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(54) A photographic processing composition and a processing process therewith

Photographische Verarbeitungszusammensetzung und zugehöriges Verarbeitungsverfahren

Composition de traitement photographique et méthode de traitement l'utilisant

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(73) Proprietor: **FUJI PHOTO FILM CO., LTD.**
Kanagawa-ken (JP)

(72) Inventors:
- **Okada, Hisashi, c/o Fuji Photo Film Co., Ltd.**
  Minami-Ashigara-shi, Kanagawa (JP)
- **Inaba, Tadashi, c/o Fuji Photo Film Co., Ltd.**
  Minami-Ashigara-shi, Kanagawa (JP)
- **Fujita, Yoshihiro, c/o Fuji Photo Film Co., Ltd.**
  Minami-Ashigara-shi, Kanagawa (JP)
- **Katsuoka, Yasuhiro, c/o Fuji Photo Film Co., Ltd.**
  Minami-Ashigara-shi, Kanagawa (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

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Description

[0001] The present invention relates to the use of a compound for processing a silver halide photographic material and a processing process therewith.

[0002] In general, a silver halide black and white photographic material is processed in the processing processes such as black and white developing, fixing and rinsing after exposing, and a silver halide color photographic material (hereinafter referred to as a color light-sensitive material) is processed in the processing processes such as color developing, desilvering, rinsing and stabilizing after exposing. A silver halide color reversal material is processed in a processing process such as black and white developing after exposing and in the processing processes such as color developing, desilvering, rinsing and stabilizing after a reversal processing.

[0003] In a color developing process of a color development processing, an exposed silver halide grain is reduced to silver by a color developing agent and at the same time a generated oxidation product of the color developing agent reacts with a coupler to form a dye image.

[0004] In the subsequent desilvering process, developed silver generated in the developing process is oxidized (bleaching) by a bleaching agent (an oxidant) having an oxidizing action to a silver salt, and further it is removed (fixing) from a light-sensitive layer together with unexposed silver halide by a fixing agent which forms soluble silver. There are a case in which bleaching and fixing are carried out independently in a bleaching process and a fixing step, respectively, and a case in which they are simultaneously carried out in a bleach-fixing process. The details of these processing processes and the compositions thereof are described in The Theory of Photographic Process written by James, the 4th edition (1977), and Research Disclosures No. 17643, pp. 28 to 29, No. 18716, 651, a left column to a right column, and No.307105, pp. 880 to 881.

[0005] In addition to the above fundamental processing processes, various auxiliary processes are supplementarily carried out for a purpose of maintaining a photographic and physical quality of a dye image or a processing stability. They include, for example, a rinsing process, a stabilizing process, a hardening process and a stopping process.

[0006] Processing is carried out in a reducer containing an oxidant in order to adjust a gradation of a silver halide black and white light-sensitive material which is subjected to a development processing.

[0007] In general, a ferric ethylenediaminetetraacetate complex salt and a ferric 1,3-diaminopropanetetraacetate complex salt are used as an oxidant for a processing solution used for the bleaching processing described above and a reducing processing. However, they are less susceptible to biodegradation. In recent years, it is desired from a viewpoint of an environmental protection to convert a photographic processing waste solution generated from these photographic processings to harmlessness. In particular, a processing composition which is easily susceptible to biodegradation is desired and an alternative for the above-mentioned bleaching agents which are not biodegraded has been investigated.

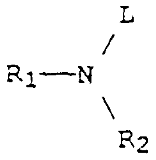
[0008] There are disclosed as a bleaching agent having a biodegradability, a ferric complex salt of N-(2-carboxymethoxyphenyl)iminodiacetic acid in German Patent Publication 3912551 and a ferric complex salt of β-alaninediacetic acid and a ferric complex salt of glycinedipropionic acid in European Patent Publication 430000A. However, the processing solutions having a bleaching ability comprising these bleaching agents do not necessarily have a sufficient desilvering property and it has been found that there are involved the problems that a continuous processing with them leads to degradation of the desilvering property as compared with that at the beginning of the continuous processing and that magenta stain is generated.

[0009] Further, it has been desired as well from a viewpoint of an environmental protection that a concentration of a metal chelate compound is lowered. However, the above bleaching agent used to have the problems that in a diluted concentration, a sufficient desilvering property is not obtained from the beginning of the continuous processing and that aging over a long period of time deteriorates the desilvering property.

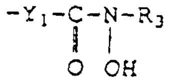
[0010] In these color processings, a rapid processing service to clients with an automatic developing machine which is called a mini lab is getting popular in recent years, and an aging stability in a processing solution and a stability in the basic performances of these bleaching agents in the continuous processing as well as a rapid bleaching performance are the inevitable problems.

[0011] EP-A-563571 describes a solid chemical and a process of processing a silver halide colour photographic material using said chemical, wherein the chemical contains a ferric complex salt of a compound represented by the following formulae (A-IV) and (A-V)

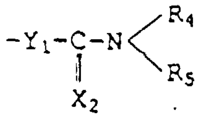
Formula (A-IV)

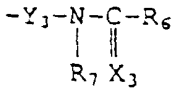


wherein R_1 and R_2 independently represent a hydrogen atom, an alkyl group or an aryl group; and L represents a group selected from the group consisting of



$$-Y_1-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{N}-R_3$$

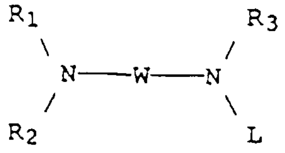




$$-Y_3-\underset{\underset{R_7}{|}}{N}-\underset{\underset{X_3}{\|}}{C}-R_6$$

wherein Y_1, Y_2 and Y_3 independently represent an alkylene group or an arylene group; X_2 and X_3 independently represent an oxygen atom or a sulfur atom; and R_3, R_4, R_5, R_6 and R_7 independently represent a hydrogen atom, an alkyl group or an aryl group;

Formula (A-V)

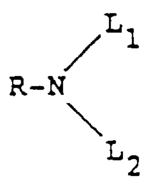


wherein R_1, R_2 and R_3 independently represent a hydrogen atom, an alkyl group or an aryl group; L is the same with those denoted in Formula (A-IV); and W represents a divalent linking group;

[0012] EP-A-461413 describes a processing composition having a bleaching ability which is used for processing silver halide colour photographic materials, and containing a metal chelate compound formed from

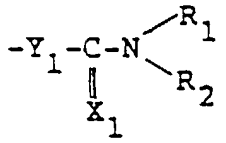
the salt of a metal selected from the group consisting of Fe(III), Mn(III), Co(III) Rh(II), Rh(III), Au(II), Au(III) and Ce(IV), and

at least one of a compound represented-by formula (I) and a compound represented by formula (II):



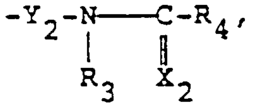
(I)

wherein L_1 and L_2 each represents



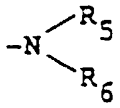
$$-Y_1-\underset{\underset{X_1}{\|}}{C}-N\begin{matrix}R_1\\R_2\end{matrix}$$

or



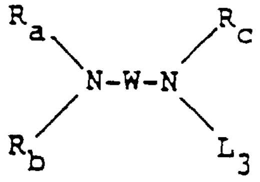
$$-Y_2-\underset{\underset{R_3}{|}}{N}-\underset{\underset{X_2}{\|}}{C}-R_4,$$

X_1 and X_2 each represents an oxygen atom or a sulfur atom, R, R_1, R_2 and R_3 each represents a hydrogen atom or an aryl or alkyl group which may be substituted, R_4 represents an aryl or alkyl group which may be substituted,



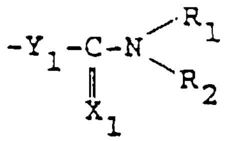
$$-N\begin{matrix}R_5\\R_6\end{matrix}$$

or $-OR_7$, R_5 and R_6 each has the same meaning as R_1, R_7 represents an aryl or alkyl group which may be substituted, Y_1 and Y_2 each represents an arylene or alkylene group which may be substituted, R, L_1 and L_2 may be joined together to form rings;



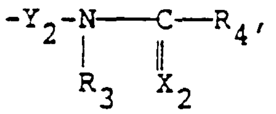
(II)

wherein L_3 represents



$$-Y_1-\underset{\underset{X_1}{\|}}{C}-N\begin{matrix}R_1\\R_2\end{matrix}$$

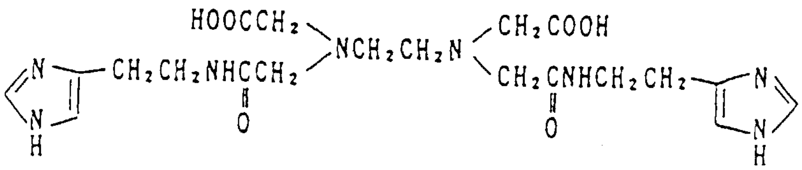
or



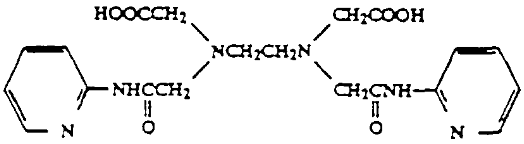
$$-Y_2-\underset{\underset{R_3}{|}}{N}-\underset{\underset{X_2}{\|}}{C}-R_4,$$

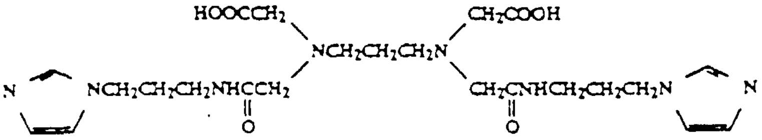
where X_1, X_2, Y_1, Y_2, R_1, R_2, R_3 and R_4 have the same meaning as in formula (I), R_a, R_b and R_c each represents a hydrogen atom or an aryl or alkyl group which may be substituted, R_a, R_b, R_c and L_3 may be joined together to form rings, and W represents a divalent linking group.

[0013] EP-A-513766 describes a method of processing a silver halide colour photographic material using an organic metal complex of compounds such as

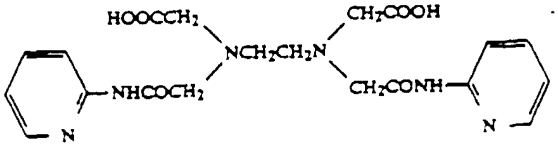


[0014] US-A-5250401 describes a method for processing a silver halide colour photographic material, wherein a processing solution contains a metal chelating compound formed by a compound such as

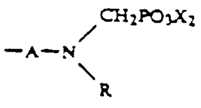




or



[0015] US-A-4894320 describes a method of processing a silver halide colour photographic material with a processing solution which contains a ferric complex salt comprising, as a complexing agent, an aromatic compound having at least one group represented by the following general formula (I):



$$-A-N(CH_2PO_3X_2)(R) \qquad (I)$$

wherein X represents a hydrogen atom or an organic or inorganic cation, A represents a single bond or a divalent linking group, and R represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic ring group, an acyl group, a sulfonyl group, A or $-CH\text{-}_2PO_3X_2$.

[0016] An object of the present invention is to provide the use of a compound which has a good handling property and is free from an environmental problem in a waste solution,for processing a silver halide photographic material and a processing process therewith.

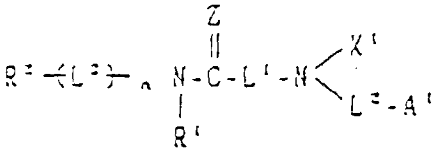
[0017] Another object of the present invention is to provide the use of a compound which is stable as well particularly in a diluted concentration and which has a bleaching ability with an excellent desilvering property,for processing a silver halide photographic material and a processing process therewith.

[0018] A further object of the present invention is to provide the use of a compound which has a bleaching ability with small aging stain,for processing a silver halide photographic material and a processing process therewith.

[0019] A still further object of the present invention is to provide the use of a compound which can stably maintain the above performances even after a continuous processing,for processing a silver halide photographic material and a processing process therewith.

[0020] A yet further object of the present invention is to provide the use of a ccmpound which is preferred particularly from the viewpoints of biodegradability and environmental protection,for processing a silver halide photographic material and a processing process therewith.

[0021] The objects described above have been achieved by the use of at least one compound selected from 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) or a salt thereof:



$$R^2-(L^3)_n-\underset{\displaystyle R^1}{\underset{|}{N}}-\overset{\displaystyle Z}{\overset{\|}{C}}-L^1-N\genfrac{}{}{0pt}{}{\diagup X^1}{\diagdown L^2-A^1} \qquad (I)$$

wherein R^1 represents a hydrogen atom, an aliphatic group or an aromatic group; R^2 represents an aromatic group; L^3 represents a divalent aliphatic group; n represents 0 or 1; X^1 represents a hydrogen atom or $-L^4-A^2$; L^1, L^2 and L^4 each represents a divalent aliphatic group, a divalent aromatic group, or a divalent linkage group consisting of a combination thereof; A^1 and A^2 each represent a carboxy group; and Z represents an oxygen atom or a sulfur atom, for processing a silver halide photographic material,
and by a method for processing a silver halide photographic material which comprises processing an imagewise exposed silver halide photographic material with a processing solution comprising 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 the above formula (I) or a salt thereof.

[0022] First of all, the compound represented by Formula (I) will be explained below in detail.

[0023] The aliphatic group represented by R^1 may be linear, branched or cyclic and is preferably linear or branched. The aliphatic group includes an alkyl group, an alkenyl group and an alkynyl group and is preferably an alkyl group, more preferably an alkyl group having 1 to 4 carbon atoms. The aliphatic group may be substituted and the substituent includes, for example, an alkyl group (for example, methyl, ethyl and isopropyl), an aralkyl group (for example, phenylmethyl), an alkenyl group (for example, allyl), an alkoxy group (for example, methoxy and ethoxy), an aryl group (for example, phenyl and p-methylphenyl), an acylamino group (for example, acetylamino), a sulfonylamino group (for example, methanesulfonylamino), a ureido group (for example, methylureido), an alkoxycarbonylamino group, an aryloxycarbonylamino group, an aryloxy group (for example, phenyloxy), a sulfamoyl group (for example, methylsulfamoyl), a carbamoyl group (for example, carbamoyl and methylcarbamoyl), a mercapto group, an alkylthio group (for example, methylthio and carboxylmethylthio), an arylthio group (for example, phenylthio), a sulfonyl group (for example, methanesulfonyl), a sulfinyl group (for example, methanesulfinyl), a hydroxy group, a halogen atom (for example, a chlorine atom, a bromine atom and a fluorine atom), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (for example, phenyloxycarbonyl), an acyl group (for example, acetyl and benzoyl), an alkoxycarbonyl group (for example, methoxycarbonyl), an acyloxy group (for example, acetoxy), an acylamino group (for example, acetylamino), a sulfonamide group (for example, methanesulfonamide), a nitro group, and a hydroxamic acid group.

[0024] In the case where the above substituents for the aliphatic group have carbon atoms, they have preferably 1 to 10 carbon atoms, more preferably 1 to 4 carbon atoms. A hydroxy group or the carboxyl group is preferred as the substituent.

[0025] The aromatic group represented by R^1 and R^2 is preferably a monocyclic or dicyclic aromatic hydrocarbon group which may have a substituent. It is more preferably a phenyl or naphthyl group which may have a substituent, most preferably a phenyl group which may have a substituent. A hydroxy group or a carboxyl group is preferred as the substituent of the aromatic group represented by R^1 and R^2.

[0026] Those enumerated as the substituents which the aliphatic group represented by R^1 may have can be applied as the substituent for the aromatic group represented by R^1 and R^2.

[0027] The divalent aliphatic group represented by L^3 may have a substituent. It is preferably an alkylene group. It has preferably 1 to 8 carbon atoms, more preferably 1 to 4 carbon atoms, and further preferably 1 to 2 carbon atoms. A methylene group is particularly preferred.

