μm, in the case of a color light-sensitive material for photographing and not more than 16.0 μm, still preferably not more than 13.0 μm, in the case of a color light-sensitive material for printing. If the film thickness is greater than that, bleach fog or postprocessing stain due to a residual developing agent after color development tends to increase. Attributed to a green-sensitive light-sensitive layer, such bleach fog and postprocessing stain would result in an outstanding increase of magenta density over an increase in cyan or yellow density.

The thickness of a light-sensitive material is desirably as small as possible as far as the photographic performance properties are not impaired perceptibly. The possible minimum dry thickness, except a support and a subbing layer, of a color light-sensitive material for photographing or printing is 12.0 μm or 7.0 μm, respectively. A color light-sensitive material for photographing usually has a layer or layers between the subbing layer of the support and the light-sensitive layer nearest to the support. The possible minimum dry thickness of such a layer or layers is 1.0 μm. Reduction in film thickness may be achieved with respect to either light-sensitive layers or light-insensitive layers.

The color light-sensitive materials applicable to the present invention preferably has a degree of swelling of from 50 to 200%, still preferably 70 to 150%. The terminology "degree of swelling" as used herein means a rate of film thickness increase when swollen with water at 25°C, which is obtained by [(a total film thickness swollen with water at 25°C to equilibrium) - (a total dry film thickness at 25°C and 55% RH)/(a total dry film thickness at 25°C and 55% RH) x 100]. If a light-sensitive material has a degree of swelling exceeding 200%, a color developing agent tends to remain in the material in a considerable amount, giving adverse influences on image quality (e.g., photographic properties and desilvering properties) and physical properties, such as film strength.

The color light-sensitive materials applicable to the present invention preferably has a rate of swelling $T_{1/2}$ of not more than 15 seconds, still preferably not more than 9 seconds. The terminology "rate of swelling $T_{1/2}$" as used herein means a time required for a light-sensitive material to be swollen to have a half of the total film thickness corresponding to 90% of the maximum swollen thickness when the light-sensitive material is immersed in a color developer at 30°C for 3 minutes and 15 seconds.

The silver halide which can be used in photographic emulsion layers of the color light-sensitive material may have any halogen composition and includes silver chloride, silver bromide, silver chlorobromide, silver iodobromide, silver iodochloride, and silver iodochlorobromide.

In color light-sensitive materials for photographing or color reversal light-sensitive materials (e.g., color negative films, reversal films or color reversal paper), silver iodobromide, silver iodochloride or silver iodochlorobromide having a silver iodide content of 0.1 to 30 mol%, particularly silver iodobromide having a silver iodide content of 1 to 25 mol%, is preferred. In direct positive color light-sensitive materials, silver bromide or silver chlorobromide are preferred, and silver chloride is also preferred for rapid processing. In light-sensitive paper, silver chloride or silver chlorobromide, particularly silver chlorobromide having a silver chloride content of not less than 80 mol%, still preferably not less than 95 mol%, and most preferably not less than 98 mol%, is preferred.

The color light-sensitive materials may contain a variety of color couplers. Examples of useful color couplers are described in the patents listed in Research Disclosure No. 17643, VII-C to G, ibid, No. 307105, VII-C to G, JP-A-62-215272, JP-A-3-33847, JP-A-2-33144, EP-A-447969, and EP-A-482552.

Specific examples of suitable yellow couplers are described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, 4,511,649, and 5,118,599, EP-A-249473, European Patent 447,969, JP-A-63-23145, JP-A-63-123047, JP-A-1-250944, JP-A-1-213648. Particularly preferred yellow couplers include those disclosed in JP-A-2-139544, p. 18, upper left col., to p. 22, lower left col., which are represented by formula (Y); acylacetamide type yellow couplers of JP-A-5-2248 or EP-A-4479696 which are characterized by their acyl group; and those disclosed in JP-A-5-27389 and EP-A-446863, which are represented by formula (Cp-2).

Magenta couplers preferably include 5-pyrazolone compounds and pyrazoloazole compounds. Examples of suitable magenta couplers are described in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (Jun., 1984), JP-A-60-33552, Research Disclosure No. 24230 (Jun., 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, and 4,556,630, and unexamined published international patent application WO 88/04795. Particularly preferred magenta couplers are pyrazoloazole type magenta couplers represented by formula (I) described in JP-A-2-139544, p. 3, lower right col. to p. 10, lower right col. and 5-pyrazolone magenta couplers represented by formula (M-1) described in JP-A-2-135944, p. 17, lower left col. to p. 21, upper left col. The most preferred of them are the above-mentioned pyrazoloazole type magenta couplers.

Useful cyan couplers include phenol couplers and naphthol couplers. Examples of suitable cyan couplers are described 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, and 4,327,173, West German Patent Publication (OLS) No. 3,329,729, EP-A-121365, EP-A-249453, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658.

Additionally, pyrazoloazole type couplers described in JP-A-64-553, JP-A-64-554, JP-A-64-555, and JP-64-556, pyrrolotriazole type couplers described in EP-A-488248 and EP-A-491197, pyrroloimidazole type couplers described in EP-A-456226, pyrazolopyrimidine type couplers described in JP-A-64-46753, imidazole couplers described in U.S. Patent 4,818,672 and JP-A-2-33144, cyclic active methylene type cyan couplers described in JP-A-64-32260, and the couplers described in JP-A-1-183658, JP-A-2-262655, JP-A-2-85851, and JP-A-3-48243 are also useful.

Typical examples of polymerized dye-forming couplers are described in U.S. Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, British Patent 2,102,137, and EP-A-341188.

Couplers which can form dye having moderate diffusibility are described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Patent Publication (OLS) No. 3,234,533.

Couplers capable of releasing a photographically useful residue on coupling reaction are also useful in the present invention. For example, DIR couplers releasing a developing inhibitor are described in the patents listed in Research Disclosure No. 17643, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, and U.S. Patents 4,248,962 and 4,782,012.

Couplers imagewise releasing a nucleating agent or a development accelerator at the time of development are described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840.

Other couplers that can be used in the color light-sensitive materials applicable to the present invention include competing couplers described in U.S. Patent 4,130,427, polyequivalent couplers described in U.S. Patents 4,283,472, 4,338,393, and 4,310,618, DIR redox compound-releasing couplers, DIR coupler-releasing couplers, DIR coupler-releasing redox compounds or DIR redox-releasing redox compounds described in JP-A-60-185950 and JP-A-62-24252, couplers releasing a dye which restores its color after release as described in EP-A-173302, couplers releasing a bleach accelerator as described in Research Disclosure No. 11449, ibid, No. 24241, and JP-A-61-201247, ligand-releasing couplers described in U.S. Patent 4,553,477, leuco dye-releasing couplers described in JP-A-63-75747, and fluorescent dye-releasing couplers described in U.S. Patent 4,774,181.

Supports which can be used suitably in the present invention are described in Research Disclosure No. 17643, p. 28 and ibid, No. 18716, p. 647, right col. to p. 648, left col.

The processing composition containing metal chelate compound (I) according to the second embodiment is also useful as a reducer for correcting a silver dot or line image which is obtained by developing a silver halide light-sensitive material for photomechanical processing.

The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the present invention is not construed as being limited thereto. Examples 1 to 6 relate to the first embodiment, and Examples 7 to 11 relate to the second one.

EXAMPLE 1

A color developer was prepared according to the following formulation.

Color Developer Formulation:

Diethylenetriaminepentaacetic acid	1.0 g
Chelating agent (see Table 1)	0.01 mol
Sodium sulfite	4.0 g
Potassium carbonate	30.0 g
Potassium bromide	1.4 g
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water to make	1000 ml
pH	10.05

To the resulting composition were added ferric chloride and calcium nitrate to give an Fe (III) ion concentration of 5 ppm and a Ca ion concentration of 150 ppm. The resulting color developers were designated samples 101 to 113.

A 5 ℓ portion each of samples 101 to 113 was put in a 10 cm wide, 25 cm long and 30 cm deep container made of rigid polyvinyl chloride, and a floating lid was put thereon to cover 200 cm^2 of the liquid surface, with the remaining 50 cm^2 being exposed to open air. The liquid in the container was kept at 38°C for 30 days while being continuously circulated at a rate of 3 ℓ/min by means of a pump (aging test). Retention (%) of the developing agent and hydroxylamine (preservative) after the aging was analyzed. Further, the aged developer was observed with the naked eye to examine if any sediment was formed.

A multi-layer color light-sensitive material prepared in the same manner as for sample 101 of Example 1 of JP-A-4-274236 was cut to a width of 35 mm and wedgewise exposed to light of 5 CMS at a color temperature of 4800°K and processed according to the following schedule. Color development was conducted using each of the developer immediately after preparation (hereinafter referred to as a fresh developer) and the aged one.

Processing Schedule

Step	Time	Temperature
Color Development	3 min 15 sec	37.8°C
Bleach	50 sec	38.0°C
Fixing	1 min 40 sec	38.0°C
Washing (1)	30 sec	38.0°C
Washing (2)	20 sec	38.0°C
Stabilization	20 sec	38.0°C

Bleaching Solution Formulation:

Ammonium 1,3-propanediaminetetraacetato ferrate	0.55 mol
Ammonium bromide	85 g
Ammonium nitrate	20 g
Glycolic acid	55 g
Water to make	1000 ml
pH	4.0

Fixer Formulation:

Diammonium ethylenediaminetetraacetate	1.7 g
Ammonium sulfite	14.0 g
Ammonium thiosulfate aqueous solution (700 g/ℓ)	260.0 ml
Water to make	1000 ml
pH	7.0

Washing Solution:

Prepared by passing tap water through a mixed bed column packed with an H type strongly acidic cation-exchange resin Amberlite IR-120B, produced by Rohm & Haas Co., and an OH type strongly basic anion-exchange resin Amberlite IRA-400, produced by Rohm & Haas Co., to reduce the Ca and Mg ions each to 3 mg/ℓ or lower and then adding to the treated water 20 mg/ℓ of sodium dichloroisocyanurate and 150 mg/ℓ of sodium sulfate. The resulting washing solution had a pH between 6.5 and 7.5.

Stabilizer Formulation:

Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene-p-monononyl phenyl ether (average degree of polymerization: 10)	0.2 g
Chelating agent (see Table 1)	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75 g
Water to make	1000 ml
pH	8.5

The exposure that gave the light-sensitive material processed with a fresh developer a blue density of 2.5 as measured under blue light was obtained, and the blue density of the light-sensitive material processed with an aged developer obtained at the same exposure was measured with a photographic densitometer X-Rite 310 to obtain a decrease in blue density due to the aging of the developer (ΔD_B).

Further, the same light-sensitive material was processed at a rate of 180 m per day for consecutive 5 days, and the developing machine was stopped for 2 days. An aliquot of the water of the final washing tank (washing tank (2)) was taken out, and the number of living bacteria per milliliter was measured.

Furthermore, the same light-sensitive material was uniformly exposed to light of 500 CMS at a color temperature of 2854°K, processed in the same manner as described above, and cut to a size of 35 mm x 40 mm. A suspension of Aspergillus niger in a 10-fold diluted M-40Y medium (400 g of sucrose, 20 g of malt extract, 5 g of yeast extract, and 1 ℓ of water) was prepared, and 0.03 ml of the cell suspension was dropped on the center of the emulsion layer side of the cut film. The spot of the cell suspension had a diameter of about 2 mm. The spotted film was placed in a sterilized plastic dish containing absorbent wadding impregnated with sterilized water and allowed to stand at 27°C for 3 weeks with a cover on the dish. After 3 weeks, the average diameter of the colony of the mold radially extending from the center of the spot was measured, and the antifungal properties of the light-sensitive material was rated as follows.

Good	No extension over the spot.
Medium	A colony of 1 cm or less in diameter.
Poor	A colony exceeding 1 cm in diameter.

The results of the above measurements and evaluation are shown in Table 1.

TABLE 1

Developer Sample No.	Chelating Agent	ΔD_B	Developing Agent Retention (%)	Hydroxylamine Retention* (%)	Sediment**	Number of Living Bacteria (/ml)	Anti-fungal Activity
101	none	-0.5	60	20	+++	8×10^1	medium
102	ethylenediamine-tetraacetic acid	-0.4	62	30	-	<10	good
103	ethylenediamine-tetramethylene-phosphonic acid	-0.05	88	70	+	3×10^2	medium
104	β-alaninediacetic acid	-0.4	65	25	++	2×10^3	poor
105	ethylenediamine-N,N'-disuccinic acid	-0.05	70	30	+	2×10^2	poor
106	Compound 1	-0.08	86	74	-	<10	good
107	Compound 4	-0.09	82	50	-	4×10^1	medium
108	Compound 6	-0.1	78	67	-	5×10^1	good
109	Compound 7	-0.2	80	58	-	9×10^1	good
110	Compound 11	-0.07	83	70	-	<10	good
111	Compound 15	-0.05	80	72	-	2×10^2	good
112	Compound 48	-0.1	85	70	-	8×10^1	good
113	Compound 49	-0.2	77	60	-	3×10^1	good

Note: *: Hydroxylamine was oxidized with iodine, and sulfanilic acid and α-naphthylamine were added to develop a red color, which was measured by spectrophotometry.

**: "-" means no sediment; "+" means formation of sediment; the degree of sedimentation becomes serious with the number of the plus marks.

As is apparent from Table 1, developers containing a conventional chelating agent or the light-sensitive materials processed with these developers suffer from some disadvantages, whereas all the testing items were satisfied by the first embodiment of the present invention.

EXAMPLE 2

To the fixer used in Example 1 was added 3 g/ℓ of Compound 1, 4, 6, 11 or 15, and an Fe (III) ion was added thereto in an amount corresponding to what would have been carried over from the preceding bleaching solution to prepare samples 201 to 205, respectively. Each sample was aged at an opening ratio of 0.1 cm^{-1} at 38 °C for 30 days, and development of turbidity was observed. As a result, all the samples containing compound (I) of the present invention maintained clearness with no sediment, whereas the untreated fixer suffered from considerable turbidity after aging.

EXAMPLE 3

To a stabilizer obtained by eliminating the chelating agent from the stabilizer used in Example 1 (designated comparative sample 301) was added, as a chelating agent, 100 mg/ℓ of Compound 1, 4, 6, 11, 15, 48 or 49 to prepare samples 302 to 309, respectively. The multi-layer color light-sensitive material as used in Example 1 was processed in the same manner as in Example 1, except for using a fresh developer 101 and each of samples 302 to 309 as a stabilizer. The processed light-sensitive material was aged at 45 °C and 70% RH for 1 week, and an increase in magenta stain (ΔD_{min}) due to the aging was measured. The results obtained are shown in Table 2.

TABLE 2

Stabilizer Sample No.	Chelating Agent	ΔD_{min}	Remark
301	none	0.25	Comparison
302	Compound 1	0.07	Invention
303	Compound 4	0.09	"
304	Compound 6	0.10	"
305	Compound 7	0.12	"
306	Compound 11	0.09	"
307	Compound 15	0.09	"
308	Compound 48	0.08	"
309	Compound 49	0.15	"

It can be seen that the stabilizer containing compound (I) of the present invention improves image preservability, suppressing an increase in stain after processing.

EXAMPLE 4

A paper support having laminated on each side a polyethylene layer was subjected to a corona discharge treatment and coated with a gelatin subbing layer containing sodium dodecylbenzenesulfonate. The following photographic layers were further provided thereon to prepare a multi-layer color paper (designated color paper 001). Coating compositions were prepared as follows.

Preparation of Coating Composition for 5th Layer:

In a mixed solvent of 0.50 g of Solv-1, 7.4 g of Solv-6, and 27.2 cc of ethyl acetate were dissolved 12.4 g of cyan coupler ExC, 0.40 g of dye image stabilizer Cpd-9, 0.40 g of dye image stabilizer Cpd-8, 7.0 g of ultraviolet absorbent UV-2, 9.5 g of dye image stabilizer Cpd-1, 0.40 g of dye image stabilizer Cpd-6, 0.40 g of dye image stabilizer Cpd-10, and 0.40 g of dye image stabilizer Cpd-11. The solution was added to 270 cc of a 10% gelatin aqueous solution containing 8 cc of sodium dodecylbenzenesulfonate, and the mixture was homogenized in an ultrasonic homogenizer to prepare coupler dispersion C.

Separately, cubic silver chlorobromide emulsion C was prepared by mixing larger size emulsion c' having an average grain size of 0.58 µm and a coefficient of variation of grain size distribution (hereinafter abbreviated as grain size CV) of 0.09 and smaller size emulsion c'' having an average grain size of 0.45 µm and a grain size CV of 0.11 at a mixing ratio of 7:3 (by silver mole). On part of the grain surface of emulsions c' and c'' was localized 0.6 mol% or 0.8 mol%, respectively, of silver bromide, with the rest of the grain comprising silver chloride. Chemical sensitization of emulsions c' and c'' was conducted by sulfur sensitization combined with gold sensitization.

Coupler dispersion C and silver chlorobromide emulsion C were mixed and dissolved to obtain a coating composition for the 5th layer having the formulation hereinafter described.

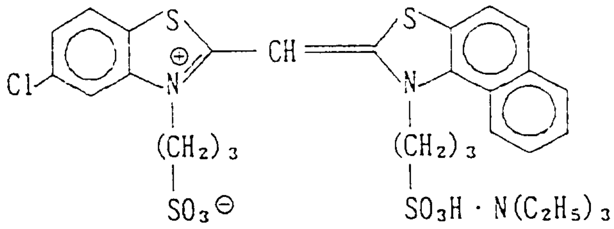
Other coating compositions for coupler-containing silver halide emulsion layers were prepared in the same manner as for the fifth layer.

To each coating composition was added sodium 1-hydroxy-3,5-dichloro-s-triazine and 1,2-bis-(vinylsulfonyl)ethane as gelatin hardening agents. To each layer were further added antiseptics Cpd-14 and Cpd-15 in an appropriate amount so as to give a total content of 25.0 mg of Cpd-14 and 50 mg of Cpd-15 per m^2 of the light-sensitive material.

Spectral sensitizing dyes and their amounts used in the silver chlorobromide emulsions for each light-sensitive emulsion layer are shown below.

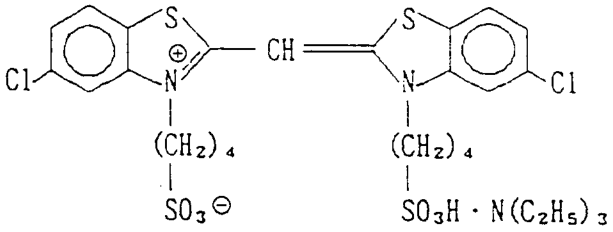
Blue-Sensitive Emulsion Layer:

Sensitizing Dye A:



and

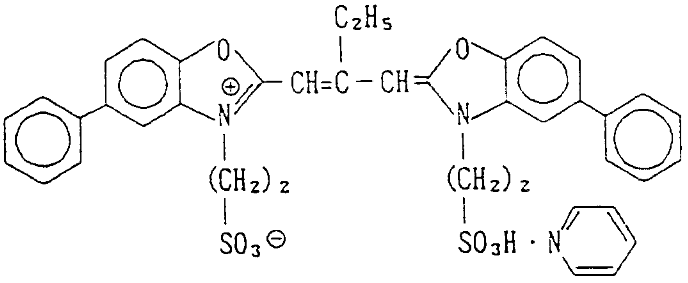
Sensitizing Dye B:



Each in an amount of 2.0 x 10^{-4} mol for emulsion a' and 2.5 x 10^{-4} mol for emulsion a", per mole of silver halide.

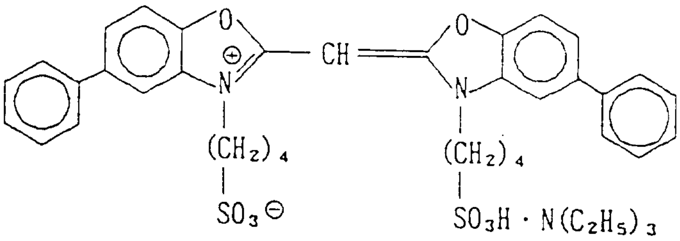
Green-Sensitive Emulsion Layer:

Sensitizing Dye C:



In an amount of 4.0 x 10^{-4} mol for emulsion b' and 5.6 x 10^{-4} mol for emulsion b", per mole of silver halide.

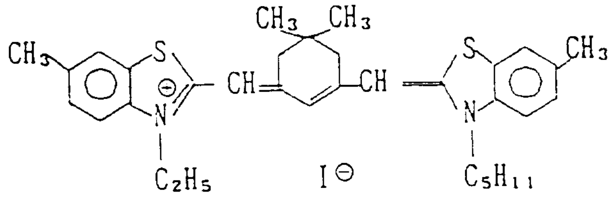
and Sensitizing Dye D:



In an amount of 7.0 x 10^{-5} mol for emulsion b' and 1.0 x 10^{-4} mol for emulsion b", per mole of silver halide.

Red-Sensitive Emulsion Layer:

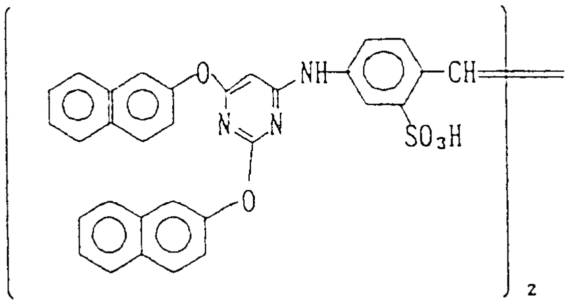
Sensitizing Dye E:



In an amount of 0.9 x 10^{-4} mol for emulsion c' and 1.1 x 10^{-4} mol for emulsion c" per mole of silver halide.

To the red-sensitive emulsion layer was further added the following compound F in an amount of 2.6 x 10^{-3} mol per mole of silver halide:

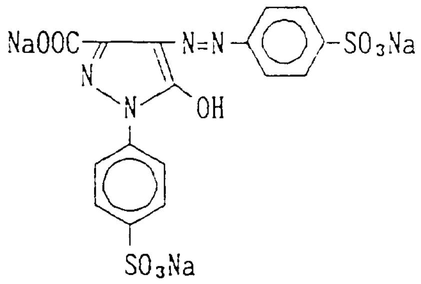
Compound F:



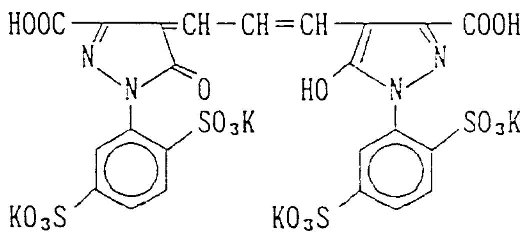
Each of the blue-sensitive emulsion layer, the green-sensitive emulsion layer, and the red-sensitive emulsion layer additionally contained 1-(5-methylureidophenyl)-5-mercaptotetrazole in an amount of 3.4 x 10^{-4} mol, 9.7 x 10^{-4} mol, and 5.5 x 10^{-4} mol, respectively, per mole of silver halide. The blue-sensitive and green-sensitive emulsion layers each furthermore contained 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene in an amount of 1 x 10^{-4} mol and 2 x 10^{-4} mol, respectively, per mole of silver halide.

For prevention of irradiation, the following dyes were added to the emulsion layers. The amount added is shown in the parentheses.

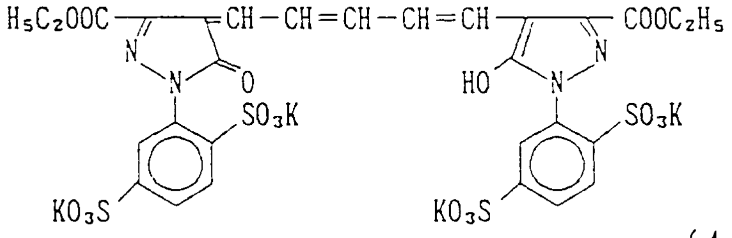
Anti-irradiation Dyes:



(12 mg/m^2)

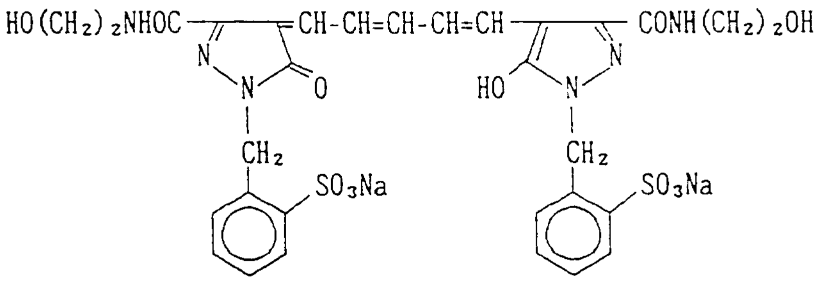


(9 mg/m^2)



(40 mg/m^2)

and



(22 mg/m^2)

The composition of each layer is shown below. The amount of a silver halide emulsion is expressed in terms of gram of silver per unit area (g-Ag/m^2). All the coating compositions were adjusted so as to provide a coating layer having a pH of 7.0.

Support:

Polyethylene-laminated paper, the polyethylene layer on which the first layer is to be provided containing 14% by weight of a white pigment (TiO_2) and a bluing dye (ultramarine).

First layer (yellow coupler-containing blue-sensitive emulsion layer):

Silver chlorobromide emulsion A (cubic; 5:5 (by Ag mole) mixture of larger size emulsion a' having an average grain size of 0.8 µm and a grain size CV of 0.08 and smaller size emulsion a'' having an average grain size of 0.5 µm and a grain size CV of 0.09; 0.4 mol% AgBr localized on part of grain surface, with the rest being AgCl in both emulsions a' and a'')	0.27 g-Ag/m^2
Gelatin	1.21 g/m^2
Yellow coupler ExY	0.79 g/m^2
Dye image stabilizer Cpd-1	0.06 g/m^2
Dye image stabilizer Cpd-2	0.04 g/m^2
Dye image stabilizer Cpd-3	0.08 g/m^2
Solvent Solv-1	0.10 g/m^2
Solvent Solv-2	0.10 g/m^2

Second Layer (color stain preventing layer):

Gelatin	0.95 g/m^2
Color stain preventing agent Cpd-4	0.08 g/m^2
Solvent Solv-7	0.01 g/m^2
Solvent Solv-2	0.20 g/m^2
Solvent Solv-3	0.25 g/m^2

Third layer (magenta coupler-containing green-sensitive emulsion layer):

Silver chlorobromide emulsion B (cubic; 6:4 (by Ag mole) mixture of larger size emulsion b' having an average grain size of 0.55 µm and a grain size CV of 0.10 and smaller size emulsion b'' having an average grain size of 0.39 µm and a grain size CV of 0.08; 0.8 mol% (in emulsion b') or 1.0 mol% (in emulsion b'') of AgBr localized on part of grain surface, with the rest being AgCl)	0.13 g-Ag/m^2
Gelatin	1.38 g/m^2
Magenta coupler ExM	0.16 g/m^2
Dye image stabilizer Cpd-5	0.07 g/m^2
Dye image stabilizer Cpd-2	0.03 g/m^2
Dye image stabilizer Cpd-6	0.01 g/m^2
Dye image stabilizer Cpd-7	0.01 g/m^2
Dye image stabilizer Cpd-8	0.07 g/m^2
Solvent Solv-3	0.30 g/m^2
Solvent Solv-4	0.05 g/m^2
Solvent Solv-5	0.10 g/m^2
Solvent Solv-8	0.20 g/m^2
Solvent Solv-9	0.10 g/m^2

Fourth Layer (color stain preventing layer):

Gelatin	0.65 g/m^2
Color stain preventing agent Cpd-4	0.06 g/m^2
Solvent Solv-7	0.01 g/m^2
Solvent Solv-2	0.15 g/m^2
Solvent Solv-3	0.18 g/m^2

Fifth layer (cyan coupler-containing red-sensitive emulsion layer):