[0028] Those enumerated as the substituents which the aliphatic group represented by R^1 may have can be applied as the substituent for the divalent aliphatic group represented by L^3.

[0029] R^1 is preferably a hydrogen atom. n is preferably 0.

[0030] The divalent aliphatic group represented by L^1, L^2 and L^4 is preferably an alkylene group or an alkenylene group.

[0031] The alkylene group represented by L^1, L^2 and L^4 may be linear, branched or cyclic and is preferably a linear alkylene group. The alkylene group may be substituted and the substituent includes, for example, an alkyl group (for example, methyl, ethyl and isopropyl), an aralkyl group (for example, phenylmethyl), an alkenyl group (for example, allyl), an alkoxy group (for example, methoxy and ethoxy), an aryl group (for example, phenyl and p-methylphenyl), an acylamino group (for example, acetylamino), a sulfonylamino group (for example, methanesulfonylamino), a ureido group (for example, methylureido), an alkoxycarbonylamino group, an aryloxycarbonyl group, an aryloxy group (for example, phenyloxy), a sulfamoyl group (for example, methylsulfamoyl), a carbamoyl group (for example, carbamoyl and methylcarbamoyl), a mercapto group, an alkylthio group (for example, methylthio and carboxylmethylthio), an arylthio group (for example, phenylthio), a sulfonyl group (for example, methanesulfonyl), a sulfinyl group (for example, methanesulfinyl), a hydroxy group, a halogen atom (for example, a chlorine atom, a bromine atom and a fluorine atom), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (for example, phenyloxycarbonyl), an acyl group (for example, acetyl and benzoyl), an alkoxycarbonyl group (for example, methoxycarbonyl), an acyloxy group (for example, acetoxy), a nitro group, and a hydroxamic acid group.

[0032] The substituents of the alkylene group represented by L^1, L^2 and L^4 are preferably a hydroxy group, a sulfo group, a carboxy group, a phosphono group, and an alkyl group having 1 to 3 carbon atoms which may be substituted (the substituents are, for example, a hydroxy group and a carboxy group) and more preferably a hydroxy group, a carboxy group, a hydroxy-substituted alkyl group, and a carboxy-substituted alkyl group. In the case where L^1, L^2 and L^4 are alkylene groups, they have preferably 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms. They are further preferably methylene and ethylene, particularly preferably methylene.

[0033] The alkenylene group represented by L^1, L^2 and L^4 may be linear, branched or cyclic and is preferably a linear alkenylene group. The alkenylene group may be substituted and those enumerated in the case where L^1, L^2 and L^4 are the alkylene groups can be applied as the substituent therefor. The alkenyl group has preferably 2 to 10 carbon atoms and is more preferably a vinylene group.

[0034] The divalent aromatic group represented by L^1, L^2 and L^4 is preferably a monocyclic or dicyclic aromatic hydrocarbon and may have a substituent. Those enumerated in the case where L^1, L^2 and L^4 are the alkylene groups can be applied as the substituent therefor, and it includes preferably an alkyl group, an acylamino group, an alkylsulfonamide group, an alkoxy group, a sulfamoyl group, a carbamoyl group, an alkylthio group, a sulfo group, a phosphono group, an acyl group, an alkoxycarbonyl group, a nitro group, a carboxy group, a hydroxy group, a halogen atom, and a hydroxamic acid group. In the case where L^1, L^2 and L^4 are arylene groups, they are preferably phenylene and naphthylene, more preferably phenylene, and particularly preferably 1,2-phenylene.

[0035] The divalent linkage group consisting of a combination of the aliphatic group and the aromatic group each represented by L^1, L^2 and L^4 is a group consisting of a combination of the aliphatic group and the aromatic group each described above and is preferably an aralkylene group having 7 to 10 carbon atoms. The aralkylene group may be substituted and those enumerated in the case where L^1, L^2 and L^4 are the alkylene groups can be applied as the substituent therefor.

[0036] An alkylene group having 1 to 6 carbon atoms or 1,2-phenylene is preferred as L^1, L^2 and L^4, methylene or ethylene is further preferred, and methylene is particularly preferred.

[0037] A^1 and A^2 each represent a carboxy group.

[0038] $-L^4-A^2$ is preferred as X^1.

[0039] Z represents an oxygen atom or a sulfur atom and is preferably the oxygen atom.

[0040] The compound represented by Formula (I) may be an ammonium salt (for example, an ammonium salt and a tetraethylammonium salt) and an alkaline metal salt (for example, a lithium salt, a potassium salt and a sodium salt).

[0041] Concrete examples of the compound represented by formula (I) or salts thereof will be listed below.

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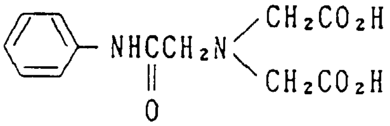

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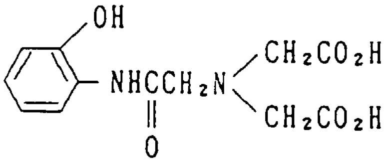

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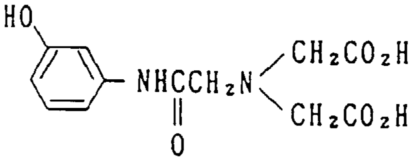

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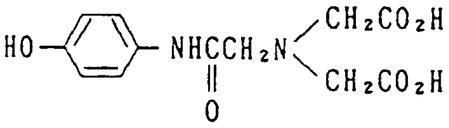

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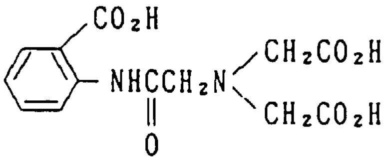

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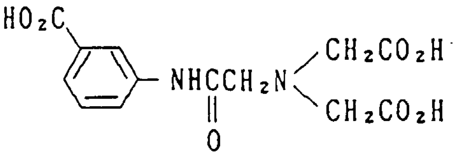

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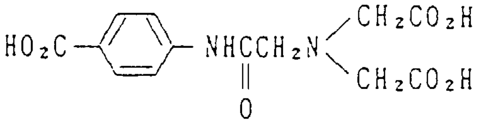

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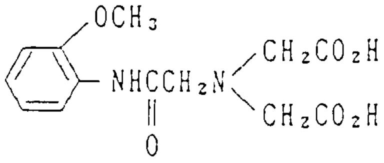

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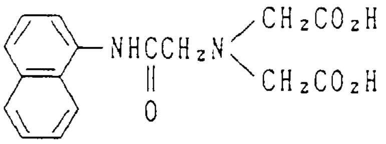

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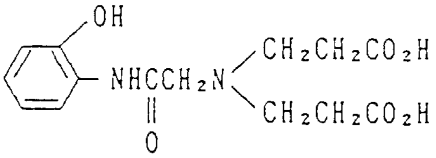

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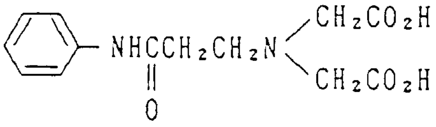

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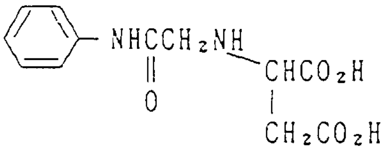

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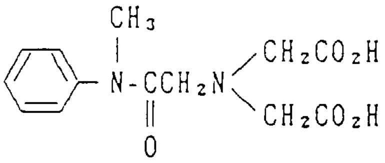

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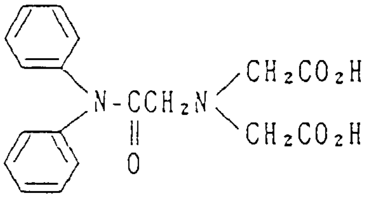

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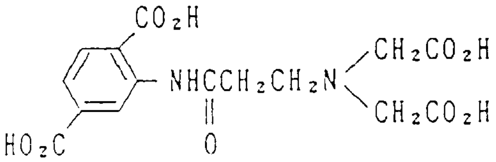

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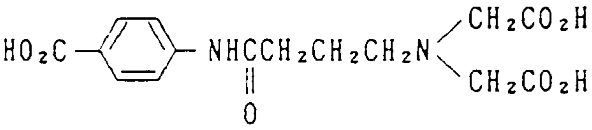

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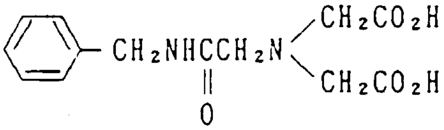

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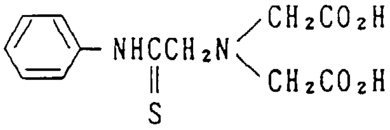

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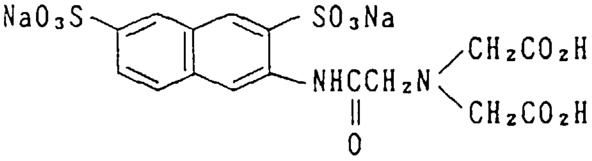

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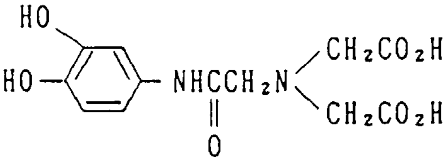

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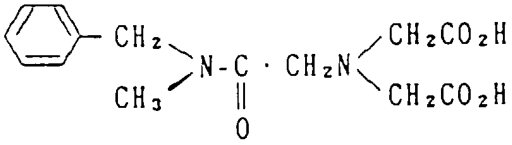

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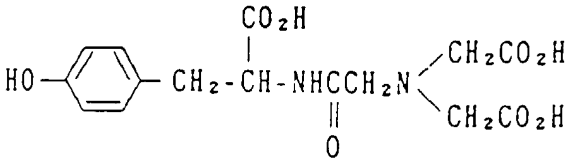

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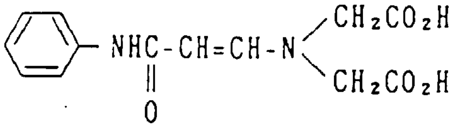

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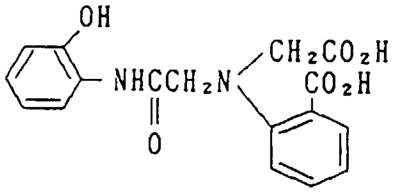

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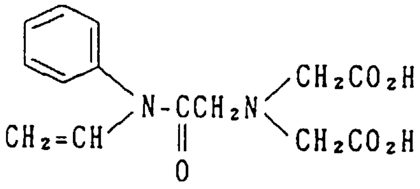

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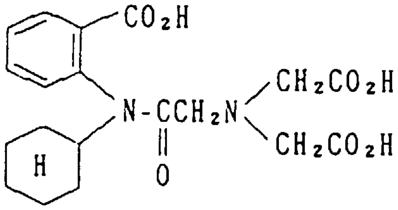

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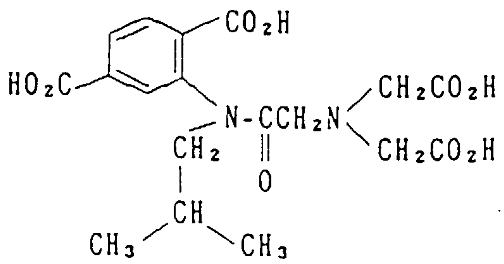
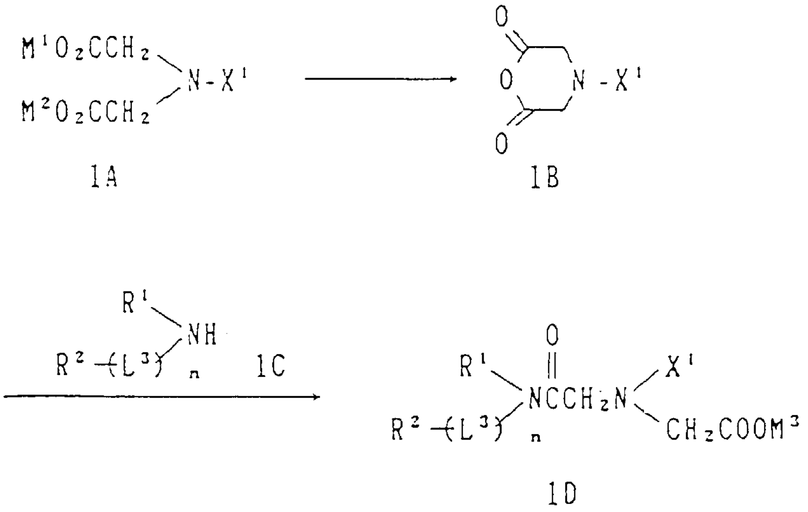


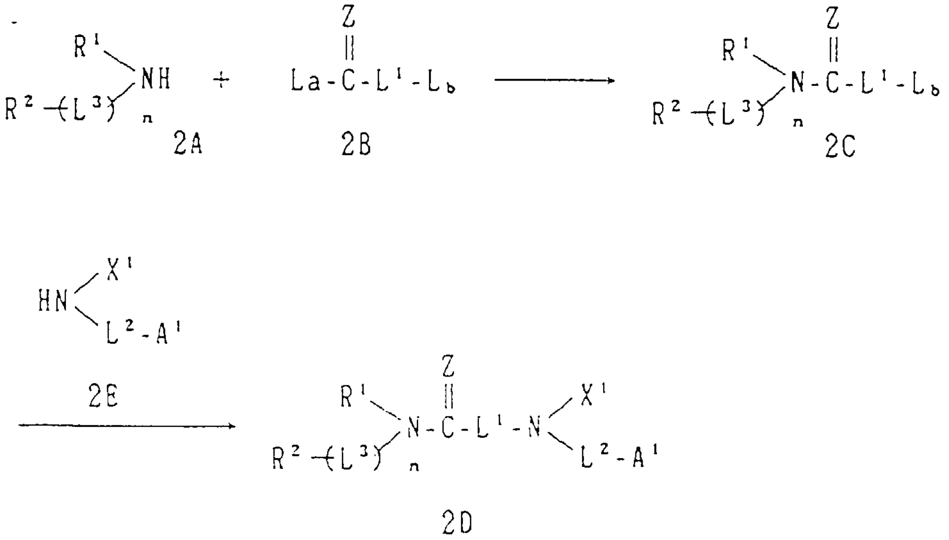
[0042] The compound used in the present invention can be synthesized by the process described in Australian Journal of Chemistry, 1982, 35, 2371 and the following process:

Synthetic process 1



wherein X^1, R^1, R^2, L^3 and n are synonymous with those in formula (I); and M^1, M^2 and M^3 each represent a hydrogen atom or a cation.

Synthetic process 2



wherein R^1, R^2, L^1, L^2, L^3, n, X^1, A^1 and Z are synonymous with those in formula (I); L_a and L_b each represents a splitting-off group (e.g., a halogen atom).

[0043] That is, in the synthetic process 1, the acid anhydride (1B) is synthesized from the iminodiacetic acid derivative (1A) and then it reacts with the amine compound (1C) to thereby synthesize the specified product (1D).

[0044] The synthetic process for the acid anhydride (1B) is not specifically limited, and a process described in, for example, "New Experimental Chemistry Course 14 (II)", pp. 1120 to 1130 (Maruzen) can be applied. Among them, a process using an acid anhydride (e.g., acetic anhydride) is preferred. A solvent may be used in this reaction and the solvent is not limited as long as it does not take part in the reaction. It includes, for example, acetonitrile, dimethylformamide, pyridine, ether, tetrahydrofuran, acetone, and benzene. Further, a base may be used and those which are not reacted with the acid anhydride are preferred as the base. Tertiary amines (e.g., triethylamine) and pyridine are more preferred. This reaction is usually carried out at 0 to 100°C, preferably 10 to 80°C.