Silver chlorobromide emulsion C (cubic; 7:3 (by Ag mole) mixture of larger size emulsion c' having an average grain size of 0.58 μm and a grain size CV of 0.09 and smaller size emulsion c'' having an average grain size of 0.45 μm and grain size CV of 0.11; 0.6 mol% (in emulsion c') or 0.8 mol% (in emulsion c'') of AgBr localized on part of grain surface, with the rest being AgCl)	0.20 g-Ag/m^2
Gelatin	0.84 g/m^2
Cyan coupler ExC	0.32 g/m^2
UV absorbent UV-2	0.18 g/m^2
Dye image stabilizer Cpd-1	0.25 g/m^2
Dye image stabilizer Cpd-9	0.01 g/m^2
Dye image stabilizer Cpd-10	0.01 g/m^2
Dye image stabilizer Cpd-11	0.01 g/m^2
Solvent Solv-6	0.19 g/m^2
Dye image stabilizer Cpd-8	0.01 g/m^2
Dye image stabilizer Cpd-6	0.01 g/m^2
Solvent Solv-1	0.01 g/m^2

Sixth layer (UV-absorbing layer):

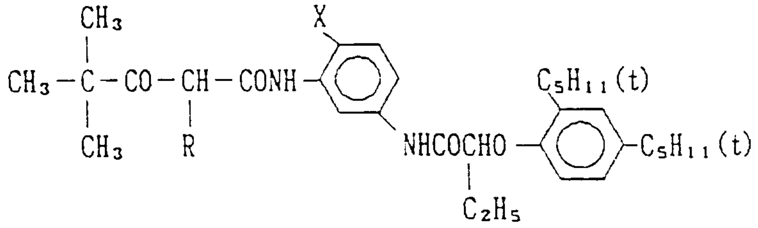
Gelatin	0.53 g/m^2
UV absorbent UV-1	0.38 g/m^2
Dye image stabilizer Cpd-12	0.15 g/m^2

Seventh layer (protective layer):

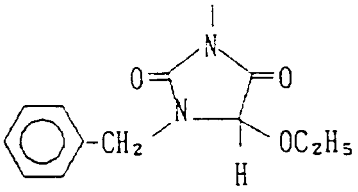
Gelatin	1.12 g/m^2
Acryl-modified polyvinyl alcohol copolymer (degree of modification: 17%)	0.07 g/m^2
Liquid paraffin	0.01 g/m^2
Dye image stabilizer Cpd-13	0.01 g/m^2

Compounds used in the above compositions are shown below.

Yellow Coupler ExY:

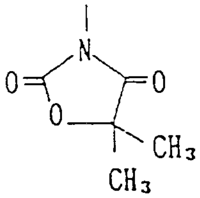


A 1:1 (by mole) mixture of
R =



;

X = Cl
and
R =

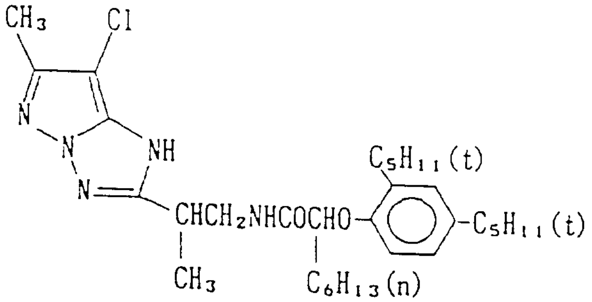


;

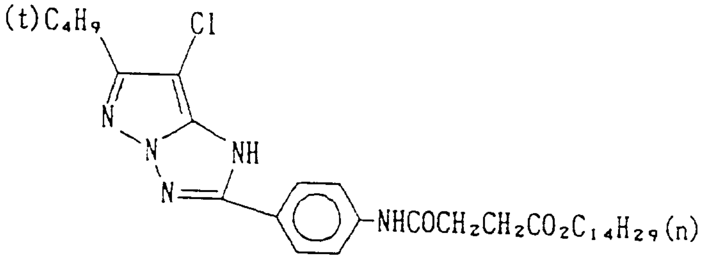
x = OCH_3

Magenta Coupler ExM:

A 1:1 (by mole) mixture of

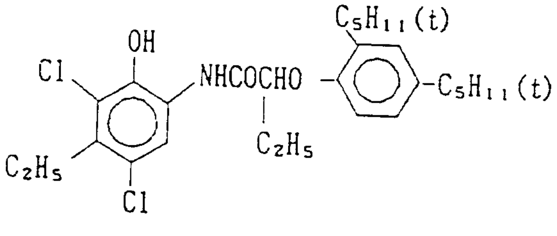


and

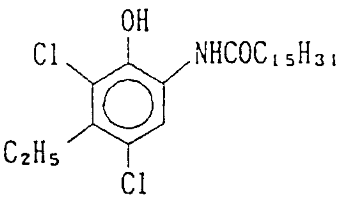


Cyan Coupler ExC:

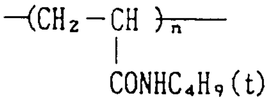
A 3:7 (by mole) mixture of



and



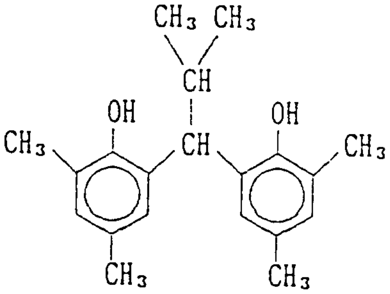
Dye Image Stabilizer Cpd-1:



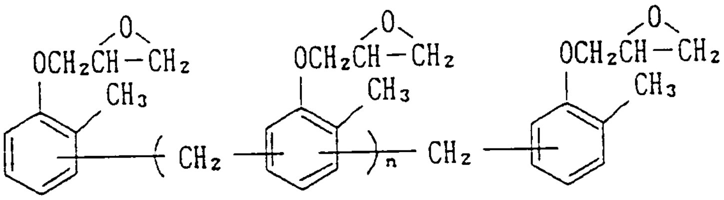
$$-\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{CH}\right)_n\!-$$

(Average molecular weight: 60,000)

Dye Image Stabilizer Cpd-2:



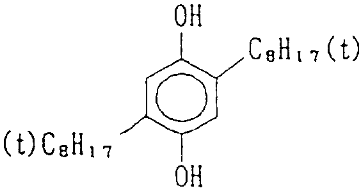
Dye Image Stabilizer Cpd-3:



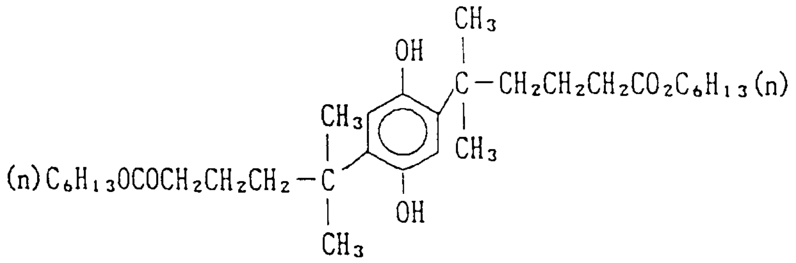
(n = 7 to 8 in average)

Color Stain Preventing Agent (Cpd-4):

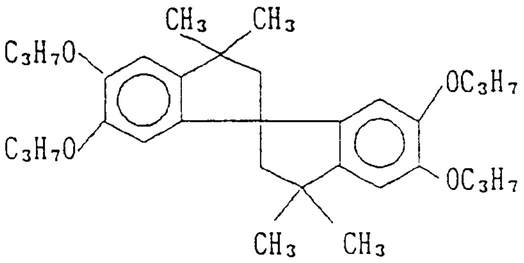
A 1:1 (by weight) mixture of



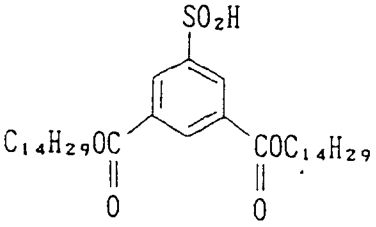
and



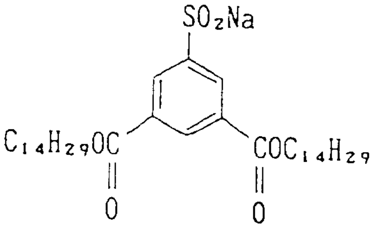
Dye Image Stabilizer Cpd-5:



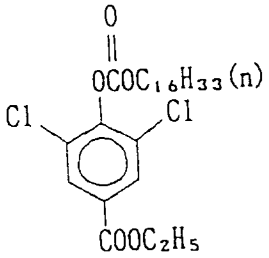
Dye Image Stabilizer Cpd-6:



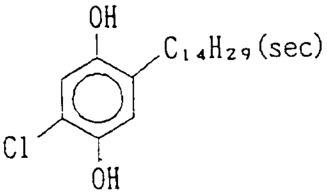
Dye Image Stabilizer Cpd-7:



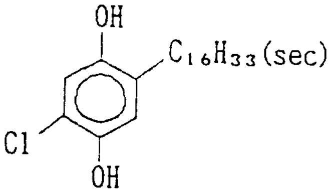
Dye Image Stabilizer Cpd-8:



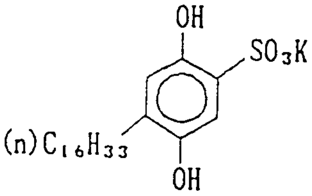
Dye Image Stabilizer Cpd-9:



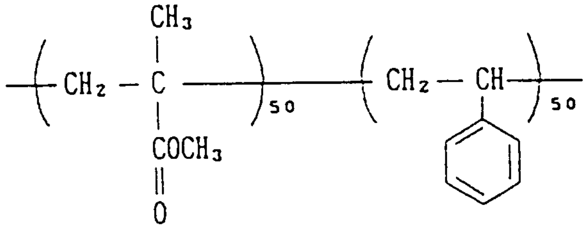
Dye Image Stabilizer Cpd-10:



Dye Image Stabilizer Cpd-11:

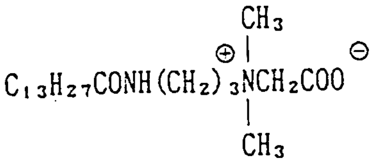


Dye Image Stabilizer Cpd-12:



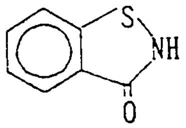
(Average molecular weight: 60,000)

Dye Image Stabilizer Cpd-13:

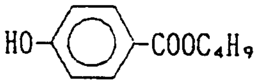


$C_{13}H_{27}CONH(CH_2)_3\overset{\oplus}{N}(CH_3)_2CH_2COO^{\ominus}$

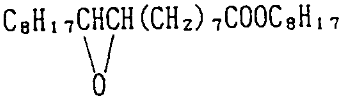
Antiseptic Cpd-14:



Antiseptic Cpd-15:

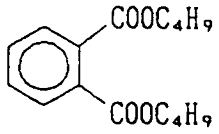


Solvent Solv-1:

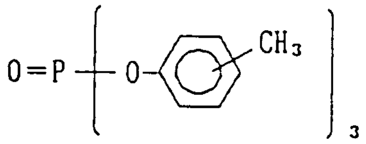


$C_8H_{17}CHCH(CH_2)_7COOC_8H_{17}$

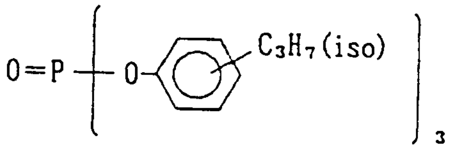
Solvent Solv-2:



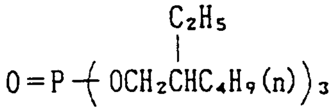
Solvent Solv-3:



Solvent Solv-4:

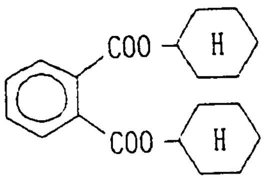


Solvent Solv-5:

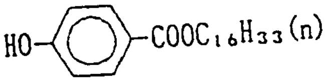


$$O=P\left(OCH_2\overset{\overset{C_2H_5}{|}}{C}HC_4H_9(n)\right)_3$$

Solvent Solv-6:



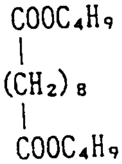
Solvent Solv-7:



Solvent Solv-8:

$O = P[OC_6H_{13}(n)]$

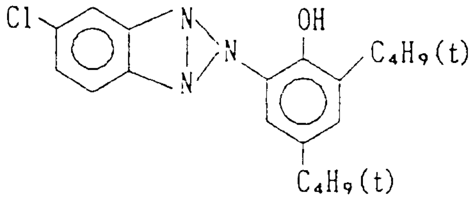
Solvent Solv-9:

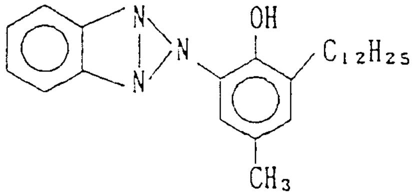


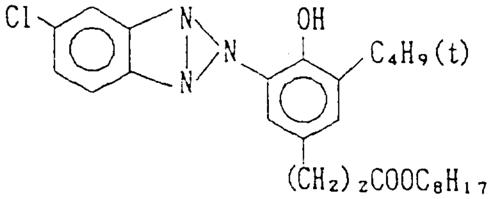
$$\begin{array}{c} COOC_4H_9 \\ | \\ (CH_2)_8 \\ | \\ COOC_4H_9 \end{array}$$

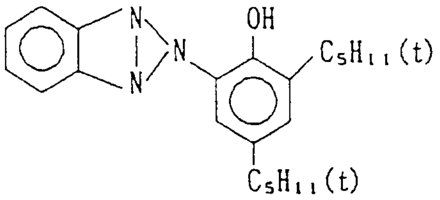
UV Absorbent UV-1:

A 1:5:10:5 (by weight) mixture of



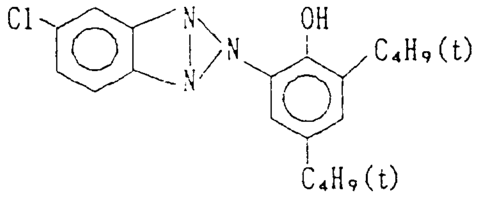


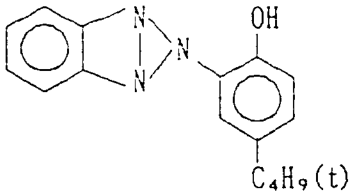


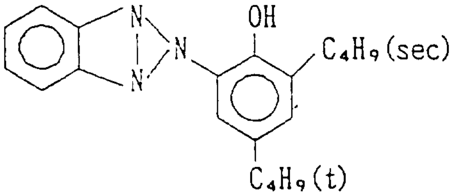


UV Absorbent UV-2:

A 1:2:2 (by weight) mixture of







A color developer having the following formulation was prepared. The resulting color developer was designated sample 401.