[0045] The synthetic process for the specified product (1D) from the acid anhydride (1B) and the amine compound (1C) is not specifically limited and a synthetic process for an amide derivative from an acid anhydride and amine can widely be utilized. For example, a process described in "New Experimental Chemistry Course 14 (II)", pp. 1145 to 1147 (Maruzen) can be applied. A solvent may be used in this reaction and the solvent includes, for example, the amine compound (1C) which is a raw material, water, alcohols, acetonitrile, dimethylformamide, pyridine, ether, tetrahydrofuran, acetone, and benzene. This reaction is usually carried out at -20 to 150°C, preferably 0 to 70°C, and more preferably 0 to 40°C.

[0046] In the synthetic process 2, the amide or thioamide compound (2C) is synthesized from the amine compound (2A) and the compound (2B) and then it can be reacted with the amine compound (2E) to thereby synthesize the specified product (2D). The synthetic process for the amide or thioamide compound (2C) is not specifically limited and there can be applied, for example, a process described in "New Experimental Chemistry Course 14 (II)", pp. 1142 to 1151 and 14 (III) pp. 1827 to 1832 (Maruzen). A solvent may be used in this reaction and the solvent includes, for example, the amine compound (2A) which is a raw material, tertiary amine, water, alcohols, acetonitrile, dimethylformamide, pyridine, ether, tetrahydrofuran, acetone, and benzene.

[0047] In order to remove an acid generated, it is preferred to use excessive amine or allow tertiary amine (e.g., triethylamine) to coexist.

[0048] This reaction is usually carried out at -20 to 150°C, preferably 0 to 70°C, and more preferably 0 to 40°C.

[0049] The synthetic process for the specified product (2D) from the compound (2C) and the amine compound (2E) is not specifically limited and there can be applied, for example, a process described in "New Experimental Chemistry Course 14 (III)", pp. 1342 to 1347 (Maruzen). A solvent may be used in this reaction. The solvent is not specifically limited as long as it does not take part in the reaction and includes, for example, water, alcohols (e.g., methanol, ethanol), acetonitrile, dimethylformamide, dimethylacetamide, and pyridine. A base is preferably allowed to coexist in order to remove an acid generated. Preferred as the base are tertiary amines (e.g., triethylamine), alkoxide (e.g., methoxide), OH^-, and CO_3^{2-}. This reaction is usually carried out at 0 to 150°C, preferably 0 to 100°C, and more preferably 20 to 80°C.

[0050] Next, the typical synthetic examples for the compound used in the present invention will be shown below.

Synthetic example 1: synthesis of Compound 1:

[0051] 158 g (1.54 mol) of acetic anhydride was dropped while stirring 287 g (1.50 mol) of nitrilotriacetic acid and 1.5 liter of pyridine at 50°C under a nitrogen atmosphere. After finishing dropping, stirring was further applied at 70°C for 2 hours, and then 140 g (1.50 mol) of aniline was added, followed by further stirring at 70°C for 4 hours. After cooling down to room temperature, the pH was adjusted to about 2 with 750 ml of water and conc. hydrochloric acid. A deposited solid matter was filtered off and recrystallized with acetone-water, whereby 319 g (1.12 mol) of the specified product monohydrate was obtained in the form of a white solid matter. Yield: 75 %. Melting point: 159 to 161°C (decomposed).

Synthetic example 2: synthesis of Compound 2:

[0052] 69.4 g (0.23 mol) of the specified product monohydrate was obtained from 95.6 g (0.50 mol) of nitrilotriacetic acid 0.5 liter of pyridine, 52.6 g (0.515 mol) of acetic anhydride and 56.2 g (0.515 mol) of o-aminophenol in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 46 %. Melting point: 117 to 119° (decomposed).

Synthetic example 3 synthesis of Compound 3:

[0053] 61.0 g (0.203 mol) of the specified product monohydrate was obtained from 65.9 g (0.345 mol) of nitrilotriacetic acid, 350 mol of pyridine, 37.0 g (0.362 mol) of acetic anhydride and 41.4 g (0.379 mol) of m-aminophenol in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 59 %. Melting point: 192 to 193°C (decomposed).

Synthetic example 4: synthesis of Compound 4:

[0054] 70.1 g (0.248 mol) of the specified product was obtained from 65.9 g (0.345 mol) of nitrilotriacetic acid, 350 ml of pyridine, 37.0 g (0.362 mol) of acetic anhydride and 41.4 g (0.379 mol) of p-aminophenol in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 72 %. Melting point: 235°C or higher (decomposed).

Synthetic example 5: synthesis of Compound 5:

[0055] 25.8 g (0.080 mol) of the specified product 1/2 hydrate was obtained from 25.0 g (0.13 mol) of nitrilotriacetic acid, 200 ml of pyridine, 13.5 g (0.13 mol) of acetic anhydride and 17.8 g (0.13 mol) of o-aminobenzoic acid in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 62 %. Melting point: 187 to 189°C.

Synthetic example 6: synthesis of Compound 6:

[0056] 73.0 g (0.235 mol) of the specified product was obtained from 65.9 g (0.345 mol) of nitrilotriacetic acid, 310 ml of pyridine, 37.0 g (0.362 mol) acetic anhydride and 52.0 g (0.379 mol) of m-aminobenzeoic acid in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 68 %. Melting point: 225°C or higher (decomposed).

Synthetic example 7: synthesis of Compound 7:

[0057] 95.7 g (0.276 mol) of the specified product dihydrate was obtained from 65.9 g (0.345 mol) of nitrilotriacetic acid, 350 ml of pyridine, 37.0 g (0.362 mol) of acetic anhydride and 52.0 g (0.379 mol) of p-aminobenzoic acid in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 80 %. Melting point: 230°C or higher (decomposed).

Synthetic example 8: synthesis of Compound 20:

[0058] 80.3 g (0.286 mol) of the specified product was obtained from 95.6 g (0.500 mol) of nitrilotriacetic acid, 500 ml of pyridine, 52.6 g (0.515 mol) of acetic anhydride and 55.2 g (0.515 mol) of benzylamine in the form of the white solid matter in the same manner as that in the synthetic example 1. Yield: 57 %. Melting point: 179 to 180°C.

[0059] The other compounds can be synthesized in the same manner.

[0060] A metal salt constituting the metal chelate compound used in the present invention is selected from Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III), and Ce (IV). More preferred are salts of Fe (III), Mn (III) and Ce (IV), and particularly preferred is a salt of Fe (III).

[0061] The metal chelate compounds used in the present invention may be prepared for use by reacting the compounds represented by formula (I) with the salts of the above metals (for example, a ferric sulfate salt, a ferric chloride salt, a ferric nitrate salt, a ferric ammonium sulfate salt, and a ferric phosphate salt) in a solution. Similarly, it may be prepared for use by reacting the ammonium salts and alkaline metal salts (for example, a lithium salt, a sodium salt and a potassium salt) of the compounds represented by formula (I) with the salts of the above metals in a solution. Further, the metal chelate compound used in the present invention, which is isolated as a metal chelate compound, may be used.

[0062] The compound represented by formula (I) is used in a mole ratio of 1.0 or more based on a metal ion constituting the chelate compound. This ratio is preferably large in the case where a stability of the metal chelate compound is low, and it is usually used in the range of 1 to 30.

[0063] The metal chelate compound used in the present invention has an effect as an oxidant for a silver halide photographic light-sensitive material (a bleaching agent for a color material and a reducing agent for a plate-making black and white light-sensitive material). In particular, it is excellent as the bleaching agent for the color light-sensitive material.

[0064] The metal chelate compound used in the present invention is used as the bleaching agent by processing an imagewise exposed silver halide color photographic material with a processing solution containing the metal chelate compound used in the present invention as the bleaching agent after it is subjected to a color development, so that developed silver is very rapidly bleached and a marked bleaching fog observed in a conventional bleaching agent which can carry out a rapid bleaching is not found.

[0065] The present invention is characterized by a oxidant in a photographic processing composition, particularly a bleaching agent in a processing composition having a bleaching ability for a color light-sensitive material, and with respect to the requisites for the other base materials, the base materials which can generally be applied can suitably be selected.

[0066] The metal chelate compound used in the present invention may be contained in any processing solution (for example, a fixing solution and an intermediate bath provided between a color developing process and a desilver process). It is particularly effective as the bleaching agent for a processing solution having a bleaching ability (a bleaching solution or a bleach-fixing solution) for a color light-sensitive material in a content of 0.005 to 1 mole per liter of the processing solution.

[0067] The processing solution having a bleaching ability of a preferred embodiment will be explained below. The metal chelate compound used in the present invention is effectively contained as a bleaching agent in a processing solution having a bleaching ability in an amount of 0.005 to 1 mole per liter of the processing solution, more preferably 0.01 to 0.5 mole, and particularly preferably 0.05 to 0.5 mole per liter of the processing solution. The use of the metal chelate compound used in the present invention even in a diluted concentration of 0.005 to 0.2 mole, preferably 0.01 to 0.2 mole and more preferably 0.05 to 0.18 mole per liter of the processing solution can demonstrate an excellent performance.

[0068] In the case where the metal chelate compound used in the present invention is used as a bleaching agent in a processing solution having a bleaching ability, it may be used in combination with the other bleaching agents in the range in which the effects of the present invention can be demonstrated (preferably, 0.01 mole or less, more preferably 0.005 mole or less per liter of the processing solution). Such bleaching agents include Fe (III), Co (III) and Mn (III) chelate series bleaching agents of the compounds shown below, persulfates (for example, peroxodisulfate), hydrogen peroxide, and bromates.

[0069] The compounds forming the above chelate series bleaching agents include ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine-N-β-hydroxyethyl)-N,N',N'-triacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, iminodiacetic acid, dihydroxyethyl glycine, ethyl ether diaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrapropionic acid, phenylenediaminetetraacetic acid, l,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 acid monopropionic acid, nitrilomonoacetic acid dipropionic acid, 2-hydroxy-3-aminopropionic acid-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-acetamide)-iminodiacetic acid, nitrilotripropionic acid, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, 1,4-diaminobutanetetraacetic acid, 2-methyl-1,3-diaminopropanetetraacetic acid, 2-dimethyl-1,3-diaminopropanetetraacetic acid, citric acid, and the alkaline metal salts (for example, a lithium salt, a sodium salt and a potassium salt) and ammonium salts thereof. In addition thereto, there can be enumerated as well the bleaching agents described in JP-A-63-80256 (the term JP-A as used herein means an unexamined published Japanese patent application), JP-A-63-97952, JP-A-63-97953, JP-A-63-97954, JP-A-1-93740, JP-A-3-216650, JP-A-3-180842, JP-A-4-73645, JP-A-4-73647, JP-A-4-127145, JP-A-4-134450, JP-A-4-174432, European Patent Publication 430000A1, and west German Patent Publication 3912551. However, they will not be limited thereto.

[0070] The processing solution containing the metal chelate compound used in the present invention and having a bleaching ability contains the metal chelate compound and in addition thereto, preferably added thereto are halides such as chloride, bromide and iodide as a rehalogenizing agent. Further, an organic ligand forming a scarcely soluble silver salt may be added in place of the halides. The halides are added in the forms of an alkaline metal salt, an ammonium salt, a guanidine salt, and an amine salt. To be concrete, there are included sodium bromide, ammonium bromide, potassium chloride, guanidine hydrochlorate, potassium bromide, and potassium chloride. In the processing solution having the bleaching ability used in the present invention, an amount of the rehalogenizing agent is suitably 2 mole/liter or less, and in case of a bleaching solution, it is preferably 0.01 to 2.0 mole/liter, further preferably 0.1 to 1.7 mole/ liter, and particularly preferably 0.1 to 0.6 mole/liter. In a bleach-fixing solution, it is preferably 0.001 to 2.0 mole/ liter, further preferably 0.001 to 1.0 mole/liter, and particularly preferably 0.001 to 0.5 mole/liter.

[0071] The processing solution having the bleaching ability used in the present invention can contain the compound (free acid) represented by formula (I) which is formed separately from the metal chelate compound used in the present invention, and the lower the stability of the metal chelate compound is, the more the compound (free acid) represented by formula (I) is preferably added. Usually, the compound (free acid) represented by formula (I) is used in a mole ratio of 0 to 30 based on the metal chelate compound used in the present invention.

[0072] In addition thereto, added to the bleaching solution or the bleach-fixing solution used in the present invention are a bleaching accelerator, a corrosion inhibitor for preventing corrosion of a processing bath, a buffer agent for keeping pH of a processing solution, a fluorescent whitening agent, and a deforming agent according to necessity.

[0073] There can be used as the bleaching accelerator, for example, the compounds having a mercapto group or a disulfide group, 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); the thiazolidine derivatives described in JP-A-50-140129; the 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; the polyamine compounds described in JP-B-45-8836 (the term JP-B as used herein means an examined Japanese patent publication); and the imidazole compounds described in JP-A-49-40493. Of them, preferred are the mercapto compounds described in British Patent 1,138,842.

[0074] The bleaching accelerator may be used in an amount of 0.01 mmole/liter to 0.1 mole/liter, preferably 0.1 mmole/liter to 0.05 mole/liter, more preferably 0.5 mmole/liter to 0.015 mole/liter.

[0075] Nitrates such as ammonium nitrate, sodium nitrate and potassium nitrate are preferably used as the corrosion inhibitor. The addition amount thereof is 0.01 to 2.0 mole/ liter, preferably 0.05 to 0.5 mole/liter.

[0076] A pH value of the bleaching solution or bleach-fixing solution used in the present invention is 2.0 to 8.0, preferably 3.0 to 7.5. In the case where bleaching or bleach-fixing is carried out immediately after a color development in a light-sensitive material for photographing, the processing solution is used at pH of 7.0 or lower, preferably 6.4 or lower in order to suppress a bleaching fog. Particularly in case of the bleaching solution, a pH of 3.0 to 5.0 is preferred. The pH value of 2.0 or lower is liable to make the metal chelate compound used in the present invention instable and accordingly, a pH of 2.0 to 6.4 is preferred. A pH of 3 to 7 is preferred for a color printing material.

[0077] Any compounds can be used as a pH buffer agent used for the above purpose as long as they are less liable to be susceptible to oxidation by a bleaching agent and have a buffer action in the above pH range. There are included, for example, 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 acid, glutaric acid, adipic acid, aspartic acid, glutamic acid, cystine, ascorbic acid, phthalic acid, terephthalic acid, picolinic acid, and salicylic acid, organic bases such as pyridine, dimethylpyrazole, 2-methyl-o-oxazoline, aminoacetonitrile, and imidazole. These buffer agents may be used in combination of plural ones. In the present invention, the organic acids having a pKa of 2.0 to 5.5 are preferred. Particularly preferred are acetic acid, glycolic acid, malonic acid, succinic acid, maleic acid, fumaric acid, picolinic acid, and the combined use thereof. These organic acids can be used as well in the forms of an alkaline metal salt (for example, a lithium salt, a sodium salt and a potassium salt) and an ammonium salt. These buffer agents may be used in an amount of suitably 3.0 mole or less, preferably 0.1 to 2.0 mole, more preferably 0.2 to 1.8 mole, and particularly preferably 0.4 to 1.5 mole per liter of a processing solution having a bleaching ability.

[0078] In order to control a pH of the processing solution having the bleaching ability, the above acids and the alkali agents (for example, aqueous ammonia, KOH, NaOH, potassium carbonate, sodium carbonate, imidazole, monoethanolamine, and diethanolamine) may be used in combination. Of them, preferred are aqueous ammonia, KOH, NaOH, potassium carbonate, and sodium carbonate.

[0079] In view of increase in recognition toward protection of a global environment in recent years, efforts for reducing a nitrogen atom discharged into an environment have been made. It is desired from such point of view that an ammonium ion is not substantially contained as well in the processing solution used in the present invention.