Formulation of Color Developer:

Water	800 ml
Potassium bromide	0.03 g
Potassium chloride	6.5 g
Disodium 4,5-dihydroxybenzene-1,3-disulfonate	0.5 g
Triethanolamine	12.0 g
Potassium carbonate	27 g
Sodium sulfite	0.1 g
Brightening agent WHITEX 4B, produced by Sumitomo Chemical Co., Ltd.	1.0 g
Preservative (disodium N,N-bis(sulfonatoethyl)hydroxylamine	45 mmol
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Water to make	1000 ml
pH (25 ° C/adjusted with potassium hydroxide and sulfuric acid).	10.00

To color developer sample 401 was added the compound shown in Table 3 below to prepare samples 402 to 408. To each of samples 401 to 408 were added 5 ppm of an iron (III) ion and 150 ppm of a calcium ion. Each sample was put in a beaker (opening ratio: 0.10 cm^{-1}) and aged at 38 ° C for 20 days.

Color paper 001 was wedgewise exposed to light through separation filters for sensitometry by using a sensitometer FWH, manufactured by Fuji Photo Film Co., Ltd. The exposure was conducted for an exposure time of 0.1 sec to give an exposure of 250 CMS. The exposed color paper was processed according to the following schedule in a small-sized automatic developing machine using the above-prepared developer immediately after preparation (fresh developer) or the aged one.

Processing Schedule

Step	Temperature	Time
Color Development	38 ° C	45 sec
Blix	35 ° C	25 sec
Rinsing (1)	35 ° C	20 sec
Rinsing (2)	35 ° C	20 sec
Rinsing (3)	35 ° C	20 sec
Drying	80 ° C	60 sec

Processing solutions other than the developer had the following formulations.

Blix Bath:

Water	600 ml
Ammonium thiosulfate (750 g/ℓ)	93 ml
Ammonium sulfite	40 g
Ammonium ethylenediaminetetraacetato ferrate	55 g
Ethylenediaminetetraacetic acid	5 g
Nitric acid (67%)	30 g
Water to make	1000 ml
pH (25 ° C/adjusted with acetic acid and aqueous ammonia)	5.8

Rinsing Solution:

Sodium dichloroisocyanurate-containing deionized water (conductivity: 5 µs/cm or lower)	1000 ml
pH	6.5

The minimum yellow density (D_{min}) and magenta sensitivity (logarithm of an exposure that gives a density of 0.5) were measured for both the color paper processed with a fresh developer and the one processed with an aged developer to obtain an increase in D_{min} (ΔD_{min}) and a change in magenta sensitivity (ΔS) due to the aging of the developer. Further, the residual amount of the developing agent in the aged developer was measured by high-performance liquid chromatography. Development of sediment of the aged developer was observed. The results obtained are shown in Table 3.

TABLE 3

Developer Sample No.	Chelating Agent (Amount Added)	Yellow ΔD_{min}	Magenta ΔS	Developing Agent Retention (%)	Sediment*	Remark
401	none	+0.07	-0.11	61	+++	Comparison
402	sodium hexametaphosphate (1 g/ℓ)	+0.04	-0.07	78	++	"
403	1-hydroxyethylidene-1,1-diphosphonic acid (60%) (1.6 g/ℓ)	+0.04	-0.05	80	++	"
404	ethylenediaminetetraacetic acid (1 g/ℓ)	+0.06	-0.08	65	-	"
405	nitrilotrimethylenephosphonic acid (1 g/ℓ)	+0.05	-0.07	75	+	"
406	Compound 1	+0.03	-0.03	85	-	Invention
407	Compound 4	+0.04	-0.04	80	-	"
408	Compound 48	+0.03	-0.05	82	-	"

Note: * "-" means no sediment; "+" means formation of sediment; the degree of sedimentation becomes serious with the number of the plus marks.

The results of Table 3 prove that addition of compound (I) according to the present invention to a developer not only suppresses variation of photographic characteristics, such as stain and sensitivity but improves aging stability of the developer. In particular, such a comparative chelating agent that is effective on prevention of sedimentation turned out to be ineffective on improvement of preservability of a developing agent, while such a comparative chelating agent that is effective to prevent decomposition of a developing agent was revealed to be insufficient in prevention of sedimentation. To the contrary, compounds (I) of the present invention provide a stable developer which is freed of sedimentation on being aged.

Further, color paper 001 was continuously processed in the same manner using developer 406 or 408 while replenishing each of the processing solutions with a respective replenisher prepared so as to maintain the composition of the running solution. The rates of replenishment were 73 ml/m^2 for a color developer, 60 ml/m^2 for a blix bath, and 360 ml/m^2 for a rinsing solution in a 3 tanks counter-current system. The processing was continued until the total amount of the developer replenisher supplied reached twice the volume of the development tank. In this case, too, the developer showed stable performance without forming sediment.

EXAMPLE 5

Developer (A) having the following formulation was prepared.

Formulation of Developer (A):

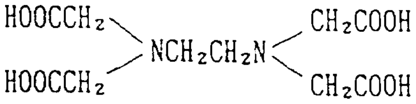
Hydroquinone	45.0 g
N-Methyl-p-aminophenol 1/2 sulfate	0.8 g
Sodium hydroxide	18.0 g
Potassium hydroxide	55.0 g
5-Sulfosalicylic acid	45.0 g
Boric acid	25.0 g
Potassium sulfite	110.0 g
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	6.0 g
5-Methylbenzotriazole	0.6 g
n-Butyldiethanolamine	15.0 g
Water to make	1000 ml
pH	11.6

Developer (B) having the same composition as developer (A), except that disodium ethylenediaminetetraacetate was replaced with the equimolar amount of Compound 1 of the present invention, was prepared. After developers (A) and (B) were aged at 40 ° C for 4 days, Sample No. B-6 of Example of JP-A-3-174148 was continuously processed with the aged developer (A) or (B). Developer (B) showed an apparent improvement over developer (A) in prevention of sedimentation. Further, as a result of analysis of the aged developers (A) and (B), it was confirmed that the addition of Compound 1 to the developer minimized the loss of hydroquinone and potassium sulfite due to air oxidation and also suppressed an increase of the pH value due to the loss of these components.

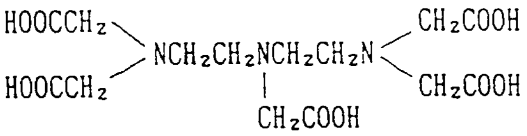
EXAMPLE 6

Compounds 4, 7, 43, 48, and 49 according to the present invention and comparative compounds A to D shown below were tested for their biodegradability according to the modified SCAS method specified in OECD chemicals test guidelines. As a result, Compounds 4, 7, 43, 48, and 49 exhibited satisfactory biodegradability, whereas compounds A to D were hardly biodegraded. Compounds (I) of the present invention were thus proved superior to the comparative compounds in biodegradability.

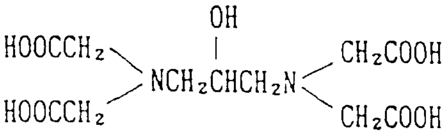
Comparative Compound A:



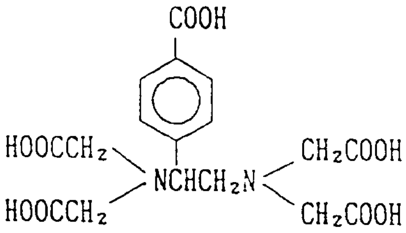
Comparative Compound B:



Comparative Compound C:



Comparative Compound D:



(described in JP-A-63-97953)

EXAMPLE 7

A cellulose triacetate film having a subbing layer was coated with the following layers to prepare a multi-layer color light-sensitive material. In the following layer structure, the amount of silver halide is expressed in terms of gram of silver per unit area (g-Ag/m^2), and the amount of sensitizers is expressed in terms of mole per mole of silver halide (mol/mol-AgX).

First layer (Anti-halation layer):

Black colloidal silver	0.18 g-Ag/m^2
Gelatin	1.40 g/m^2
Magenta coupler ExM-1	0.18 g/m^2
ExF-1	2.0x10^{-3} mol/mol-AgX
Solvent HBS-1	0.20 g/m^2

Second layer (Intermediate layer):

Silver iodobromide emulsion G	0.065 g-Ag/m^2
2,5-Di-t-pentadecylhydroquinone	0.18 g/m^2
Cyan coupler ExC-2	0.020 g/m^2
UV absorbent UV-1	0.060 g/m^2
UV absorbent UV-2	0.080 g/m^2
UV absorbent UV-3	0.10 g/m^2
Solvent HBS-1	0.10 g/m^2
Solvent HBS-2	0.020 g/m^2
Gelatin	1.04 g/m^2

Third layer (Low sensitivity red-sensitive emulsion layer):

Silver iodobromide emulsion A	0.25 g-Ag/m^2
Silver iodobromide emulsion B	0.25 g-Ag/m^2
Sensitizing dye ExS-1	6.9x10^{-5} mol/mol-AgX
Sensitizing dye ExS-2	1.8x10^{-5} mol/mol-AgX
Sensitizing dye ExS-3	3.1x10^{-4} mol/mol-AgX
Cyan coupler ExC-1	0.17 g/m^2
Cyan coupler ExC-3	0.030 g/m^2
Cyan coupler ExC-4	0.10 g/m^2
Cyan coupler ExC-5	0.020 g/m^2
Cyan coupler ExC-7	0.0050 g/m^2
Cyan coupler ExC-8	0.010 g/m^2
Additive Cpd-2	0.025 g/m^2
Solvent HBS-1	0.10 g/m^2
Gelatin	0.87 g/m^2

Fourth Layer (Middle sensitivity red-sensitive emulsion layer):

Silver iodobromide emulsion D	0.70 g-Ag/m^2
Sensitizing dye ExS-1	3.5×10^{-4} mol/mol-AgX
Sensitizing dye ExS-2	1.6×10^{-5} mol/mol-AgX
Sensitizing dye ExS-3	5.1×10^{-4} mol/mol-AgX
Cyan coupler ExC-1	0.13 g/m^2
Cyan coupler ExC-2	0.060 g/m^2
Cyan coupler ExC-3	0.0070 g/m^2
Cyan coupler ExC-4	0.090 g/m^2
Cyan coupler ExC-5	0.025 g/m^2
Cyan coupler ExC-7	0.0010 g/m^2
Cyan coupler ExC-8	0.0070 g/m^2
Additive Cpd-2	0.023 g/m^2
Solvent HBS-1	0.10 g/m^2
Gelatin	0.75 g/m^2

Fifth layer (High sensitivity red-sensitive emulsion layer):

Silver iodobromide emulsion E	1.40 g-Ag/m^2
Sensitizing dye ExS-1	2.4×10^{-4} mol/mol-AgX
Sensitizing dye ExS-2	1.0×10^{-4} mol/mol-AgX
Sensitizing dye ExS-3	3.4×10^{-4} mol/mol-AgX
Cyan coupler ExC-1	0.12 g/m^2
Cyan coupler ExC-3	0.045 g/m^2
Cyan coupler ExC-6	0.020 g/m^2
Cyan coupler ExC-8	0.025 g/m^2
Additive Cpd-2	0.050 g/m^2
Solvent HBS-1	0.22 g/m^2
Solvent HBS-2	0.10 g/m^2
Gelatin	1.20 g/m^2

Sixth layer (Intermediate layer):

Additive Cpd-1	0.10 g/m^2
Solvent HBS-1	0.50 g/m^2
Gelatin	1.10 g/m^2

Seventh layer (Low sensitivity green-sensitive emulsion layer):

Silver iodobromide emulsion C	0.35 g-Ag/m^2
Sensitizing dye ExS-4	3.0×10^{-5} mol/mol-AgX
Sensitizing dye ExS-5	2.1×10^{-4} mol/mol-AgX
Sensitizing dye ExS-6	8.0×10^{-4} mol/mol-AgX
Magenta coupler ExM-1	0.010 g/m^2
Magenta coupler ExM-2	0.33 g/m^2
Magenta coupler ExM-3	0.086 g/m^2
Yellow coupler ExY-1	0.015 g/m^2
Solvent HBS-1	0.30 g/m^2
Solvent HBS-3	0.010 g/m^2
Gelatin	0.72 g/m^2

Eighth layer (Middle sensitivity green-sensitive emulsion layer):

Silver iodobromide emulsion D	0.80 g-Ag/m^2
Sensitizing dye ExS-4	3.2×10^{-5} mol/mol-AgX
Sensitizing dye ExS-5	2.2×10^{-4} mol/mol-AgX
Sensitizing dye ExS-6	8.4×10^{-4} mol/mol-AgX
Magenta coupler ExM-2	0.13 g/m^2
Magenta coupler ExM-3	0.030 g/m^2
Yellow coupler ExY-1	0.018 g/m^2
Solvent HBS-1	0.16 g/m^2
Solvent HBS-3	8.0×10^{-3} g/m^2
Gelatin	0.89 g/m^2

Ninth layer (High sensitivity green-sensitive emulsion layer):

Silver iodobromide emulsion E	1.25 g-Ag/m^2
Sensitizing dye ExS-4	3.7×10^{-5} mol/mol-AgX
Sensitizing dye ExS-5	8.1×10^{-5} mol/mol-AgX
Sensitizing dye ExS-6	3.2×10^{-4} mol/mol-AgX
Cyan coupler ExC-1	0.010 g/m^2
Magenta coupler ExM-1	0.030 g/m^2
Magenta coupler ExM-4	0.040 g/m^2
Magenta coupler ExM-5	0.019 g/m^2
Additive Cpd-3	0.040 g/m^2
Solvent HBS-1	0.25 g/m^2
Solvent HBS-2	0.10 g/m^2
Gelatin	1.40 g/m^2

Tenth layer (Yellow filter layer):

Yellow colloidal silver	0.030 g-Ag/m^2
Additive Cpd-1	0.16 g/m^2
Solvent HBS-1	0.60 g/m^2
Gelatin	0.60 g/m^2

Eleventh layer (Low sensitivity blue-sensitive emulsion layer):

Silver iodobromide emulsion C	0.18 g-Ag/m^2
Sensitizing dye ExS-7	8.6x10^{-4} mol/mol-AgX
Yellow coupler ExY-1	0.020 g/m^2
Yellow coupler ExY-2	0.22 g/m^2
Yellow coupler ExY-3	0.50 g/m^2
Yellow coupler ExY-4	0.020 g/m^2
Solvent HBS-1	0.28 g/m^2
Gelatin	1.08 g/m^2

Twelfth layer (Middle sensitivity blue-sensitive emulsion layer):

Silver iodobromide emulsion D	0.40 g-Ag/m^2
Sensitizing dye ExS-7	7.4x10^{-4} mol/mol-AgX
Cyan coupler ExC-7	7.0x10^{-3} g/m^2
Yellow coupler ExY-2	0.050 g/m^2
Yellow coupler ExY-3	0.10 g/m^2
Solvent HBS-1	0.050 g/m^2
Gelatin	0.78 g/m^2

Thirteenth layer (High sensitivity blue-sensitive emulsion layer):

Silver iodobromide emulsion F	1.00 g-Ag/m^2
Sensitizing dye ExS-7	4.0x10^{-4} mol/mol-AgX
Yellow coupler ExY-2	0.10 g/m^2
Yellow coupler ExY-3	0.10 g/m^2
Solvent HBS-1	0.070 g/m^2
Gelatin	0.86 g/m^2

Fourteenth layer (1st protective layer):

Silver iodobromide emulsion G	0.20 g-Ag/m^2
UV absorbent UV-4	0.11 g/m^2
UV absorbent UV-5	0.17 g/m^2
Solvent HBS-1	5.0×10^{-2} g/m^2
Gelatin	1.00 g/m^2

Fifteenth layer (2nd protective layer):

Hardening agent H-1	0.40 g/m^2
Additive B-1 (diameter: 1 7 µm)	5.0×10^{-2} g/m^2
Additive B-2 (diameter: 1.7 µm)	0.10 g/m^2
Additive B-3	0.10 g/m^2
Additive S-1	0.20 g/m^2
Gelatin	1.20 g/m^2

For improving preservability, processability, pressure resistance, antifungal and antibacterial properties, antistatic properties, and coating properties, each layer contained appropriately W-1, W-2, W-3, B-4, B-5, B-6, F-1 to 17, an iron salt, a lead salt, a gold salt, a platinum salt, an iridium salt, and a rhodium salt.

Silver iodobromide emulsions A to G used in the light-sensitive material are shown in Table 4.

TABLE 4

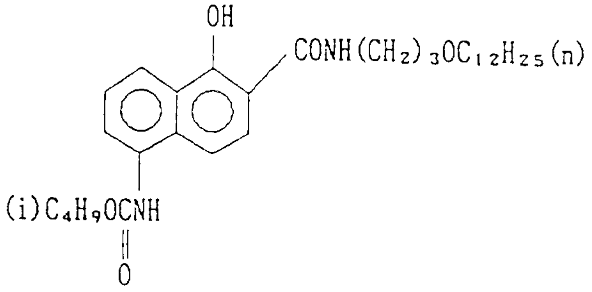
Emulsion No.	Average AgI Content (%)	Average Grain Size (μm)	Grain Size CV (%)	Diameter/ Thickness Ratio	Core/(Intermediate)/ Shell Ag Content Ratio (AgI Content Ratio)	Grain Structure/Shape
A	4.0	0.45	27	1	1/3 (13/1)	double-layered/ octahedral grains
B	8.9	0.70	14	1	3/7 (25/2)	"
C	2.0	0.55	25	7	-	homogeneous/ tabular grains
D	9.0	0.65	25	6	12/59/29 (0/11/8)	triple-layered/ tabular grains
E	9.0	0.85	23	5	8/59/33 (0/11/8)	"
F	14.5	1.25	25	3	37/63 (34/3)	double-layered/ plate-like grains
G	1.0	0.07	15	1	-	homogeneous/fine particles

Emulsions A to F had been sensitized during grain formation by reduction sensitization using thiourea dioxide and thiosulfonic acid in accordance with Example of JP-A-2-191938. Emulsions A to F had been sensitized by gold sensitization, sulfur sensitization and selenium sensitization in the presence of the respective spectral sensitizing dyes and sodium thiocyanate in accordance with Example of JP-A-3-237450. Tabular silver halide grains were prepared by using low-molecular weight gelatin according to Example of

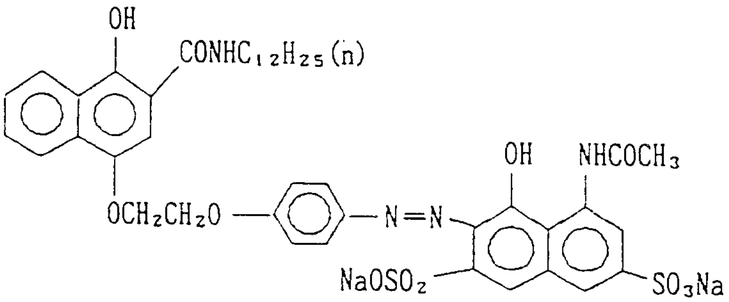
JP-A-1-158426. Tabular grains and normal crystal grains having a grain structure were observed to have a dislocation line as described in JP-A-3-237450 under a high-voltage electron microscope.

Compounds used in the light-sensitive material are shown below.

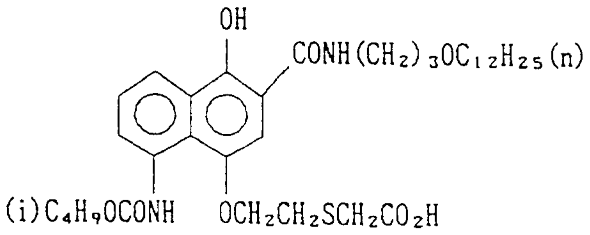
ExC-1



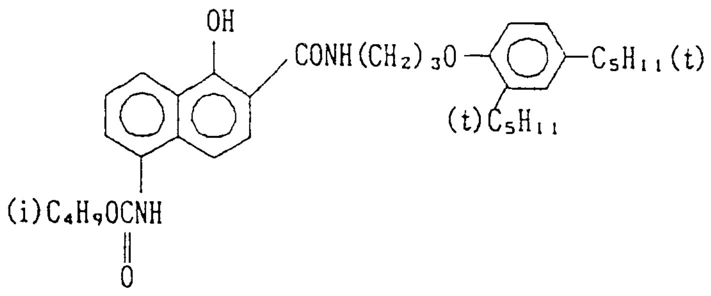
ExC-2



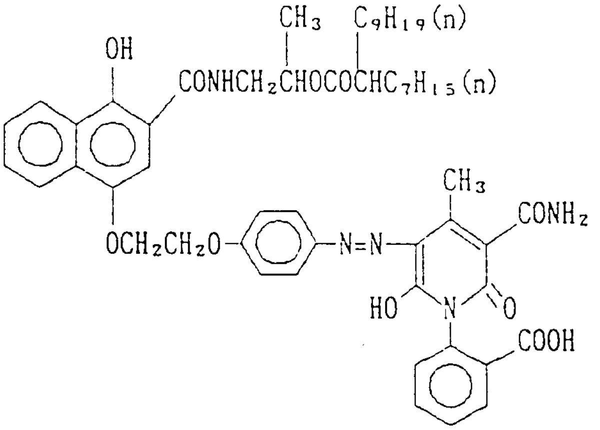
ExC-3



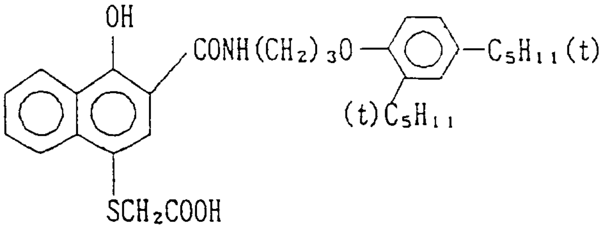
ExC-4



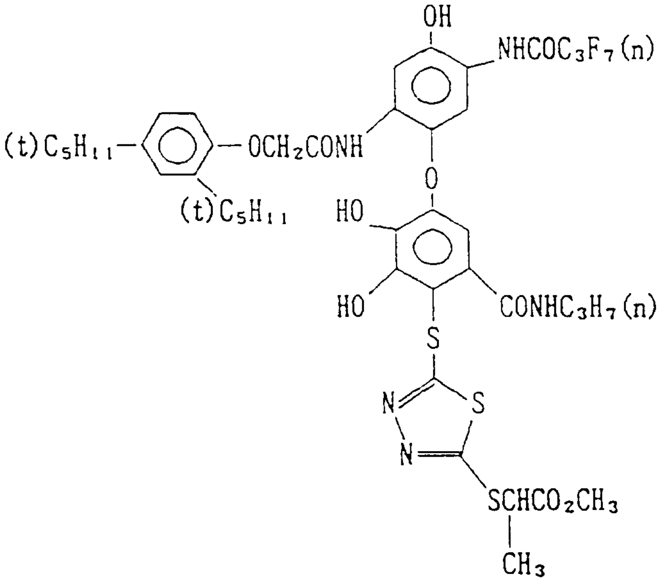
ExC－5



ExC－6



ExC－7



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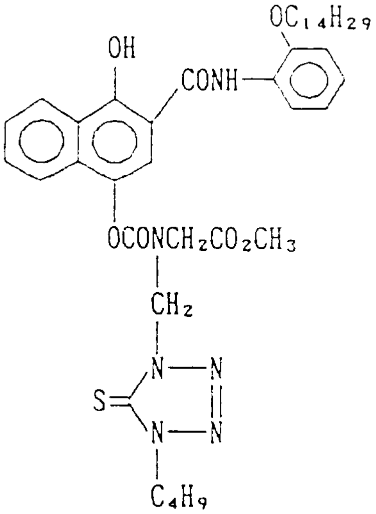
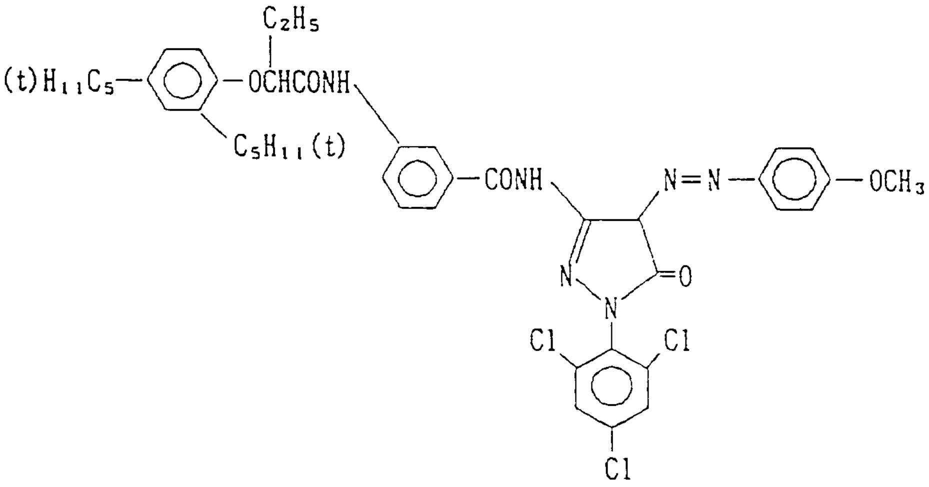
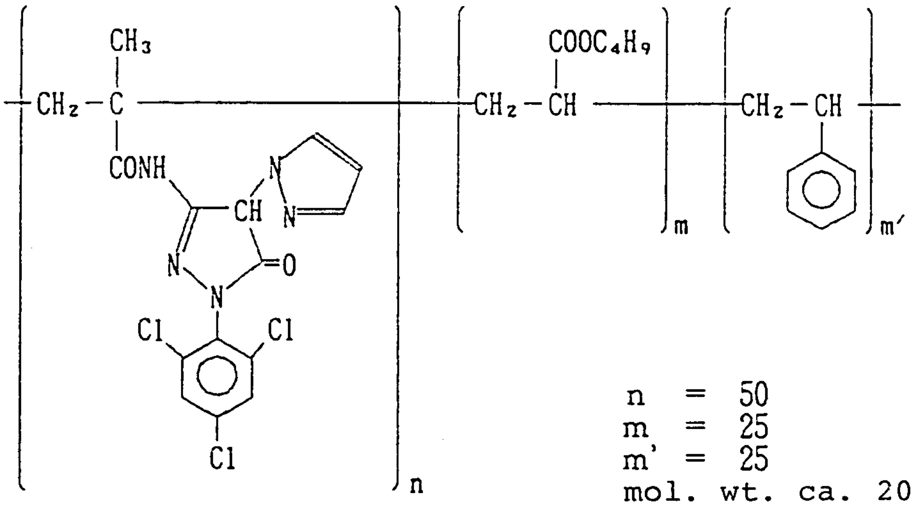