[0080] In the present invention, "substantially containing no ammonium ion" means a status that a concentration of the ammonium ion is 0.1 mole/liter or less, preferably 0.08 mole/ liter or less, more preferably 0.01 mole/liter or less and it is particularly preferably not contained at all.

[0081] An alkaline metal ion and an alkaline earth metal ion are preferred as an alternative cation specimen for reducing an ammonium ion concentration to the range used in the present invention, and the alkaline metal ion is particularly preferred. Of them, a lithium ion, a sodium ion and a potassium ion are particularly preferred. To be concrete, in addition to a sodium salt and a potassium salt of an organic acid ferric complex as a bleaching agent and potassium bromide and sodium bromide as a rehalogenizing agent contained in a processing solution having a bleaching ability, potassium nitrate and sodium nitrate are included.

[0082] Potassium hydroxide, sodium hydroxide, potassium carbonate and sodium carbonate are preferred as an alkali agent used for controlling the pH.

[0083] In processing, the processing solution having the bleaching ability used in the present invention is particularly preferably subjected to an aeration since the photographic performances can be very stably maintained. A conventional means publicly known in the art can be applied to the aeration, and the blowing of air into the processing solution having the bleaching ability and the absorption of air utilizing an ejector can be carried out.

[0084] In blowing air, air is preferably discharged in a solution through a diffusion tube having fine pores. Such diffusion tube is widely used for an aeration tank and the others in an active sludge treatment. With respect to the aeration, there can be utilized the items described in Z-121, Using Process published by Eastman Kodak Co., Ltd., C-41 the 3rd edition (1982), pp. BL-1 to BL-2. In processing with the processing solution having the bleaching ability used in the present invention, stirring is preferably strengthened and in carrying out it, the content described at page 8, a right upper column, the sixth line to a left lower column, the second line of JP-A-3-33847 can be utilized as it is.

[0085] The bleaching or bleach-fixing process can be carried out at a temperature range of 30 to 60°C, preferably 35 to 50°C.

[0086] A processing time at the bleaching or bleach-fixing process is in a range of 10 seconds to 7 minutes, preferably 10 seconds to 4 minutes in case of a light-sensitive material for photographing. Also, it is 5 to 70 seconds, preferably 5 to 60 seconds, and more preferably 10 to 45 seconds in case of a light-sensitive material for printing. A rapid processing and the excellent results without increase in a stain have been achieved in these preferred processing conditions.

[0087] A light-sensitive material which was processed in the processing solution having the bleaching ability is subjected to a fixing or bleach-fixing processing. Those described at page 6, a right lower column, the sixteenth line to page 8, a left upper column, the fifteenth line of JP-A-3-33847 are preferred for such fixing solution or bleach-fixing solution.

[0088] In general, ammonium thiosulfate has been used as a fixing agent in a desilvering process but it may be substituted with the other conventional fixing agents, for example, a mesoion series compound, a thioether series compound, thioureas, a lot of iodides, and hypo. They 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. There are included, for example, ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, guanidine thiosulfate, ammonium thiocyanate, sodium thiocyanate, potassium thiocyanate, dihydroxyethyl-thioether, 3,6-dithia-1,8-octanediol, and imidazole. Among them, thiosulfates and mesoions are preferred. Ammonium thiosulfate is preferred from a viewpoint of a rapid fixability. However, in light of an environmental problem as described previously, sodium thiosulfate and mesoions are further preferred from a viewpoint that an ammonium ion is not substantially contained in a processing solution. Further, combined use of two or more kinds of the bleaching agents enables a further rapid fixing to be carried out. For example, in addition to ammonium thiosulfate and sodium thiosulfate, preferred as well is the combined use of ammonium thiocyanate, imidazole, thiourea, and thioether each described above. In this case, the second fixing agent is added preferably in a range of 0.01 to 100 mole % based on ammonium thiosulfate and sodium thiosulfate.

[0089] An addition amount of the fixing agent is 0.1 to 3.0 mole, preferably 0.5 to 2.0 mole per liter of a bleach-fixing solution or a bleaching solution. A pH value of a fixing solution depends on the kind of a fixing agent, and it is generally 3.0 to 9.0. Particularly in the case where thiosulfates are used, it is preferably 5.8 to 8.0 in terms of obtaining a stable bleaching performance.

[0090] A preservative can be added to a bleach-fixing solution and a fixing solution to increase an aging stability of the solution. In case of the bleach-fixing solution or fixing solution containing thiosulfate, effective as the preservative are sulfite and/or hydroxylamine, hydrazine, and a bisulfite adduct of aldehyde (for example, a bisulfite adduct of acetaldehyde, particularly preferably the bisulfite adducts of aromatic aldehydes described in JP-A-1-298935). Further, the sulfinic acid compounds described in JP-A-62-143048 also are preferably used as well.

[0091] Further, a buffer agent is preferably added to the bleach-fixing solution and the fixing solution in order to keep a pH uniform. There are included, for example, phosphate, imidazole, imidazoles such as 1-methyl-imidazole, 2-methyl-imidazole and 1-ethyl-imidazole, triethanolamine, N-allylmorpholine, and N-benzoylpiperazine.

[0092] Further, in the fixing solution, various chelate compounds can be added to mask the iron ions carried over from a bleaching solution to achieve the improvement in a stability of the solution. Such preferred chelate compound includes 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilomethylenephosphonic acid, 2-hydroxy-1,3-hydroxy-1,3-diaminopropanetetraacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, iminodiacetic acid, dihydroxyethyl glycine, 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'-tetramethylene-phosphonic 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-acetamide)-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, hydrazidediacetic acid, and N-hydroxy-iminodipropionic acid, and the alkaline metal salts (for example, a lithium salt, a sodium salt and a potassium salt) and ammonium salts thereof.

[0093] A preferred addition amount of the chelate compounds described above is 0.3 to 10 times, more preferably 0.5 to 3 times in terms of a mole ratio based on an iron ion carried over. An amount of the above chelate compounds which are incorporated into a fixing solution of 1 liter is preferably 0.01 to 0.5 mole, particularly preferably 0.03 to 0.2 mole.

[0094] The fixing process can be carried out in a range of 30 to 60°C, preferably 35 to 50°C.

[0095] Time in a fixing processing process is 15 seconds to 2 minutes, preferably 25 seconds to 1 minute and 40 seconds in case of a light-sensitive material for photographing, and 8 to 80 seconds, preferably 10 to 45 seconds in case of a light-sensitive material for printing.

[0096] In general, a desilvering process is carried out in a combination of a bleaching process, a bleach-fixing (blixing) process and a fixing process, and to be concrete, the following ones are included:

(1) bleaching-fixing,
(2) bleaching-blixing,
(3) bleaching-blixing-fixing,
(4) bleaching-rinsing-fixing,
(5) blixing, and
(6) fixing-blixing.

[0097] Preferred for a light-sensitive material for photographing is (1), (2), (3) or (4), more preferably (1), (2) or (3). Preferred for a light-sensitive material for printing is (5).

[0098] The present invention can be applied as well to a desilvering processing in which, for example, a controlling bath, a terminating bath and a rinsing bath are put after a color development processing.

[0099] The processing process according to the present invention is preferably carried out with an automatic developing machine. A transporting method in such automatic developing machine is described in JP-A-60-191257, JP-A-60-191258, and JP-A-60-191259. Further, a crossover is preferably shortened in the automatic developing machine in order to carry out a rapid processing. The automatic developing machine in which the crossover time is shortened to 5 seconds or shorter is described in JP-A-1-319038.

[0100] In carrying out a continuous processing with the automatic developing machine according to a processing process of the present invention, a replenishing solution is preferably added according to an amount of a processed light-sensitive material in order to replenish the components in a processing solution consumed in the processing of a light-sensitive material and control the accumulation of undesirable components eluted from a light-sensitive material in a processing solution. Two or more processing baths may be provided at the respective processing processes. In this case, a countercurrent system is preferably applied in which a replenishing solution is flowed from a following bath to a preceding bath. Particularly in a rinsing process and a stabilizing process, a cascade of 2 to 4 stages is preferably applied.

[0101] An amount of a replenishing solution is preferably reduced as long as a composition change in the respective processing solutions does not cause inconvenience in the photographic properties and a stain of the solutions.

[0102] An amount of a replenishing solution for a developing solution is 50 to 3000 ml, preferably 50 to 2200 ml per m^2 of a light-sensitive material in case of a color photographing material, and 15 to 500 ml, preferably 20 to 350 ml per m^2 of the light-sensitive material in case of a color printing material.

[0103] An amount of a replenishing solution for a bleaching solution is 10 to 1000 ml, preferably 50 to 550 ml per m^2 of the light-sensitive material in case of the color photographing material, and 15 to 500 ml, preferably 20 to 300 ml per m^2 of the light-sensitive material in case of the printing material.

[0104] An amount of a replenishing solution for a bleach-fixing solution is 200 to 3000 ml, preferably 250 to 1300 ml per m^2 of the light-sensitive material in case of the color photographic material, and 20 to 300 ml, preferably 50 to 200 ml per m^2 of the light-sensitive material in case of the printing material. The bleach-fixing solution may be replenished as a single solution or may be replenished dividing into a bleaching composition and a fixing composition or as a bleach-fixing replenishing solution prepared by mixing the overflowing solutions from a bleaching bath and/or a fixing bath.

[0105] An amount of a replenishing solution for a fixing solution is 300 to 3000 ml, preferably 300 to 1200 ml per m^2 of the light-sensitive material in case of the color photographing material, and 20 to 300 ml, preferably 50 to 200 ml per m^2 of the light-sensitive material in case of the printing material.

[0106] A replenishing amount of a rinsing solution or a stabilizing solution is 1 to 50 times, preferably 2 to 30 times and more preferably 2 to 15 times as much as an amount carried over from a preceding bath per a unit area.

[0107] Further, the processing solution having the bleaching ability used in the present invention can be reused after recovering an overflowed solution used for the processing and adding the components to adjust the components. Usually, such use method is called regeneration and in the present invention, such generation can be preferably carried out. With respect to the details of the regeneration, there can be applied the matters described in Processing Manual, Fuji Color Negative Film, CN-16 Processing (revised in August 1990), pp. 39 to 40, published by Fuji Photo Film Co., Ltd.

[0108] A kit used for preparing the processing solution having the bleaching ability used in the present invention may be either of a liquid form or of a powder form. The powder form is easy to prepare since almost all raw materials are supplied in a powder form and less hygroscopic in the case where an ammonium salt is removed.

[0109] The above kit for regeneration is preferably of the powder form from a viewpoint of reduction of an amount of a waste solution since it can be directly added without using extra water.

[0110] In addition to the aeration described previously, the methods described in "The Base of Photographic Engineering-Silver Salt Photograph" edited by Japan Photographic Academy, published by Corona Co., Ltd. can be used for the generation of the processing solution having the bleaching ability. To be concrete, in addition to an electrolysis regeneration, there are included the methods for regenerating the bleaching solution by means of bromic acid, chlorous acid, bromine, a bromine precursor, persulfate, hydrogen peroxide, hydrogen peroxide utilizing a catalyst, bromous acid, and ozone.

[0111] In the regeneration by electrolysis, an anode and a cathode are put in the same bleaching bath or the regeneration is carried out with an anode bath and a cathode bath each separated to different baths with a diaphragm. In addition thereto, a bleaching solution and a developing solution and/or a fixing solution can be simultaneously subjected to a regeneration processing with a diaphragm.

[0112] A bleaching solution and a bleach-fixing solution are regenerated by subjecting the accumulated silver ions to an electrolytic reduction. In addition thereto, the accumulated halogen ions are preferably removed with an anionic ion exchange resin in terms of maintaining a fixing performance.

[0113] An ion exchange or a ultrafiltration is used in order to reduce an amount of rinsing water, and the ultrafiltration is particularly preferably used.

[0114] In the present invention, a color light-sensitive material is subjected to a color development processing before a desilvering processing after an imagewise exposure. A color developing solution which can be used in the present invention includes those described at page 9, a left upper column, the sixth line to page 11, a right lower column, the sixth line of JP-A-3-33847 and those described in JP-A-5-197107.

[0115] A publicly known aromatic primary amine color developing agent can be applied as a color developing agent used in a color developing process. A preferred example is a p-phenylenediamine derivative, and the representative examples thereof include 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methylaniline, 4-amino-N-ethyl-N-(3-hydroxypropyl)-3-methylaniline, 4-amino-N-ethyl-N-(4-hydroxybutyl)-3-methylaniline, 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-3-methylaniline, 4-amino-N-(3-carbamoylpropyl-N-n-propyl)-3-methylaniline, and 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methoxyaniline. In addition thereto, those described in European Patent Publication No. 410450 and JP-A-4-11255 can preferably be used as well.

[0116] Further, they may be the sulfate, chlorate, sulfite, naphthalenedisulfonic acid and p-toluenesulfonic acid salts of these p-phenylenediamine derivatives. A use amount of the aromatic primary amine developing agent is preferably 0.0002 to 0.2 mole, more preferably 0.001 to 0.1 mole per liter of a color developing solution.

[0117] A processing temperature in the color developing solution in the present invention is 20 to 55°C, preferably 30 to 55°C. A processing time is 20 seconds to 5 minutes, preferably 30 seconds to 3 minutes and 20 seconds, and further preferably 1 minute to 2 minutes and 30 seconds in a light-sensitive material for photographing. In a material for printing, it is 10 seconds to 1 minute and 20 seconds, preferably 10 seconds to 60 seconds, and further preferably 10 seconds to 40 seconds.

[0118] The processing method of the present invention can be applied as well to a color reversal processing. A black/white developing solution used for the above processing is a so-called first black/white developing solution used for the reversal processing of a conventional color light-sensitive material. Various well known compounds which are added to a black/white developing solution used for a processing solution for a black/white silver halide light-sensitive material can be incorporated into the first black/white developing solution used for the color reversal light-sensitive material.

[0119] There can be enumerated as the representative additives, a developing agent such as l-phenyl-3-pyrazolidone, metol and hydroquinone, a preservative such as sulfite, an accelerator consisting of an alkali such as sodium hydroxide, sodium carbonate and potassium carbonate, an inorganic or organic inhibitor such as potassium bromide, 2-methylbenzimidazole and methylbenzothiazole, a water softening agent such as polyphosphate, and a development inhibitor consisting of a trace amount of iodide and a mercapto compound.

[0120] In the present invention, a light-sensitive material which is subjected to a desilvering processing is subjected to a washing or stabilizing process. With respect to the washing or stabilizing process applied, a stabilizing solution described in U.S. Patent 4,786,583 can be enumerated. In the stabilizing solution, formaldehyde is used as a stabilizing agent, and preferred from a viewpoint of a working environmental safety are N-methylolazole, hexamethylenetetramine, a formaldehyde bisulfite adduct, dimethylolurea, and an azolylmethylamine derivative. These are described in JP-A-2-153348, JP-A-4-270344, and European Patent Publication 504609A2. In particular, preferably used in combination are azoles such as 1,2,4-triazole described in European Patent Publication 519190A2, and azolylmethylamine and the derivatives thereof, such as 1,4-bis(1,2,4-triazole-1-ylmethyl) piperazine since an image stability is high and a vapor pressure of formaldehyde is low.

[0121] In the present invention, stirring is preferably strengthened as much as possible in terms of more effectively demonstrating the effects of the present invention.

[0122] The concrete method for strengthening stirring includes the methods described in JP-A-62-183460, JP-A-62-183461, and JP-A-3-33847 (page 8), that is, a method employed for a color negative film processor FP-560B manufactured by Fuji Photo Film Co., Ltd., in which a jet stream of a processing solution is struck against an emulsion side of a light-sensitive material, a method described in JP-A-62-183461, in which a stirring effect is increased with a rotating means, a method in which a stirring effect is improved by moving a light-sensitive material (film) while contacting an emulsion layer side thereof to a wiper blade to cause a turbulent flow on an emulsion layer surface, and a method in which a circulating flow amount of a whole processing solution is increased. Of them, the method in which a jet stream of a processing solution is struck is most preferred, and this method is preferably employed in the whole processing baths.

[0123] A light-sensitive material which can be applied to the processing of the present invention includes a color negative film, a color reversal film, a color paper, a color reversal paper, a direct positive color light-sensitive material, a color negative film for a movie, and a color positive film for a movie. They are described in, for example, JP-A-3-33847, JP-A-3-293662, and JP-A-4-130432. There are no specific limitations to a support for the light-sensitive material used in the present invention; a coating method; the kind of silver halides used for a silver halide emulsion layer and a surface protective layer (for example, silver iodobromide, silver iodochlorobromide, silver bromide, silver chlorobromide, and silver chloride), the grain forms thereof (for example, cube, plate and sphere), the grain sizes thereof, the fluctuations thereof, the crystal structures thereof (for example, a core/shell structure, a multi-layer structure, and a uniform layer structure), the manufacturing processes thereof (for example, a single jet process and a double jet process), a binder (for example, gelatin), a hardener, an anti-foggant, a metal doping agent, a silver halide solvent, a thickener, an emulsion breaker, a dimension stabilizer, an anti-adhesion agent, a stabilizer, an anti-contamination agent, a dye image stabilizer, an anti-stain agent, a chemical sensitizer, a spectral sensitizer, a sensitivity improver, a supersensitizer, a nucleus forming agent, a coupler (for example, pivaloyl acetanilide type and benzoyl acetanilide type yellow couplers, 5-pyrazolone type and pyrozoloazole type magenta couplers, the phenol type and naphthol type cyan couplers, a DIR coupler, a bleaching accelerator-releasing coupler, a competitive coupler, and a colored coupler), a coupler dispersing method (for example, an oil-in-water dispersing method using a high boiling solvent), a plasticizer, an anti-static agent, a lubricant, a coating aid, a surface active agent, a whitening agent, a formalin scavenger, a light scattering agent, a matting agent, a light absorber, an ultraviolet absorber, a filter dye, an irradiation dye, a development improver, a delustering agent, a fungicide (for example, 2-phenoxyethanol), and an anti-mold agent. They can be referred to, for example, Product Licensing, vol. 92, pp. 107 to 110 (December 1971-), Research Disclosure (hereinafter referred to as RD) No. 17643 (December 1978), RD No. 18716 (November 1979), and RD No. 307105 (November 1989).

[0124] The processing composition used in the present invention can be applied to any color light-sensitive materials. In the present invention, a dry film thickness of the whole constitutional layers of a color light-sensitive material excluding a support and a subbing layer and a back layer each provided on the support is preferably 20.0 μm or less,more preferably 18.0 μm or less in case of a color light-sensitive material for photographing, and preferably 16.0 μm or less, more preferably 13.0 μm or less in case of a printing material in terms of achieving the objects of the present invention.

[0125] In an outside of the range of the above preferred layer thickness, a bleaching fog and a stain after processing are increased, which are attributable to a developing agent remaining in a light-sensitive material after a color development processing. The generation of these bleaching fog and stain is attributable to a green-sensitive layer, and a magenta color is resultingly liable to increase as compared with the other cyan and yellow colors.

[0126] A lower limit in a layer thickness regulation is desirably reduced from the above regulation within the range in which the properties of a light-sensitive material are not damaged to a large extent. The lower limit of the whole dry layer thickness of the constitutional layers excluding those of a support and a subbing layer provided on the support is 12.0 μm in case of a color light-sensitive material for photographing and 7.0 μm in case of a printing material. In case of the light-sensitive material for photographing, a layer is usually provided between a light-sensitive layer closest to a support and a subbing layer, and the lower limit of the whole dry layer thickness of this layer (may be plural layers) is 1.0 μm. The layer thickness may be reduced either in a light-sensitive layer or a non-light-sensitive layer.

[0127] A swelling rate of the color light-sensitive material used in the present invention is preferably 50 to 200 %, more preferably 70 to 150 %, wherein the swelling rate is defined by the following equation:

$$\text{Swelling rate} = [(\text{equilibrium swollen layer thickness in water at } 25^\circ\text{C}) - (\text{whole dry layer thickness at } 25^\circ\text{C and } 55\ \%\ \text{RH})]/(\text{whole dry layer thickness at } 25^\circ\text{C and } 55\ \%\ \text{RH}) \times 100.$$

[0128] The swelling rate deviated from the above values will increase a residual amount of a color developing agent and exert an adverse influence to a photographic performance, an image quality such as a desilvering performance and a film property such as a film strength.

[0129] Further, a swelling speed $T_{1/2}$ of the color light-sensitive material used in the present invention is preferably

15 seconds or less, more preferably 9 seconds or less, wherein the swelling speed is defined by the time in which the layer thickness is swollen to 1/2 of a saturated swollen layer thickness defined by 90 % of the maximum swollen layer thickness in a color developing solution (30°C, 3 minutes and 15 seconds).

[0130] Silver halide contained in a photographic emulsion layer of the color light-sensitive material used in the present invention may be of any silver halide composition. For example, it is silver chloride, silver bromide, silver chlorobromide, silver iodobromide, silver iodochloride, or silver iodochlorobromide.

[0131] In case of a color light-sensitive material for photographing and a color reversal light-sensitive material (for example, a color negative film, a reversal film and a color reversal paper), preferred is silver iodobromide, silver iodochloride or silver iodochlorobromide each containing 0.1 to 30 mole % of sliver iodide. Particularly preferred is silver iodobromide containing 1 to 25 mole % of silver iodide. In case of a direct positive light-sensitive material, silver bromide or silver chlorobromide is preferred. Silver chloride is preferred as well for carrying out a rapid processing. In case of a light-sensitive material for paper, silver chloride or silver chlorobromide is preferred. Particularly preferred is silver chlorobromide containing silver chloride of 80 mole % or more, more preferably 95 mole % or more, most preferably 98 mole % or more.

[0132] Various color couplers can be used for the color light-sensitive material applied to the processing according to the present invention. The-concrete examples thereof are described in the patents described in above RD No. 17643, VII-C to G and No. 307105, VII-C to G, and JP-A-62-215272, JP-A-3-33847, JP-A-2-33144, and European Patent Publications 447969A and 482552A.

[0133] A yellow coupler includes those described in, for example, 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, European Patents 249,473A and 0,477,969, JP-A-63-23145, JP-A-63-123047, JP-A-1-250944, and JP-A-1-213648.

[0134] The particularly preferred yellow coupler includes the yellow couplers represented by formula (Y) described in a left upper column at page 18 to a left lower column at page 22 of JP-A-2-139544, the acyl acetamide series yellow couplers characterized by an acyl group, described in JP-A-5-2248 and European Patent Publication 0447969, and the yellow couplers represented by Formula (Cp-2) described in JP-A-5-27389 and European Patent Publication 0446863A2.

[0135] The 5-pyrazolone series and pyrazoloazole series compounds are preferred as a magenta coupler. More preferred are the compounds 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 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, U. S. Patents 4,500,630, 4,540,654, and 4,556,630, and International Publication WO88/04795.

[0136] The particularly preferred magenta coupler includes the pyrazoloazole series magenta couplers described in a right lower column at page 3 to a right lower column at page 10 of JP-A-2-139544 and the 5-pyrazolone magenta couplers represented by Formula (M-I) described at a left lower column at page 17 to a left upper column at page 21 of JP-A-2-139544. Most preferred are the pyrazoloazole series magenta couplers described above.

[0137] A cyan coupler includes the phenol series and naphthol series couplers. Preferred are the compounds 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 3,329,729, European Patents 0,121,365A and 0,249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658. Further, there can be used as well the pyrazoloazole series couplers described in JP-A-64-553, 64-554, 64-555, and 64-556, the pyrrolotriazole series couplers described in European Patent Publications 0,488,248 and 0,491,197, the pyrroloimidazole series couplers described in European Patent Publication 0,456,226A, the pyrazolopyrimidine series couplers described in JP-A-64-46753, the imidazole series couplers described in U.S. Patent 4,818,672 and JP-A-2-33144, the cyclic active methylene series 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.

[0138] The typical examples of a polymerized dye-forming coupler 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 European Patent 341,188A.

[0139] Preferred as a coupler capable of forming a dye having an appropriate dispersing property are the compounds described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Patent (published) 3,234,533.

[0140] In the present invention, there can be used as well the compounds releasing a photographically useful residue upon coupling. Preferred as a DIR coupler releasing a development inhibitor are the compounds described in the patents described in above RD No. 17643, Item 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.

[0141] Preferred as a coupler releasing imagewise a nucleus-forming agent or a development accelerator in developing are the compounds described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840.

[0142] In addition thereto, the compounds capable of being used for the color photographic element used in the present invention include the competitive couplers described in U.S. Patent 4,130,427; the polyequivalent couplers described in U.S. Patents 4,283,472, 4,338,393 and 4,310,618; the DIR redox compound-releasing couplers, DIR coupler-releasing couplers, DIR coupler-releasing redox compounds, or DIR redox-releasing redox compounds described in JP-A-60-185950 and JP-A-62-24252; the couplers releasing a dye the color of which is recovered after splitting off, described in European Patent 173,302A; the bleaching accelerator-releasing couplers described in RD No. 11449 and No. 24241, and JP-A-61-201247; the ligand-releasing couplers described in U.S. Patent 4,555,477; the couplers releasing a leuco dye, described in JP-A-63-75747; and the couplers releasing a fluorescent dye, described in U.S. Patent 4,774,181.

[0143] The suitable supports which can be used in the present invention are described in, for example, above Research Disclosures (RD) No. 17643, pp. 28 and No. 18716, pp. 647, right column to pp. 648, left column.

[0144] In particular, also preferred as the support in case of using it for a color negative film are those having a layer which has a conductivity and a transparent magnetic substance layer on one face as described in JP-A-4-62543, those having a magnetic recording layer, described in International Patent Publication WO90/04205, FIG. 1A, and those having a stripe magnetic recording layer and a transparent magnetic recording layer which is adjacent to the stripe magnetic recording layer, described in JP-A-4-124628. The protective layer described in JP-A-4-73737 is preferably provided on these magnetic recording layers.

[0145] A thickness of the support is preferably 70 µm to 120 µm. There can be used as a raw material for the support, various plastic films described at page 5, right upper column, the first line to page 6, right upper column, the fifth line of JP-A-4-124636, and the preferred one includes a cellulose derivative (for example, diacetyl-, triacetyl-, propionyl-, butanoyl-, and acetylpropionyl-acetates) and polyesters described in JP-B-48-40414 (for example, polyethylene terephthalate, poly-1,4-cyclohexanedimethylene terephthalate, and polyethylene naphthalate). Polyester is preferably used as the support of a film used in the present invention since a higher liquid-flashing effect can be obtained.

[0146] A package (patrone) in which the color negative film of the present invention is stored may be any one of existing or publicly known ones. In particular, preferred are those having the forms described in U.S. Patent 4,834,306, Fig. 1 to Fig. 3 and those described in U.S. Patent 4,846,418, Fig. 1 to Fig. 3.

[0147] In addition thereto, preferred as the color negative film are those having the contents described at page 14, left upper column, the first line to page 18, left lower column, the eleventh line of JP-A-4-125558.

[0148] Incidentally, the present invention can also be applied as a reducing solution which corrects a silver image consisting of a halftone dot and/or a line drawing which is obtained by subjecting a silver halide light-sensitive material for plate making to a development processing after exposing.

[0149] The present invention will be explained below in further details with reference to the examples.

EXAMPLE 1

[0150] The respective layers of the compositions shown below were simultaneously coated on a cellulose triacetate film support which was subjected to subbing to thereby prepare the multi-layer color light-sensitive material 101.

Composition of the light-sensitive layer

[0151] The base materials used for the respective layers are classified as follows:

ExC	Cyan coupler	UV	UV absorber
ExM	Magenta coupler	HBS	High boiling solvent
ExY	Yellow coupler	H	Gelatin hardener
ExS	Sensitizing dye		

[0152] The numerals corresponding to the respective components show the coated amounts in terms of a g/m^2 unit and the coated amounts converted to silver in case of silver halide. Provided that in case of the sensitizing dyes, the coated amount per mole of silver halide contained in the same layer is shown in terms of a mole unit.

Sample 101 :		
First layer (an anti-halation layer)		
Black colloidal silver	silver	0.18
Gelatin		1.38

(continued)

Sample 101 :		
First layer (an anti-halation layer)		
ExM-1		0.11
ExF-1		$3.4x10^{-3}$
HBS-1		0.16
Second layer (an intermediate layer)		
ExC-2		0.030
UV-1		0.020
UV-2		0.020
UV-3		0.060
HBS-1		0.05
HBS-2		0.020
Polyethyl acrylate latex		0.080
Gelatin		0.89
Third layer (a low red-sensitive emulsion layer)		
Emulsion A	silver	0.22
Emulsion B	silver	0.22
EXS-1		$5.0x10^{-4}$
ExS-2		$1.8x10^{-5}$
ExS-3		$5.0x10^{-4}$
ExC-1		0.050
ExC-3		0.030
ExC-4		0.14
ExC-5		$3.0x10^{-3}$
ExC-7		$1.0x10^{-3}$
ExC-8		0.010
Cpd-2		0.005
HBS-1		0.10
Gelatin		0.89
Fourth layer (a middle red-sensitive emulsion layer)		
Emulsion C	silver	0.69
EXS-1		$3.4x10^{-4}$
ExS-2		$1.2x10^{-5}$
ExS-3		$4.0x10^{-4}$
ExC-1		0.15
ExC-2		0.060
ExC-4		0.050
ExC-5		0.010
ExC-8		0.010
Cpd-2		0.023
HBS-1		0.11
Gelatin		0.59
Fifth layer (a high red-sensitive emulsion layer)		
Emulsion D	silver	1.61
ExS-1		$2.4x10^{-4}$
ExS-2		$1.0x10^{-5}$
ExS-3		$3.4x10^{-4}$

(continued)

Sample 101 :		
Fifth layer (a high red-sensitive emulsion layer)		
EXC-1		0.10
ExC-3		0.050
ExC-5		2.0x10^{-3}
ExC-6		0.010
ExC-8		0.010
Cpd-2		0.025
HBS-1		0.20
HBS-2		0.10
Gelatin		1.29
Sixth layer (an intermediate layer)		
Cpd-1		0.090
HBS-1		0.05
Polyethyl acrylate latex		0.15
Gelatin		1.09
Seventh layer (a low green-sensitive emulsion layer)		
Emulsion E	silver	0.23
Emulsion F	silver	0.23
ExS-4		4.0x10^{-5}
ExS-5		1.8x10^{-4}
ExS-6		6.5x10^{-4}
ExM-1		5.0x10^{-3}
ExM-2		0.27
ExM-3		0.086
ExM-4		0.030
EXY-1		0.015
HBS-1		0.30
HBS-3		0.010
Gelatin		0.83
Eighth layer (a middle green-sensitive emulsion layer)		
Emulsion G	silver	0.93
ExS-4		2.0x10^{-5}
ExS-5		1.4x10^{-4}
ExS-6		5.4x10^{-4}
ExM-2		0.13
ExM-3		0.045
ExM-5		0.020
EXY-1		7.0x10^{-3}
ExY-4		2.0x10^{-3}
ExY-5		0.020
HBS-1		0.16
HBS-3		8.0x10^{-3}
Gelatin		0.79
Ninth layer (a high green-sensitive emulsion layer)		
Emulsion H	silver	1.28
ExS-4		3.7x10^{-5}

(continued)

Sample 101 :		
Ninth layer (a high green-sensitive emulsion layer)		
ExS-5		8.1x10^{-5}
ExS-6		3.2x10^{-4}
EXC-1		0.010
ExM-1		0.020
ExM-4		0.050
ExM-5		0.020
ExY-4		5.0x10^{-3}
Cpd-3		0.050
HBS-1		0.20
HBS-2		0.08
Polyethyl acrylate latex		0.26
Gelatin		1.43
Tenth layer (a yellow filter layer)		
Yellow colloidal silver	silver	7.5x10^{-3}
Cpd-1		0.13
Cpd-4		7.5x10^{-3}
HBS-1		0.60
Gelatin		0.58
Eleventh layer (a low blue-sensitive emulsion layer)		
Emulsion I	silver	0.25
Emulsion J	silver	0.25
Emulsion K	silver	0.10
ExS-7		8.0x10^{-4}
ExC-7		0.010
ExY-1		5.0x10^{-3}
ExY-2		0.40
ExY-3		0.45
ExY-4		6.0x10^{-3}
ExY-6		0.10
HBS-1		0.30
Gelatin		1.64
Twelfth layer (a high blue-sensitive emulsion layer)		
Emulsion L	silver	1.30
ExS-7		3.0x10^{-4}
ExY-2		0.15
ExY-3		0.06
ExY-4		5.0x10^{-3}
Cpd-2		0.10
HBS-1		0.070
Gelatin		1.19
Thirteenth layer (the first protective layer)		
UV-2		0.10
UV-3		0.12
UV-4		0.30
HBS-1		0.10

(continued)

Sample 101 :		
Thirteenth layer (the first protective layer)		
Gelatin		2.49
Fourteenth layer (the second protective layer)		
Emulsion M	silver	0.10
H-1		0.37
B-1 (diameter: 1.7 µm)		5.0×10^{-2}
B-2 (diameter: 1.7 µm)		0.15
B-3		0.05
S-1		0.20
Gelatin		0.71

[0153] Further, W-1 to W-3, B-4 to B-6, and F-1 to F-17, an iron salt, a lead salt, a gold salt, a platinum salt, an iridium salt, a palladium salt, and a rhodium salt were appropriately incorporated into the respective layers in order to improve a preservation performance, a processing performance, an anti-pressure performance, anti-mold and fungicidal performances, an anti-static performance, and a coating performance.