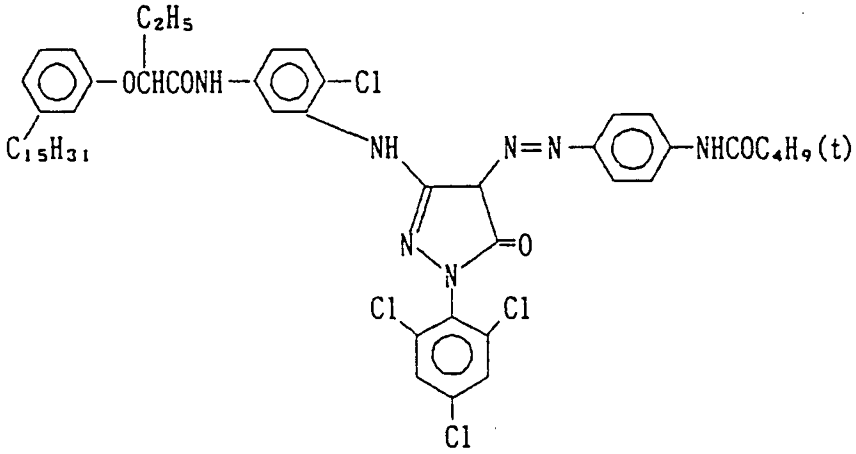
ExM-1



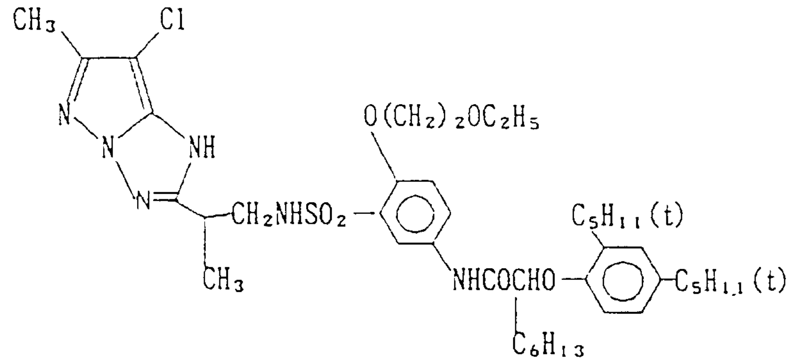
ExM-2



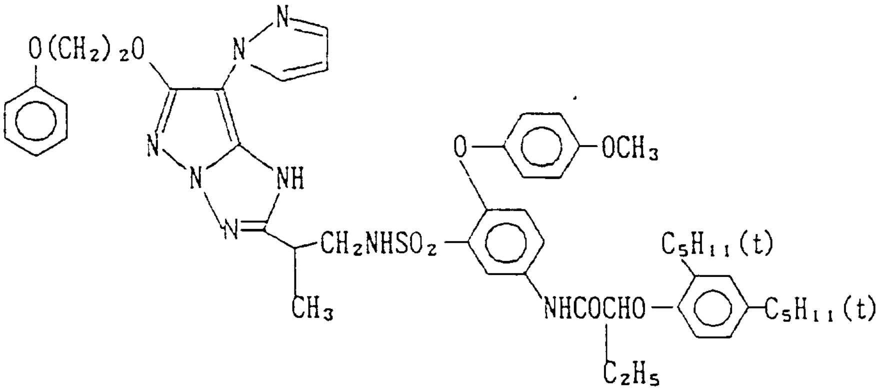
ExM-3



ExM－4



ExM－5



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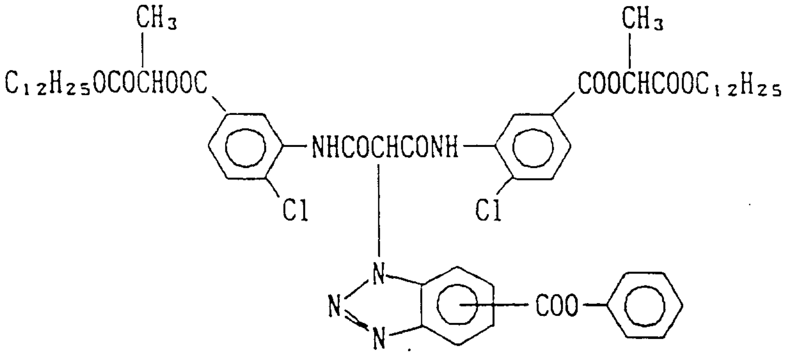
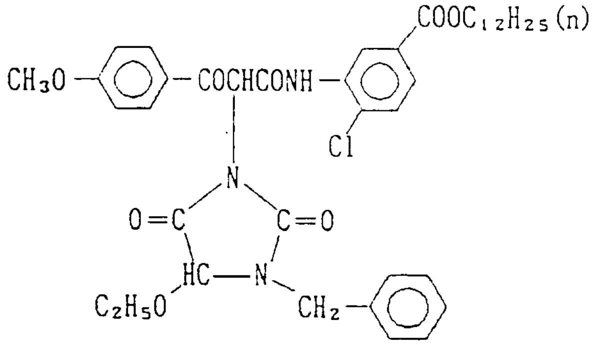
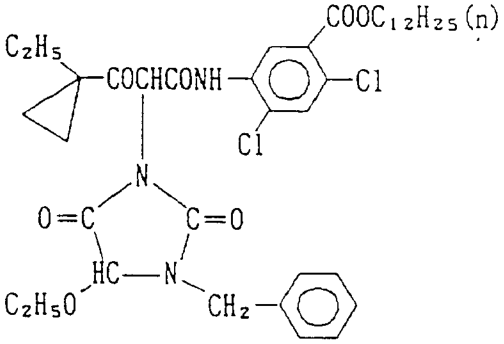


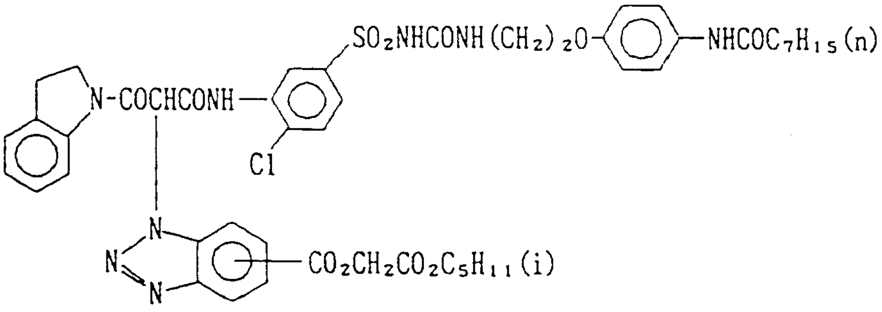
ExY－2



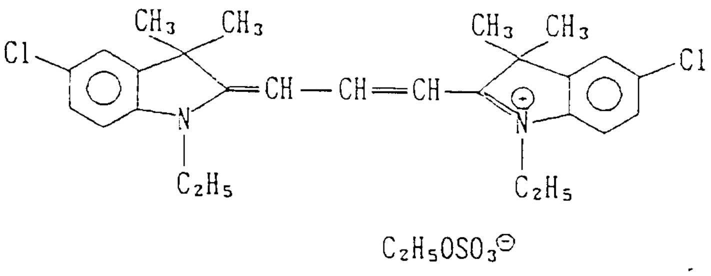
ExY－3



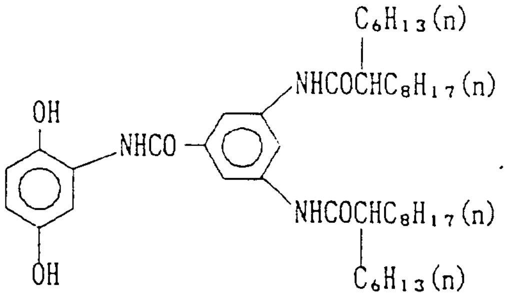
ExY－4



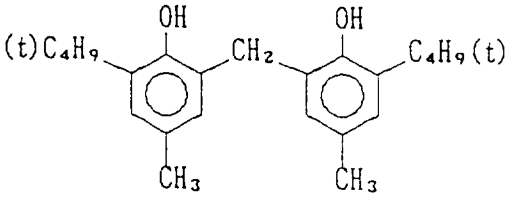
ExF－1



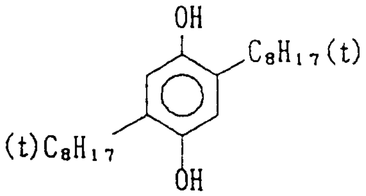
Cpd－1



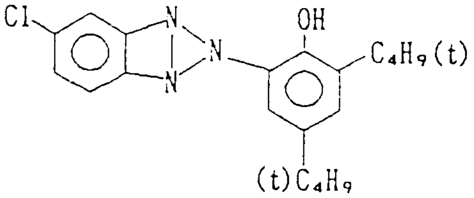
Cpd－2



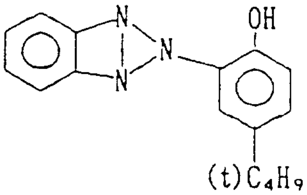
Cpd－3



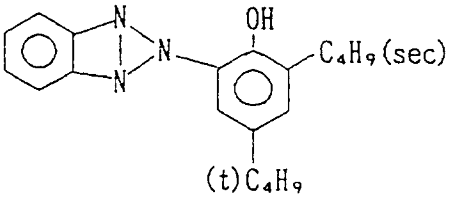
UV－1



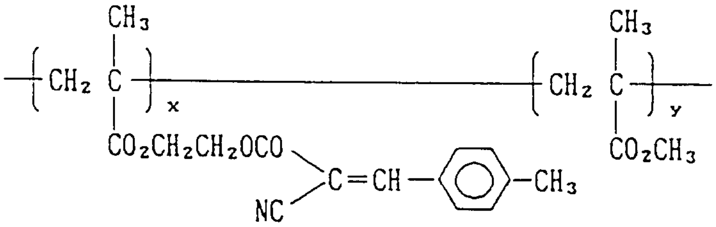
UV－2



UV－3

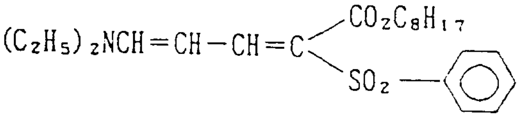


UV－4



x : y =70 : 30 (wt%)

UV-5:



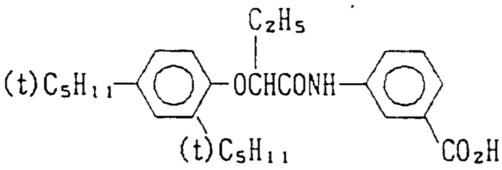
HBS-1:

Tricresyl phosphate

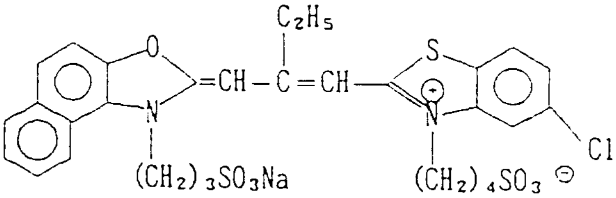
HBS-2:

Di-n-butyl phthalate

HBS-3:



ExS-1



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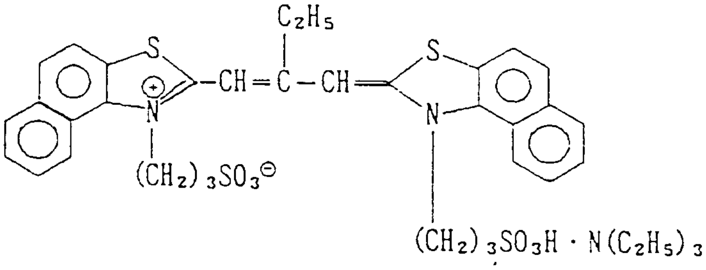
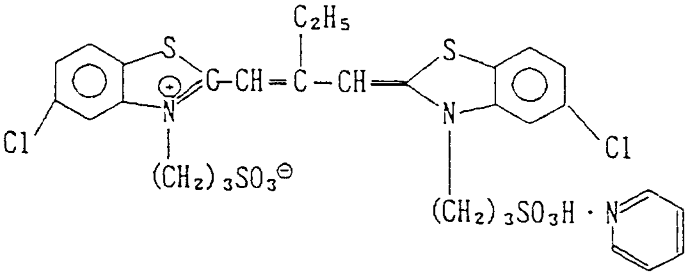
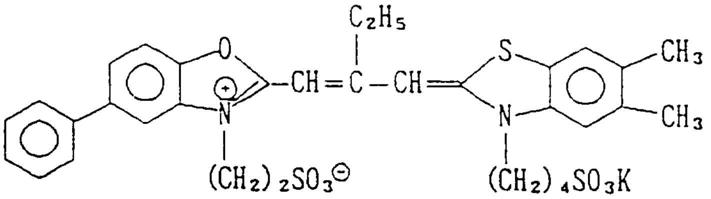