[0154] Cpd-4 was dispersed in a form of a solid matter according to the process described in International Patent 88-4794.

Table 1

Emulsion	Grain form (halogen structure)	(I)	(II)	(III)	(IV)	(V)
A	Circular plate (uniform structure)	0	-	0.45	15	5.5
B	Cube (shell-high iodide double structure)	1.0	-	0.20	8	1
C	Tetradecahedron (middle shell-high iodide triple structure)	4.5	25	0.85	18	1
D	Hexagonal plate (outside-high iodide structure)	2.0	16	1.10	17	7.5
E	Circular plate (outside-high iodide structure)	1.0	-	0.45	15	3.0
F	Octahedron (core-high iodide double structure)	6.0	22	0.25	8	1
G	Tetradecahedron (middle shell-high iodide triple structure)	4.5	19	0.85	19	1
H	Hexagonal plate (outside-high iodide structure)	3.5	16	1.10	16	6.8
I	Circular plate (center-high iodide structure)	2.0	15	0.45	15	6.0
J	Cube (uniform structure)	1.0	10	0.30	8	1
K	Tetradecahedron (core-high iodide double structure)	18.0	8	0.80	18	1
L	Hexagonal plate (middle shell-high iodide triple structure)	12.0	12	1.35	22	12.0
M	Light-insensitive fine grain (uniform structure)	1.0	-	0.04	15	1

Remarks: (I): Average AgI content (%).
(II): Intergrain iodide distribution fluctuation coefficient (%).
(III): Average grain diameter sphere-corresponding diameter (μm).
(IV): Fluctuation coefficient in a grain diameter (%).
(V): Diameter/thickness ratio.

[0155] In Table 1,

(1) Emulsions I to L are subjected to reduction sensitization with thiourea dioxide and thiosulfonic acid in preparing grains according to the examples described in JP-A-2-191938.
(2) Emulsions A to L are subjected to gold sensitization, sulfur sensitization and selenium sensitization in the presence of the spectral sensitizing dyes described in the respective layers and sodium thiocyanate according to the examples described in JP-A-3-237450.
(3) Low molecular weight gelatin is used for preparing the tabular grains according to the examples described in JP-A-1-158426.
(4) The dislocation lines described in JP-A-3-237450 are observed on the tabular grains with a high pressure electron microscope.

[0156] The couplers and the additives each contained in the respective layers were dispersed in a gelatin solution by the methods shown in Table 2. The addition methods in the respective layers are shown in Table 3.

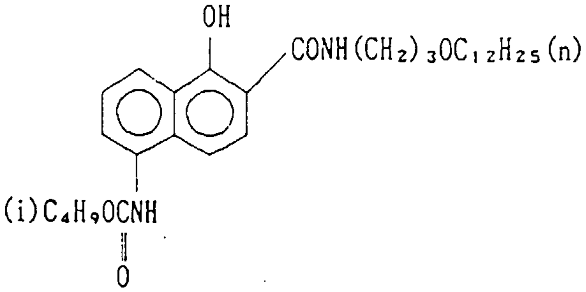
Table 2

Dispersing method	Method
A	A method in which a uniform aqueous solution of a coupler, a high boiling organic solvent, a surface active agent, NaOH, n-propanol, and the other additives is neutralized for depositing and dispersing
B	A method in which a uniform n-propanol solution of a coupler, a high boiling organic solvent, and the other additives is added to a surface active agent agueous solution for depositing and dispersing
C	A method in which a solution of a coupler, a high boiling organic solvent, a surface active agent, a low boiling organic solvent, and the other additives is mixed with an aqueous solution of gelatin and a surface active agent and stirred for emulsion-dispersing and the low boiling organic solvent is removed by evaporation
D	A method in which in C, the organic solvents are removed by washing with water or ultrafiltration after dispersing

Table 3

Layer	Dispersing method	Average dispersed grain diameter (nm)
3rd layer	C	133
4th layer	C	130
5th layer	D	40
7th layer	C	135
8th layer	C	60
9th layer	A	40
11th layer	C	125
12th layer	B	80

ExC-1



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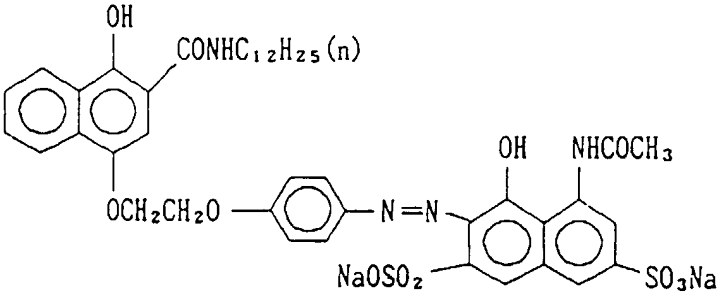

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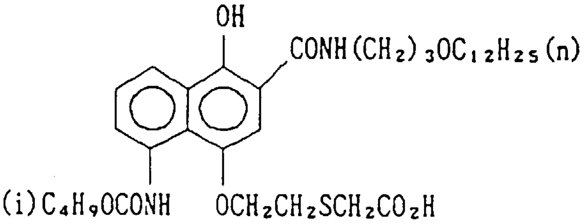

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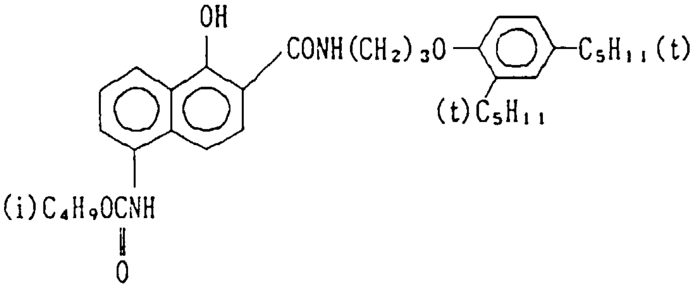

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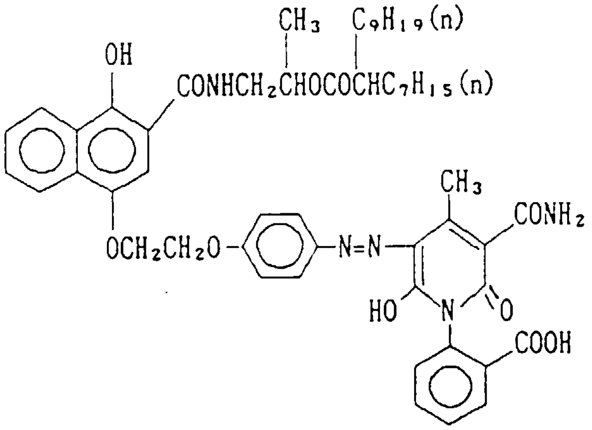

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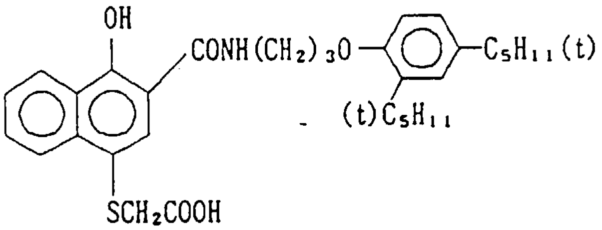

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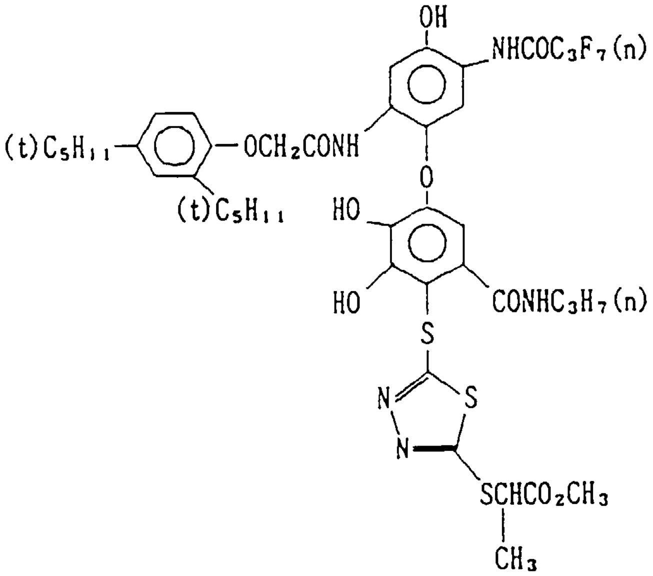

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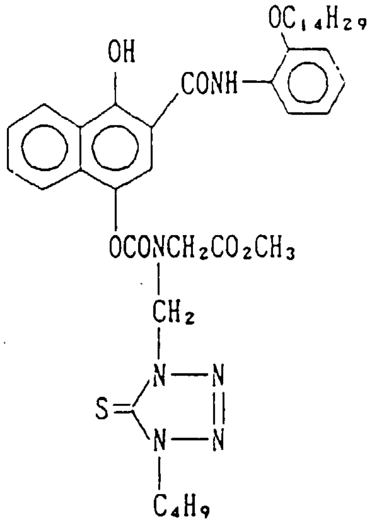
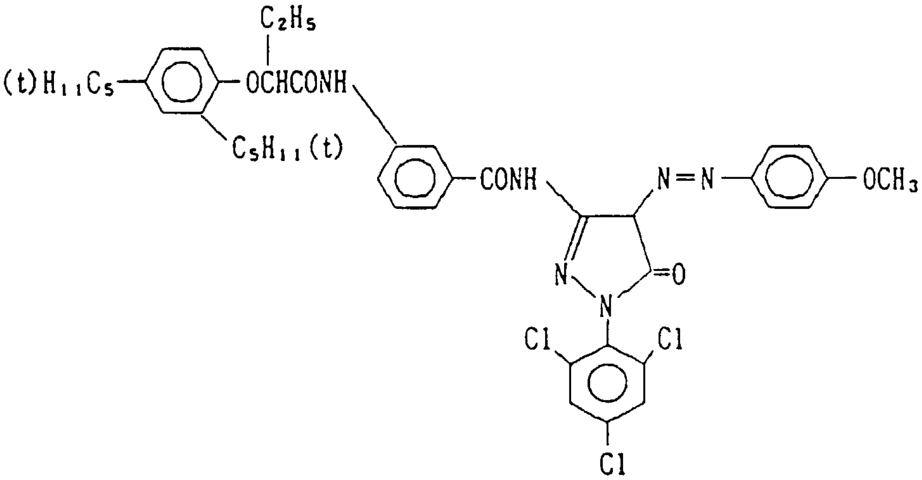


ExM-1



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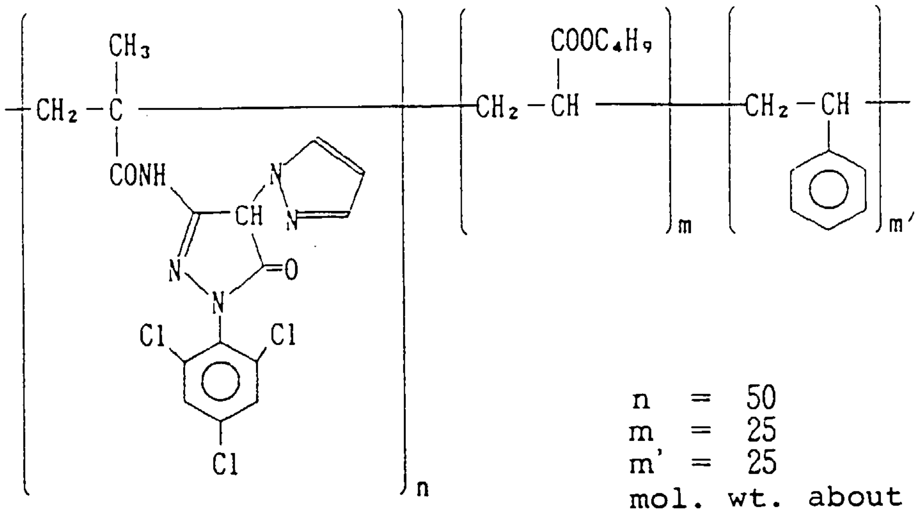
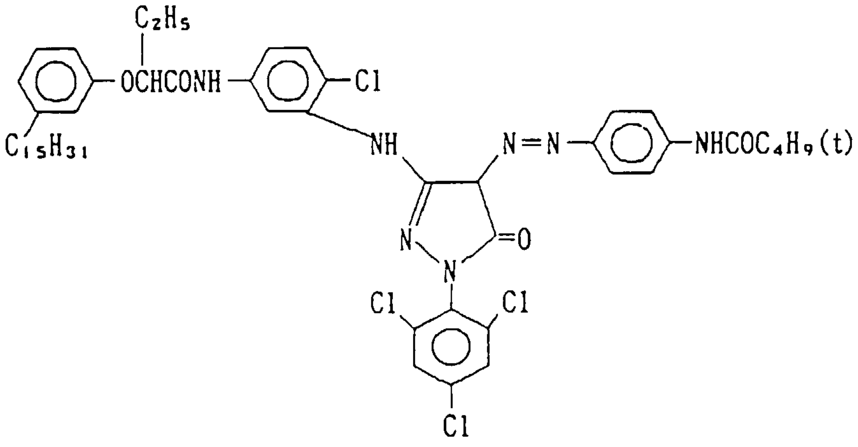


n = 50
m = 25
m' = 25
mol. wt. about 20,000

ExM-3



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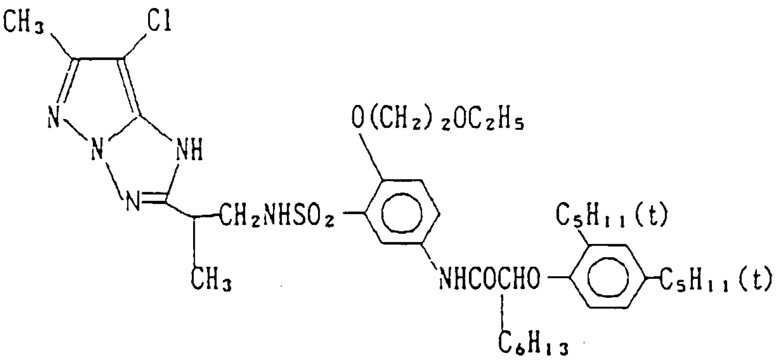