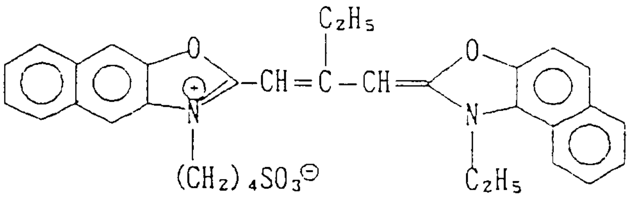
ExS-3



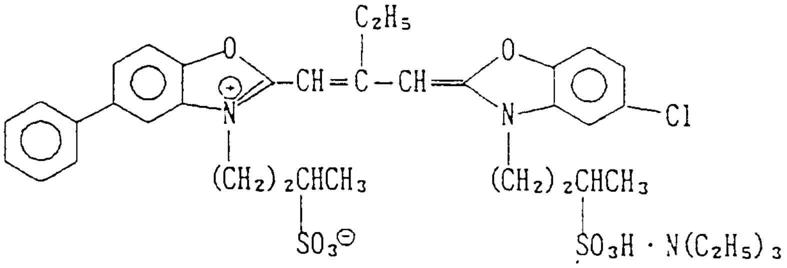
ExS-4



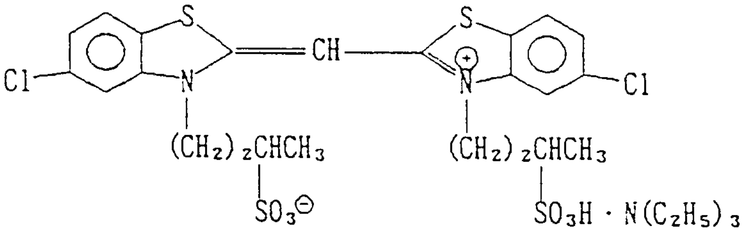
ExS-5



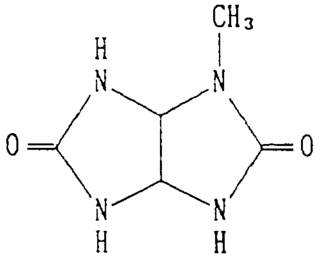
ExS-6



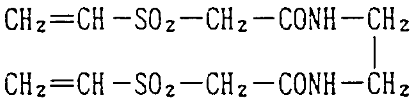
ExS-7



S-1

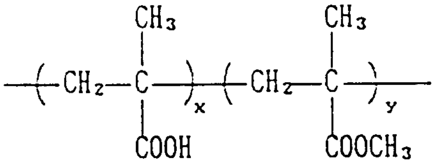


H - 1



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

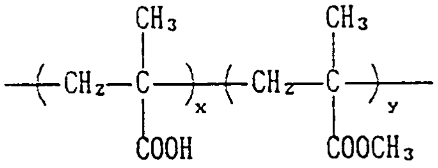
B - 1



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

x/y=10/90

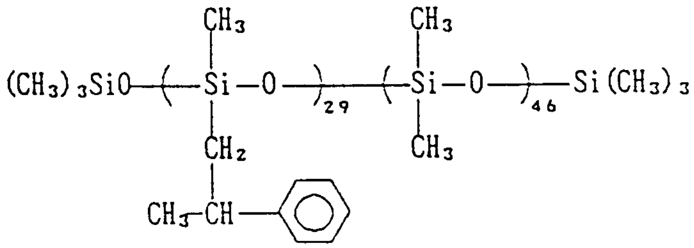
B - 2



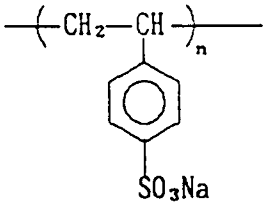
$$-\!\left(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right)_x\!\left(\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right)_y\!-$$

x/y=40/60

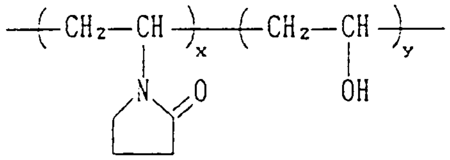
B - 3



B - 4

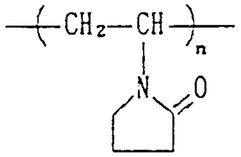


B − 5



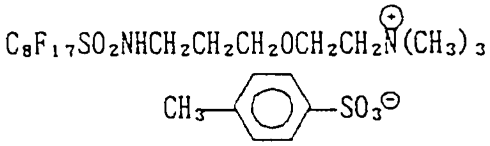
x/y=70/30

B − 6

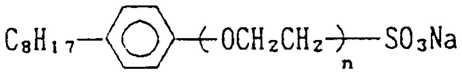


(mol. wt. ca. 10,000)

W − 1

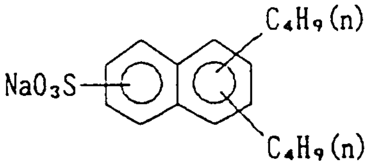


W − 2

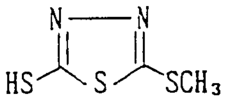


n = 2 ∼ 4

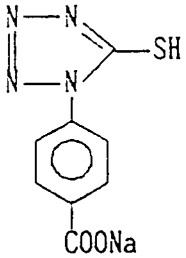
W − 3



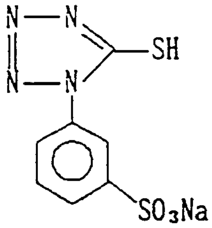
F－1



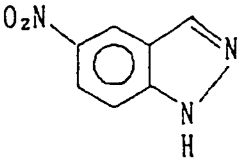
F－2



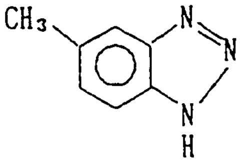
F－3



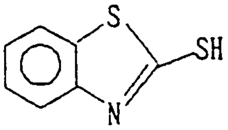
F－4



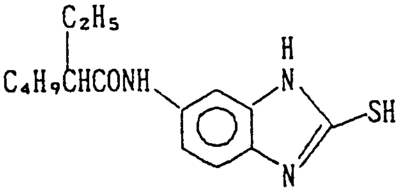
F－5



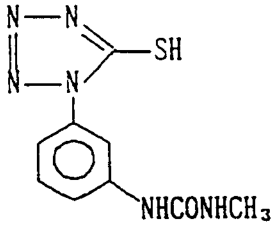
F－6



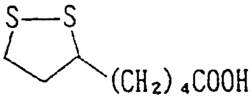
F－7



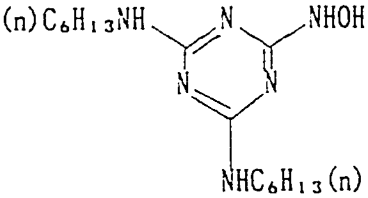
F－8



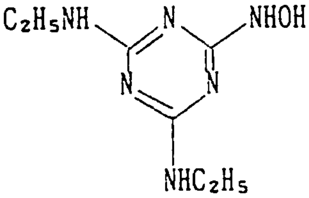
F－9



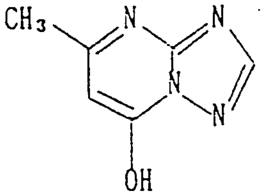
F－10



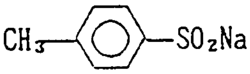
F－11



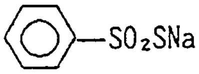
F－12



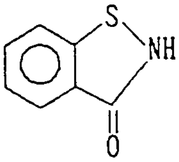
F－13



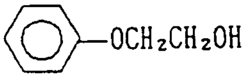
F－14



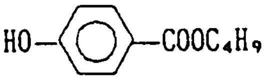
F－15



F－16



F－17



The light-sensitive material was exposed to light and continuously processed by means of an automatic developing machine according to the following schedule until the accumulated amount of the developer replenisher supplied reached three times the tank volume.

Step	Time	Temp. (°C)	Rate of Replenishment (mℓ/350 cm^{2*})	Tank Volume (ℓ)
Color development	3′ 10″	38	20	20
Bleach	3′00″	38	25	40
Washing (1)	15″	24	counter-flow system from (2) to (1)	10
Washing (2)	15″	24	15	10
Fixing	3′00″	38	15	30
Washing (3)	30″	24	counter-flow system from (4) to (3)	10
Washing (4)	30″	24	1200	10
Stabilization	30″	38	20	10
Drying	4″20″	55		

Note: * Per meter of a 35 mm wide light-sensitive material.

Compositions of the processing solutions used are described below.

Color Developer:

	Running Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	1.0	1.3
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.3
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 (Sample 701 to 716):

	Running Solution	Replenisher
Compound shown in Table 5	0.28 mol	0.34 mol
Ferric nitrate nonahydrate	0.25 mol	0.30 mol
3-Mercapto-1,2,4-triazole	0.03 g	0.08 g
Ammonium bromide	140.0 g	160.0 g
Ammonium nitrate	30.0 g	35.0 g
Aqueous ammonia (27%)	6.5 ml	4.0 ml
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with aqueous ammonia and nitric acid)	6.0	5.7

Fixer:

	Running Solution (g)	Replenisher (g)
Disodium ethylenediaminetetraacetate	0.5	0.7
Ammonium sulfite	20.0	22.0
Ammonium thiosulfate aqueous solution (700 g/ℓ)	295.0 ml	320.0 ml
Acetic acid (90%)	3.3	4.0
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	6.7	6.8

Stabilizer:

Common to running solution and replenisher:

Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene p-monononylphenyl ether (average degree of polymerization: 10)	0.2 g
Disodium ethylenediaminetetraacetate	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75 g
Water to make	1.0 ℓ
pH	8.5

The amount of silver remaining on the maximum density area of the thus processed light-sensitive material was measured by X-ray fluorometry. The results obtained are shown in Table 5. The minimum density (D_{min}) was measured with green (G) light.

Then, the light-sensitive material was processes in the same manner as described above, except for using a bleach fog-free standard bleaching solution having the following formulation and changing the bleaching time to 390 seconds.

Standard Bleaching Solution:

	Running Solution (g)	Replenisher (g)
Sodium ethylenediaminetetraacetato ferrate trihydrate	1000.0	120.0
Disodium ethylenediaminetetraacetate	10.0	11.0
Ammonium bromide	100	120
Ammonium nitrate	30.0	35.0
Aqueous ammonia (27 wt%)	6.5 ml	4.0 ml
Water to make	1000 ml	1000 ml
pH	6.0	5.7

The D_{min} of the thus processed light-sensitive material was 0.60 as measured in the same manner as described above. This value was taken as a standard D_{min}, and bleach fog (ΔD_{min}) was obtained as a difference between D_{min} of the light-sensitive material processed with each of bleaching solutions 701 to 716 and the standard D_{min}. The results obtained are also shown in Table 5.

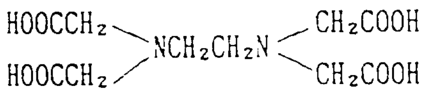
The processed light-sensitive material was preserved at 60 °C and 70% RH for 4 weeks in a dark room, and the increase in stain (ΔD) (i.e., D_{min} in the white background) due to the preservation was obtained. The results obtained are shown in Table 5.

Separately, the light-sensitive material was processed in the same manner as described above, except that 1 ml of the running solution of each bleaching bath per liter of the color developer was added to the formulation of the color developer. The increase in D_{min} (ΔD_{min}) due to incorporation of the bleaching bath into the color developer was obtained. The results obtained are shown in Table 5.

TABLE 5

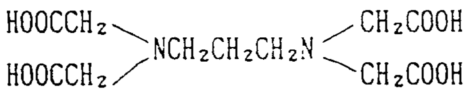
Bleaching Bath No.	Chelating Compound	Residual Silver ($\mu g/cm^2$)	Bleach Fog $\Delta D_{min}(G)$	Stain Increase $\Delta D(G)$	$\Delta D_{min}(G)$ due to Incorporation of Bleaching Bath into Developer	Remark
701	Comparative compound A	3.2	0.00	0.04	0.03	Comparison
702	Comparative compound B	1.7	0.15	0.06	0.05	"
703	Comparative compound C	2.5	0.10	0.07	0.05	"
704	Comparative compound D	1.9	0.14	0.06	0.06	"
705	Compound 1	1.9	0.00	0.04	0.00	Invention
706	Compound 7	1.8	0.01	0.03	0.01	"
707	Compound 8	1.7	0.00	0.03	0.01	"
708	Compound 10	1.6	0.03	0.04	0.02	"
709	Compound 20	1.5	0.01	0.04	0.04	"
710	Compound 22	1.6	0.02	0.04	0.04	"
711	Compound 42	1.4	0.02	0.03	0.01	"
712	Compound 43	1.7	0.02	0.04	0.05	"
713	Compound 49	1.7	0.03	0.04	0.03	"
714	Compound 50	1.4	0.02	0.03	0.05	"
715	Compound 51	1.6	0.01	0.03	0.03	"
716	Compound 52	1.3	0.03	0.04	0.06	"

Comparative Compound A:



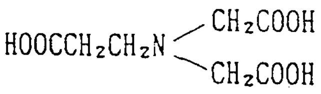
$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$$

Comparative Compound B:



$$(HOOCCH_2)_2NCH_2CH_2CH_2N(CH_2COOH)_2$$

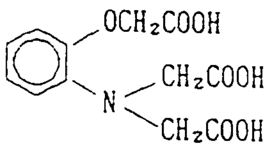
Comparative Compound C:



$$HOOCCH_2CH_2N(CH_2COOH)_2$$

(described in EP-A-430000)

Comparative Compound D:



(described in West German Patent Publication (OLS) No. 39125511)

It is seen from Table 5 that the metal chelate of compound (I) reduces the residual silver amount more than the metal chelate of the comparative compound and, at the same time, exhibits excellent effects on prevention of bleach fog or stain increase after processing. It is also seen that the bleaching solution containing the metal chelate of the present invention suppresses an increase in D_{min} even when incorporated into the preceding color developer.

EXAMPLE 8

A light-sensitive material (the same as sample 103 prepared in JP-A-4-145433) was processed as follows.

Processing Schedule

Step	Temperature	Time
Color Development	38 ° C	45 sec
Blix	35 ° C	25 sec
Rinsing (1)	35 ° C	20 sec
Rinsing (2)	35 ° C	20 sec
Rinsing (3)	35 ° C	20 sec
Drying	80 ° C	60 sec

Processing solutions had the following formulations.

Color Developer:

Water	600 ml
Ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid	2.0 g
Potassium bromide	0.015 g
Potassium chloride	3.1 g
Triethanolamine	10.0 g
Potassium carbonate	27 g
Brightening agent WHITEX 4B, produced by Sumitomo Chemical Co., Ltd.	1.0 g
Diethylhydroxylamine	4.2 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Water to make	1000 ml
pH (25 ° C)	10.05

Blix Bath (Sample 801 to 813):

Water	400 ml
Ammonium thiosulfate (700 g/ℓ)	100 ml
Sodium sulfite	17 g
Iron chloride	0.50 mol
Chelating compound (see Table 6)	0.55 mol
Ammonium bromide	40 g
Water to make	1000 ml
pH (25 ° C)	6.8

Rinsing Solution:

Ion exchanged water (Ca and Mg ions each reduced to 3 ppm or less).

The light-sensitive material was uniformly exposed to light at such an exposure as to give a gray density of 1.5 and then processed in the same manner as described above, and the silver amount remaining in the maximum density area was measured by X-ray fluorometry. The results obtained are shown in Table 6.