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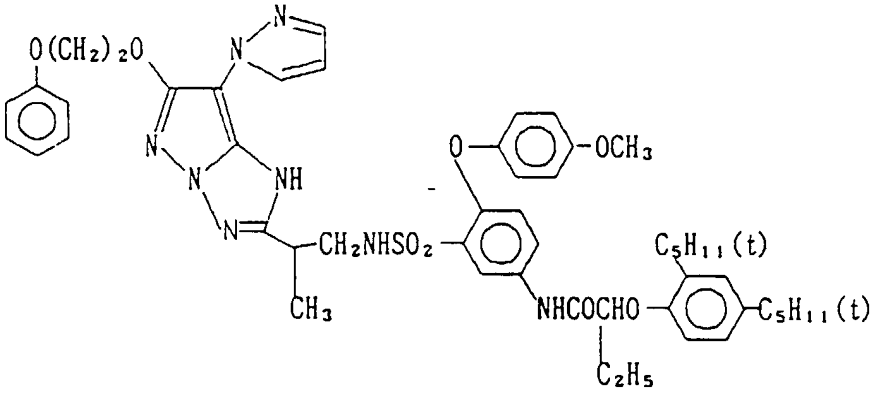

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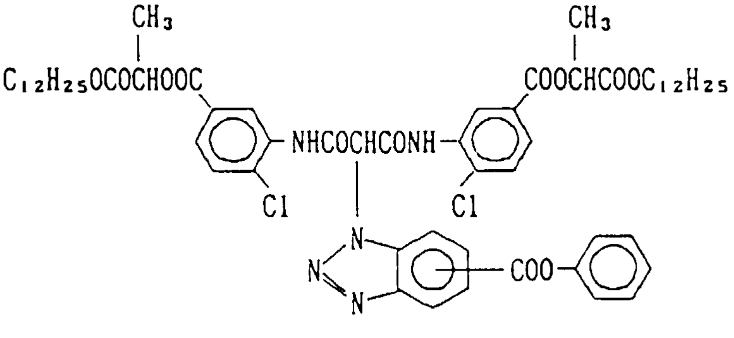
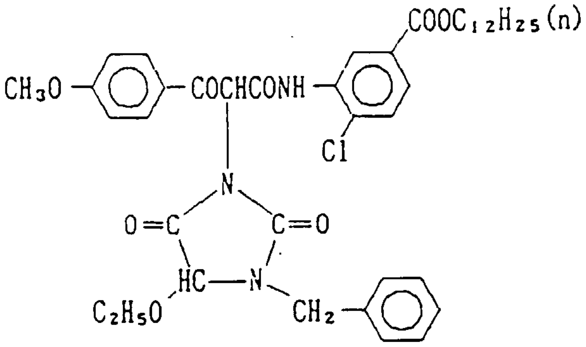


ExY-2



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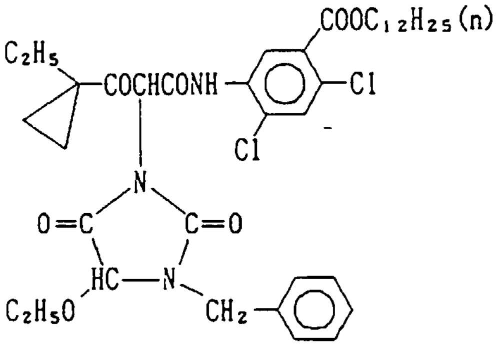

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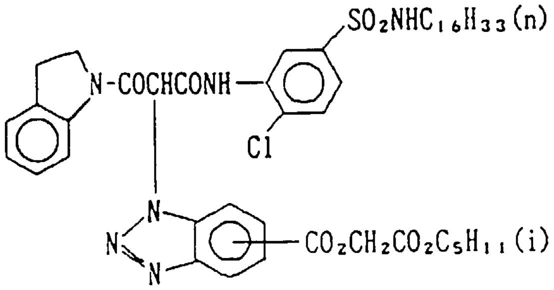

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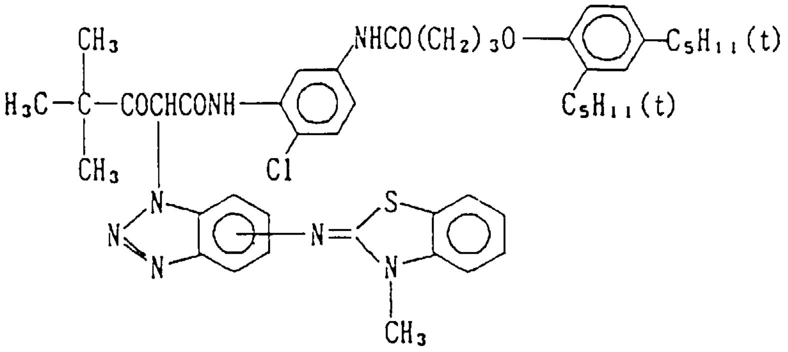

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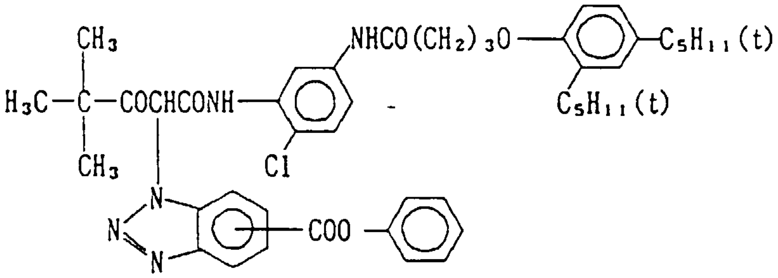

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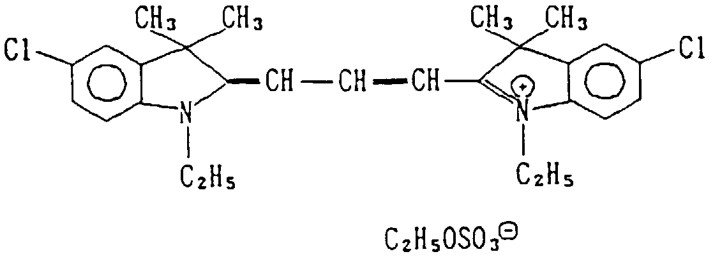
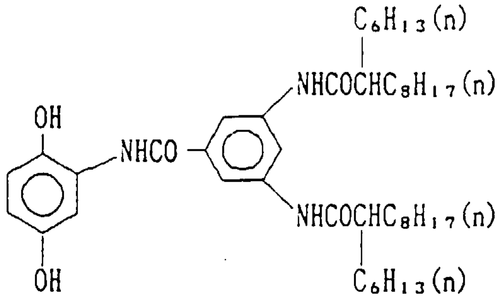
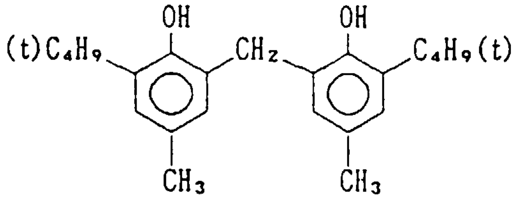


Cpd−1



Cpd−2



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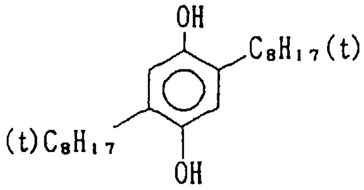
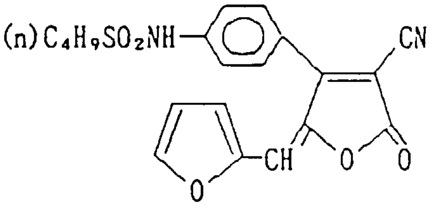
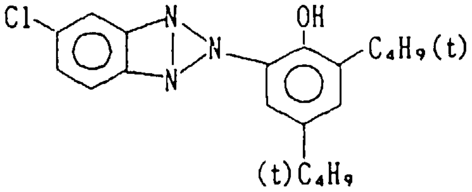


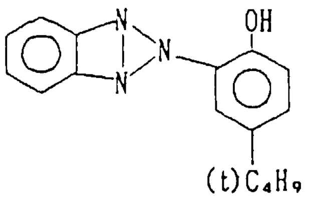
Cpd−4



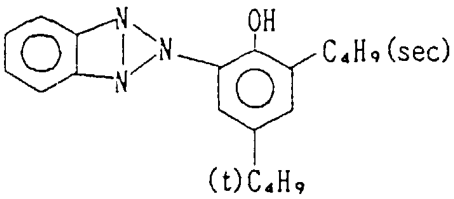
UV−1



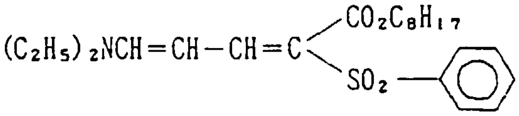
UV－2



UV－3



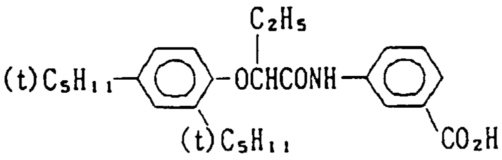
UV－4



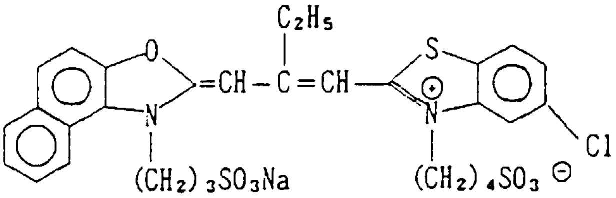
HBS-1 tricresylphosphate

HBS-2 di-n-butylphthalate

HBS－3



ExS－1



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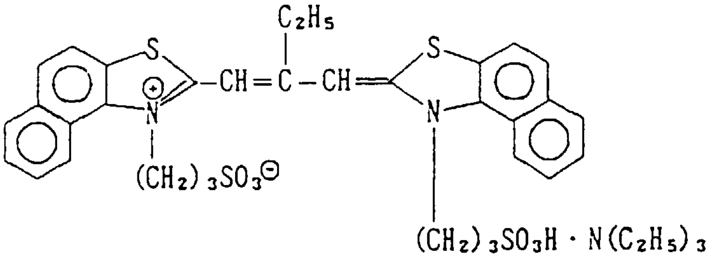

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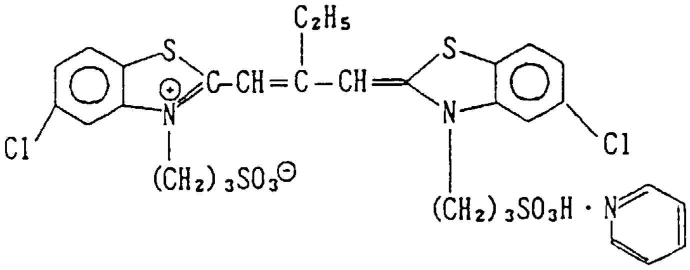

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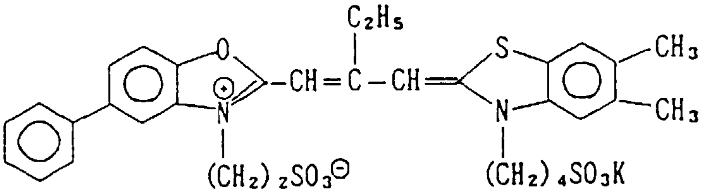

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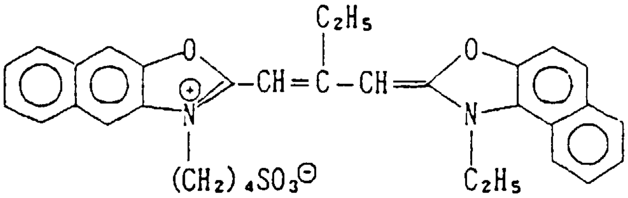

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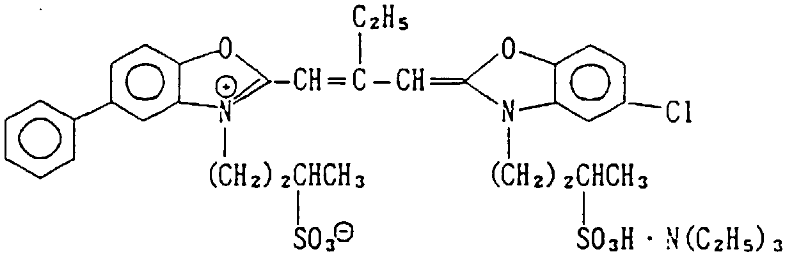

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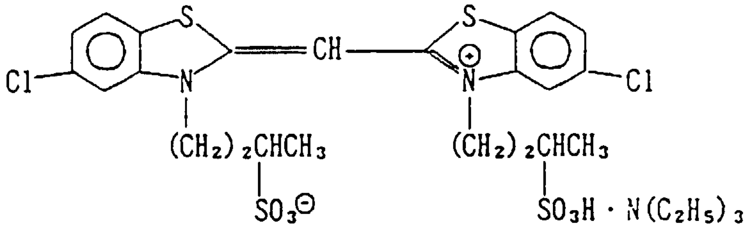
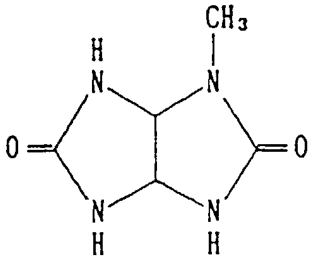
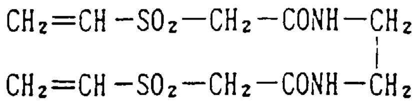


S-1

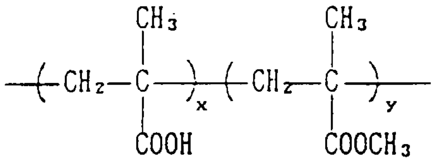


H-1



$$\begin{array}{l} CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \\ \hspace{9em}| \\ CH_2{=}CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

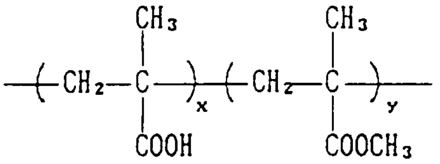
B-1



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

x/y=10/90

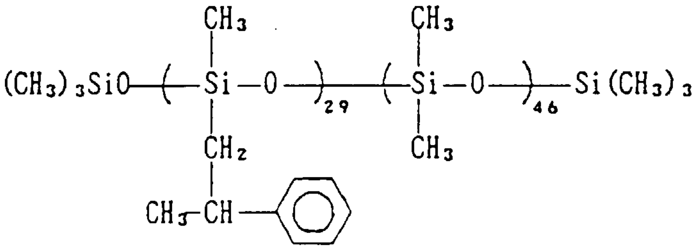
B − 2



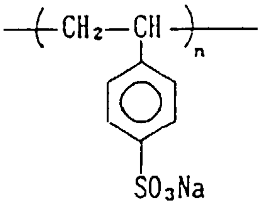
$-\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y-$

x/y=40/60

B − 3



B − 4



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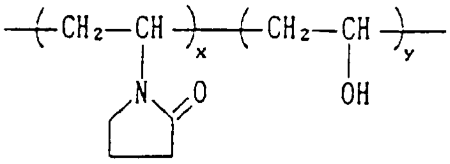
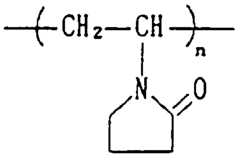