TABLE 6

Blix Bath No.	Chelating Compound	Residual Silver ($\mu g/cm^2$)	Remark
801	Comparative Compound A*	14.0	Comparison
802	Compound 1	10.5	Invention
803	Compound 7	9.0	"
804	Compound 8	8.8	"
805	Compound 10	5.5	"
806	Compound 20	5.3	"
807	Compound 22	5.8	"
808	Compound 42	5.0	"
809	Compound 43	12.0	"
810	Compound 49	5.6	"
811	Compound 50	8.5	"
812	Compound 51	11.0	"
813	Compound 52	5.0	"

Note: Comparative compound A is the same as used in Example 7.

The results in Table 6 prove that the blix bath containing metal chelate compound (I) according to the second embodiment of the present invention reduces the amount of residual silver more than those containing the comparative metal chelate compound.

EXAMPLE 9

The experiment of Example 7 using bleaching solution 710 was repeated with the following exceptions. The amount each of Compound 22 and ferric nitrate nonahydrate in bleaching solution 710 was reduced by half. The bleaching solution for running solution and the replenisher therefor were adjusted to pH 4.2 and 4.0, respectively. To the running bleaching solution and the replenisher therefor were added 0.2 mol/ℓ and 0.3 mol/ℓ, respectively, of succinic acid; 0.45 mol/ℓ and 0.67 mol/ℓ, respectively, of glutaric acid; and 0.05 mol/ℓ and 0.075 mol/ℓ, respectively, of malonic acid.

As a result, the so modified bleaching bath still exhibited excellent performance, such as desilvering effects, even if the concentration of the bleaching agent was reduced by half.

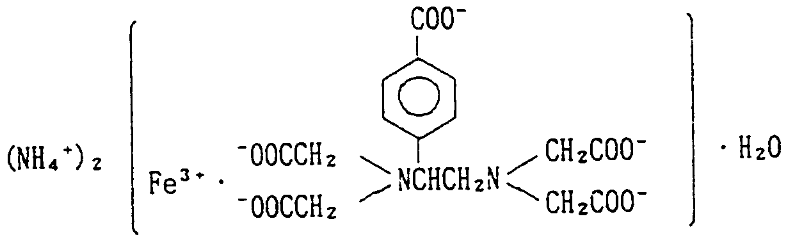
EXAMPLE 10

The same experiment as in Processing J (light-sensitive material sample No. 405) of Example 4 of JP-A-5-216191 was repeated, except for replacing ammonium 1,3-diaminopropanetetraacetato ferrate monohydrate of the bleaching solution as used in JP-A-5-216191 with an ammonium salt of an iron (III) complex of Compound 22 of a molar amount half as much as the former. As a result, excellent desilvering effects were obtained even if the concentration of the bleaching agent was reduced by half.

EXAMPLE 11

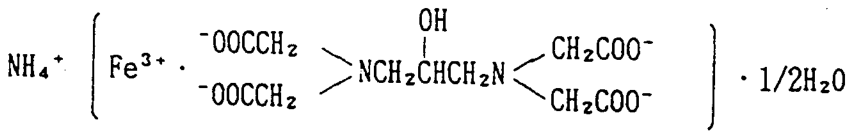
Compounds K-2, K-3, K-7, and K-8 according to the present invention, ammonium ethylenediaminetetraacetato ferrate, ammonium ethylenediaminedisuccinato ferrate, and comparative compounds E and F shown below were tested for their biodegradability according to the modified SCAS method specified in OECD chemicals test guidelines. As a result, Compounds K-2, K-3, K-7, and K-8 exhibited satisfactory biodegradability, whereas the other compounds tested were hardly biodegraded. The metal chelate compounds of the present invention were thus proved superior to the comparative metal chelate compounds in biodegradability.

Comparative Compound E:



(described in JP-A-63-97953)

Comparative Compound F:



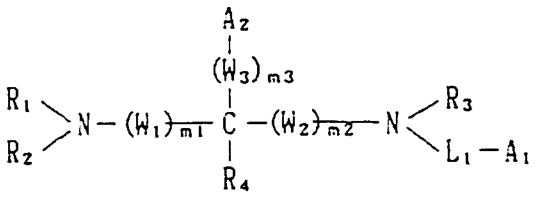
A processing solution containing compound (I) according to the first embodiment of the present invention prevents the active component from being oxidized or decomposed due to a metallic ion and therefore maintains its performance for an extended period of time. The processing solution suffers from neither sedimentation due to accumulation of a metallic ion nor growth of mold or bacteria and therefore causes no such troubles as contamination of films or clogging of filters of an automatic developing machine. In addition, compounds (I) contribute to environmental protection owing to their biodegradability.

The metal chelate compounds (I) according to the second embodiment of the present invention are also biodegradable. A processing solution having bleaching ability containing metal chelate compound (I) causes no bleach fog, reduces staining after processing, is capable of rapid processing for desilvering, and, even when incorporated into a color developer, brings about little variation in processing performance of the color developer.

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

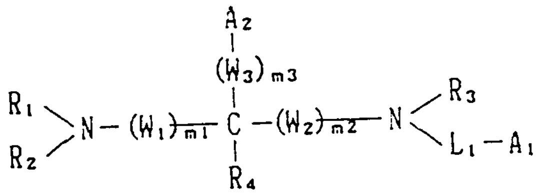
1. A photographic processing composition for a silver halide light-sensitive material, said processing composition containing at least one of a compound represented by formula (I):



(I)

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

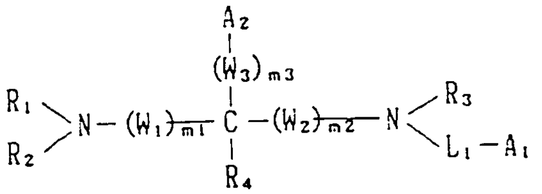
2. A method for processing a silver halide light-sensitive material comprising processing an imagewise exposed silver halide light-sensitive material with a photographic processing composition containing at least one of a compound represented by formula (I):



(I)

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

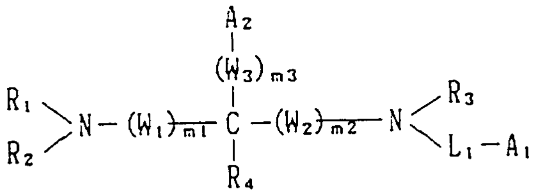
3. A photographic processing composition for a silver halide light-sensitive material, said processing composition containing at least one of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) and Ce (IV) chelate compounds of a compound represented by formula (I):



(I)

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

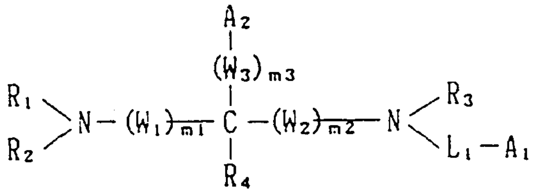
4. A method for processing a silver halide light-sensitive material comprising processing an imagewise exposed silver halide light-sensitive material with a photographic processing composition containing at least one of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) and Ce (IV) chelate compounds of a compound represented by formula (I):



$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N-(W_1)_{m1}-\underset{\displaystyle R_4}{\underset{|}{\overset{\displaystyle A_2}{\overset{|}{\overset{\displaystyle (W_3)_{m3}}{\overset{|}{C}}}}}}-(W_2)_{m2}-N\!<\!\begin{matrix} R_3 \\ L_1-A_1 \end{matrix} \qquad (\mathrm{I})$$

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

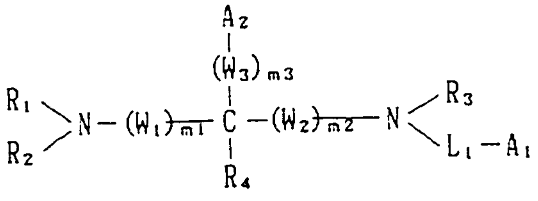
5. A photographic processing composition having bleaching ability for a silver halide color light-sensitive material, wherein said processing composition having bleaching ability contains as a bleaching agent at least one of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) and Ce (IV) chelate compounds of a compound represented by formula (I):



$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N-(W_1)_{m1}-\underset{\displaystyle R_4}{\underset{|}{\overset{\displaystyle A_2}{\overset{|}{\overset{\displaystyle (W_3)_{m3}}{\overset{|}{C}}}}}}-(W_2)_{m2}-N\!<\!\begin{matrix} R_3 \\ L_1-A_1 \end{matrix} \qquad (\mathrm{I})$$

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

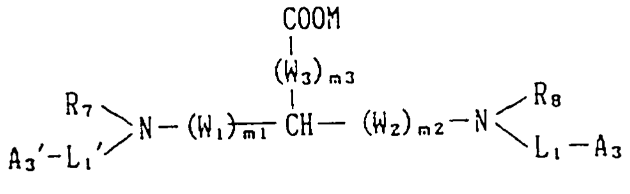
6. A method for processing a silver halide color light-sensitive material comprising processing an imagewise exposed and color-developed silver halide color light-sensitive material with a processing composition containing a bleaching agent and thereby having bleaching ability, wherein said bleaching agent is at least one of Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) and Ce (IV) chelate compounds of a compound represented by formula (I):



$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N-(W_1)_{m1}-\underset{\displaystyle R_4}{\underset{|}{\overset{\displaystyle A_2}{\overset{|}{\overset{\displaystyle (W_3)_{m3}}{\overset{|}{C}}}}}}-(W_2)_{m2}-N\!<\!\begin{matrix} R_3 \\ L_1-A_1 \end{matrix} \qquad (\mathrm{I})$$

wherein R_1 represents an aliphatic group or an aromatic group; R_2, R_3, and R_4 each represents a hydrogen atom, an aliphatic group or an aromatic group; L_1 represents a divalent linking group selected from an alkylene group, an arylene group, and a combination thereof; W_1 and W_2 each represents a divalent linking group containing an alkylene group or an arylene group; W_3 represents a divalent linking group containing an alkylene group; A_1 represents a carboxyl group, a phosphono group, a sulfo group or a hydroxyl group; A_2 represents a carboxyl group, a phosphono group or a sulfo group; and m_1, m_2, and m_3 each represents 0 or 1, provided that m_1 and m_2 do not simultaneously represent 0, or a salt thereof.

7. The photographic processing composition as claimed in claim 1, 3 or 5, wherein said at least one of a compound represented by formula (I) is selected from those represented by formula (II):

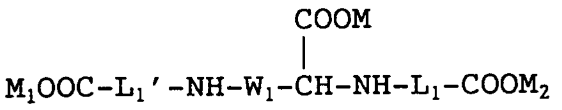


(II)

wherein W_1, W_2, W_3, m_1, m_2, m_3, and L_1 are as defined in formula (I); R_7 and R_8 each independently represents a hydrogen atom or $-L_1''-A_3''$; L_1' and L_1'' each has the same meaning as L_1 defined in formula (I); L_1, L_1', and L_1'' may be the same or different; A_3, A_3', and A_3'' each represents a carboxyl group or a salt thereof, a phosphono group or a salt thereof, or a combination thereof, the counter cation in the salt being an alkali metal, ammonium or pyridinium; and M represents a hydrogen atom or a cation.

8. The photographic processing composition as claimed in claim 1, 3 or 5, wherein m_1 represents 1; and m_2 and m_3 each represents 0.

9. The photographic processing composition as claimed in claim 1, 3 or 5, wherein said at least one of a compound represented by formula (I) is selected from those represented by formula (III):



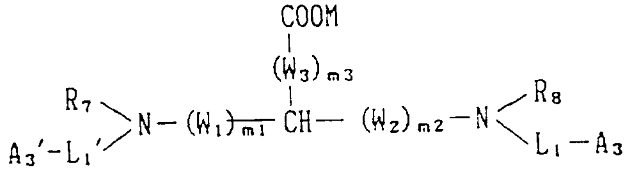
$$M_1OOC-L_1'-NH-W_1-\overset{\overset{\displaystyle COOM}{|}}{CH}-NH-L_1-COOM_2 \qquad \text{(III)}$$

wherein W_1 and L_1 are as defined in formula (I); L_1' has the same meaning as L_1 in formula (I); L_1 and L_1' may be the same or different; and M, M_1 and M_2, which may be the same or different, each represents a hydrogen atom or a cation.

10. The photographic processing composition as claimed in claim 1, 3 or 5, wherein A_1 and A_2 each represents a carboxyl group.

11. The photographic processing composition as claimed in claim 1, 3 or 5, wherein W_1, W_2 and W_3 each represents an alkylene group.

12. The method as claimed in claim 2, 4 or 6, wherein said at least one of a compound represented by formula (I) is selected from those represented by formula (II):

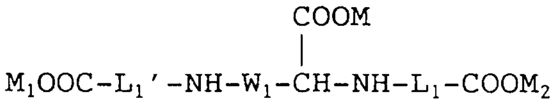


(II)

wherein W_1, W_2, W_3, m_1, m_2, m_3, and L_1 are as defined in formula (I); R_7 and R_8 each independently represents a hydrogen atom or $-L_1''-A_3''$; L_1' and L_1'' each has the same meaning as L_1 defined in formula (I); L_1, L_1', and L_1'' may be the same or different; A_3, A_3', and A_3'' each represents a carboxyl group or a salt thereof, a phosphono group or a salt thereof, or a combination thereof, the counter cation in the salt being an alkali metal, ammonium or pyridinium; and M represents a hydrogen atom or a cation.

13. The method as claimed in claim 2, 4 or 6, wherein m_1 represents 1; and m_2 and m_3 each represents 0.

14. The method as claimed in claim 2, 4 or 6, wherein said at least one of a compound represented by formula (I) is selected from those represented by formula (III):



$$M_1OOC-L_1'-NH-W_1-\overset{\displaystyle COOM \atop |}{CH}-NH-L_1-COOM_2 \qquad \text{(III)}$$

wherein W_1 and L_1 are as defined in formula (I); L_1' has the same meaning as L_1 in formula (I); L_1 and L_1' may be the same or different; and M, M_1 and M_2, which may be the same or different, each represents a hydrogen atom or a cation.

15. The method as claimed in claim 2, 4 or 6, wherein A_1 and A_2 each represents a carboxyl group.

16. The method as claimed in claim 2, 4 or 6, wherein W_1, W_2 and W_3 each represents an alkylene group.