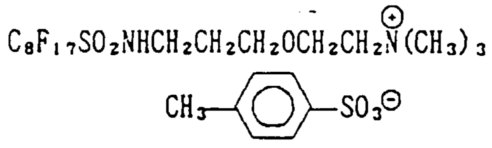
x/y=70/30

B − 6

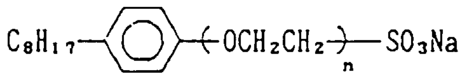


(mol. wt. about 10,000)

W－1

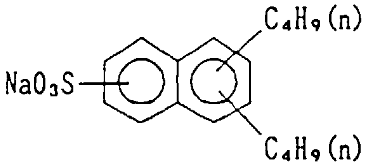


W－2

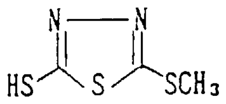


n =2 ～ 4

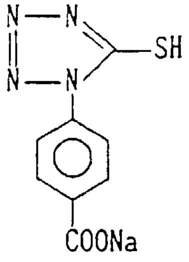
W－3



F－1



F－2



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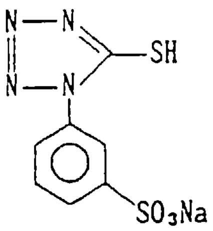

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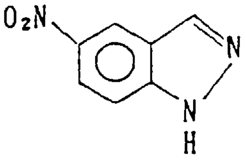
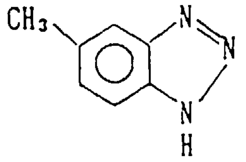


F－5



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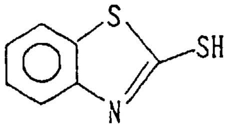
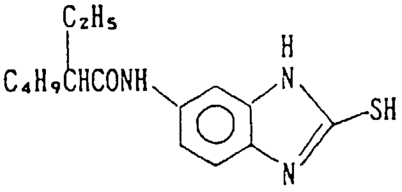
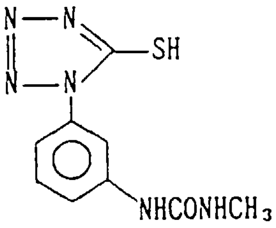


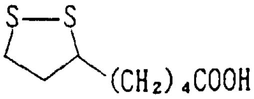
F－7



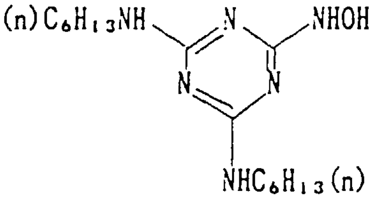
F－8



F－9



F－10



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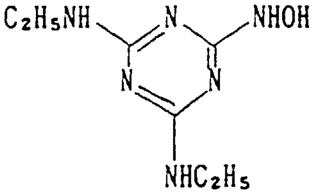

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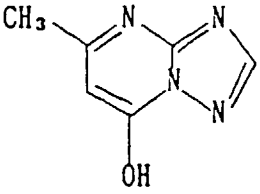

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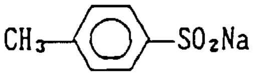

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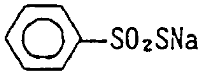
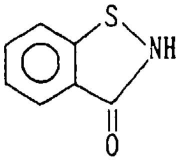
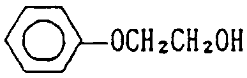


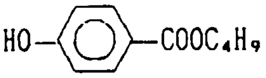
F-15



F-16



F-17



[0157] The multi-layer color light-sensitive material 101 prepared was cut to a 35 mm width and subjected to wedge exposing to a white light (a color temperature of a light source: 4800°K and an exposure: 5CMS). Then, it was processed in the processing processes shown below with a cine type automatic developing machine. Provided that the samples to be evaluated for the performances thereof were processed after the imagewise exposed samples were processed until an accumulated replenishing amount of a color developing solution reached a three times as much amount as a tank capacity of the base solution thereof.

[0158] As for an aeration condition for a bleaching solution in this case, the processing was carried out while bubbles were discharged at 200 ml/minute from the pores of 0.2 mm ϕ provided at a bottom of a bleaching solution tank.

Process	Processing time	Processing temperature	Replenishing amount*	Tank capacity
Color developing	3 minutes & 15 seconds	37.8°C	20 ml	10 l
Bleaching	3 minutes	38.0°C	5 ml	10 l
Rinsing	30 seconds	27.0°C	15 ml	5 l
Fixing	2 minutes & 40 seconds	38.0°C	15 ml	10 l
Rinsing (1)	1 minute	25.0°C	-	5 l
Rinsing (2)	1 minute	25.0°C	30 ml	5 l
Stabilizing	45 seconds	36.0°C	20 ml	5 l
Drying	1 minute	55.0°C		

*The replenishing amount is per meter of 35 mm width.

[0159] The rinsing is of a counter current system from (2) to (1).

[0160] An amount of the color developing solution carried over to the bleaching process and an amount of the fixing solution to the rinsing process were 2.5 ml and 2.0 ml per meter of the light-sensitive material having a 35 mm width, respectively.

[0161] A time for a crossover is 5 seconds at any process and this time is included in a processing time of a preceding process.

[0162] The compositions of the processing solutions are shown below:

Color developing solution	Mother solution	Replenishing solution
Diethylenetriaminepentacetic acid	1.0 g	1.1 g
1-Hydroxyethylidene-1,1-diphosphonic acid	3.0 g	3.2 g
Sodium sulfite	4.0 g	4.9 g
Potassium carbonate	30.0 g	30.0 g
Potassium bromide	1.4 g	0.4 g

(continued)

Color developing solution	Mother solution	Replenishing solution
Potassium iodide	1.5 mg	-
Hydroxylamine sulfate	2.4 g	3.6 g
4-(N-ethyl-N-β-hydroxyethylamino) 2-methylaniline sulfate	4.5 g	6.4 g
Water was added to	1000 ml	1000 ml
pH	10.05	10.15

Bleaching solution	Mother solution	Replenishing solution
Ferric nitrate nonahydrate	0.15 mol	0.23 mol
Chelate compound (shown in Table 4)	0.16 mol	0.24 mol
Sodium bromide	0.3 mol	0.45 mol
Sodium nitrate	0.2 mol	0.30 mol
Acetic acid	0.50 mol	0.75 mol
Water was added to	1000 ml	1000 ml
pH	4.5	4.0

wherein the chelate compound is reacted with ferric nitrate in the solution to form an organic acid ferric sodium salt which becomes a bleaching agent.

Fixing solution (common to both of the base solution and the replenishing solution)	
1,3-Diaminopropanetetraacetic acid	1.7 g
Ammonium sulfite	14.0 g
Ammonium thiosulfate aqueous solution (700 g/liter)	260.0 ml
Water was added to	1000 ml
pH	7.0

<u>Rinsing water between bleaching and fixing and rinsing water after fixing</u> (common to both of the base solution and replenishing solution)

[0163] City water was introduced into a mixed bed type column filled with an H type strong acidic cation exchange resin (Amberlite IR-120B) and an OH type strong base anion exchange resin (Amberlite IRA-400) each manufactured by Rohm & Haas Co., Ltd. to reduce the ion concentrations of calcium and magnesium to 3 mg/liter or less, respectively, and subsequently sodium dichloroisocyanurate 20 mg/liter and sodium sulfate 150 mg/liter were added. The pH of this solution resided in the range of 6.5 to 7.5.

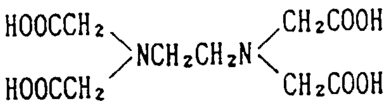
Stabilizing solution (common to both of the mother solution and replenishing solution)	
Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10)	0.2 g
Disodium ethylenediaminetetraacetate	0.05 g
1,2-Benzoisothiazoline-3-one	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazole-1-ylmethyl)piperazine	0.75 g
Water was added to	1000 ml
pH	8.5

[0164] The multi-layer color light-sensitive material 101 which was subjected to the above processings was measured for a residual silver amount at a maximum color developing part by an X-ray fluorescence analysis.

Table 4

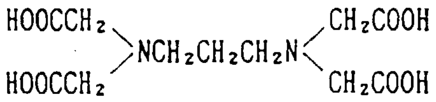
Sample No.	Chelate compound	Residual silver amount (µg/cm^2)
101 (Comp.)	Comparative compound A	45.0
102 (Comp.)	Comparative compound B	7.6
103 (Comp.)	Comparative compound C	12.3
104 (Comp.)	Comparative compound D	9.0
105 (Comp.)	Comparative compound E	11.0
106 (Inv.)	Exemplified compound 1	4.2
107 (Inv.)	Exemplified compound 2	4.0
108 (Inv.)	Exemplified compound 3	3.9
109 (Inv.)	Exemplified compound 4	4.2
110 (Inv.)	Exemplified compound 20	4.5

Comparative Compound A



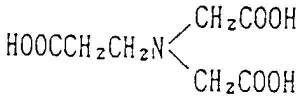
$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$$

Comparative Compound B



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

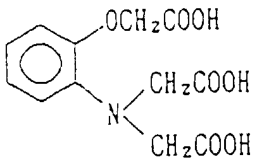
Comparative Compound C



$$HOOCCH_2CH_2N(CH_2COOH)_2$$

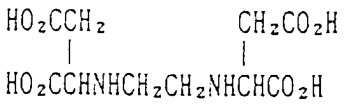
(the compound described in European Patent Publication No. 430000A1)

Comparative Compound D



(the compound described in German Patent Publication No. 39125511)

Comparative Compound E



$$\overset{HO_2CCH_2}{\overset{|}{HO_2CCH}}NHCH_2CH_2NH\overset{CH_2CO_2H}{\overset{|}{CH}}CO_2H$$

(the compound described in JP-A-5-72695)

[0165] It can be found from the results shown in Table 4 that the chelate compounds used in the present invention can reduce the residual silver amount as compared with the comparative chelate compounds.

EXAMPLE 2

[0166] Sample 103 described in JP-A-4-145433 was processed in the following manner.

Processing process	Temperature	Time
Color developing	38°C	45 seconds
Blixing	35°C	25 seconds
Rinsing (1)	35°C	20 seconds
Rinsing (2)	35°C	20 seconds
Rinsing (3)	35°C	20 seconds
Drying	80°C	60 seconds

Color developing solution:	
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
Fluorescent whitening agent (WHITEX 4B manufactured by Sumitomo Chem. Ind. Co., Ltd.)	1.0 g
Diethylhydroxylamine	4.2 g
N-ethyl-N-(β-methanesulfonamidethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Water was added to	1000 ml
pH (25°C)	10.05

Blixing solution:	
Water	400 ml
Ammonium thiosulfate (700 g/liter)	100 ml
Sodium sulfite	17.0 g
Iron chloride	0.11 mole
Chelate compound (shown in Table 5)	0.13 mole
Ammonium bromide	40 g
Water was added to	1000 ml
pH (25°C)	6.8

wherein the chelate compound is reacted with iron chloride in the solution to form an organic acid ferric ammonium salt which becomes a bleaching agent.

Rinsing solution:

Ion-exchanged water (contents of calcium and magnesium: each 3 ppm or lower)

[0167] Further, the samples which were evenly exposed so that a gray color density became 1.5 were processed in the same manner using a solution obtained by allowing the above blixing solution to be left for standing at 35°C for 2 weeks. The silver amounts remaining at the maximum density parts of these samples were determined by a fluorescence X-ray method. The results are shown in Table 5.

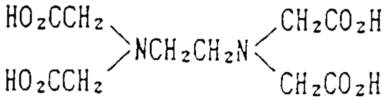
Table 5

	Residual silver mount (μg/cm^2)		
Sample No.	Chelate compound	Fresh solution	2 weeks aging solution
201 (Comp.)	A*	15.0	21.0
202 (Comp.)	F*	3.9	19.0
203 (Comp.)	G*	3.8	17.9
204 (Inv.)	1**	3.0	4.2
205 (Inv.)	3**	3.4	4.9
206 (Inv.)	7**	3.6	4.7
207 (Inv.)	20**	3.8	4.8

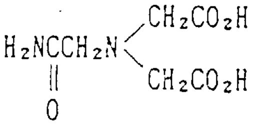
* Comparative compound

** Exemplified compound

Comparative Compound A

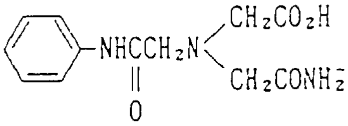


Comparative Compound F



(the compound described in JP-A-1-93740)

Comparative Compound G



(the compound described in JP-A-4-73647)

[0168] It was found from the above results that in the case where the chelate compounds used in the present invention were used, the residual silver amounts were decreased as compared with the chelate compound of Comparative Compound A and that particularly even after leaving for standing, the effects thereof were revealed.

EXAMPLE 3

[0169] In Example 1, 0.15 mole of malonic acid was added to the bleaching solution, whereby magenta stain after aging was improved as compared with a case where malonic acid was not added.

EXAMPLE 4

[0170] There are shown in Table 6, the results obtained by carrying out a biodegradability test based on the 302B revised Zahn-Wellens method prescribed in the OECD chemicals test guide line.

Table 6

Sample No.	Compound	Decomposition rate (%)
301 (Comp.)	Ethylenediaminetetraacetic acid	≒0
302 (Comp.)	1,3-Propanediaminetetraacetic acid	≒0
303 (Inv.)	Exemplified Compound 1	70 % or more
304 (Inv.)	Exemplified Compound 5	70 % or more
305 (Inv.)	Exemplified Compound 7	90 % or more

[0171] It was confirmed from the above results that the compounds represented by formula (I) forming the metal chelate compounds used in the present invention were excellent in terms of the biodegradability.

EXAMPLE 6

[0172] Sample 101 was cut to a 35 mm width and subjected to photographing with a camera. Then, it was subjected to the following processing by every 1 m^2 per day over a period of 15 days (running processing).

[0173] The respective processings were carried out with the automatic developing machine FP-560B manufactured by Fuji Photo Film Co., Ltd. in the following manner. Remodeling was made so that an overflowed solution from a bleaching bath was not flowed in the following bath and all discharged in a waste solution tank.

[0174] The processing processes and the processing solution compositions are shown below.

Processing processes

Process	Processing time	Processing temperature	Replenishing amount*	Tank capacity
Color developing	3 minute & 5 seconds	37.6°C	15 ml	17 l
Bleaching	50 seconds	38.0°C	5 ml	5 l
Fixing (1)	50 seconds	38.0°C	-	5 l
Fixing (2)	50 seconds	38.0°C	8 ml	5 l
Rinsing	30 seconds	38. 0°C	17 ml	3.5 l
Stabilizing(1)	20 seconds	38.0°C	-	3 l
Stabilizing(2)	20 seconds	38.0°C	15 ml	3 l
Drying	1 minute & 30 seconds	60°C		

*Replenishing amount is per 1.1 meter of the light-sensitive material with a 35 mm width (corresponding to 24 Ex. one roll).

[0175] A stabilizing solution and a fixing solution are of a countercurrent system from (2) to (1), and all of the overflowed solution from the rinsing bath was introduced into the fixing bath (2). The amounts of the developing solution carried over to the bleaching process, the bleaching solution carried over to the bleach-fixing process, the bleach-fixing solution carried over to the fixing process, and the fixing solution carried over to the rinsing process were 2.5 ml, 2.0 ml, 2.0 ml, and 2.0 ml per 1.1 meter of the light-sensitive material with a 35 mm width, respectively. A crossover time is 6 seconds at either processes, and this time is included in a processing time of the preceding process.

[0176] The aperture areas in the processing machine described above were 120 cm^2 in the color developing solution, 120 cm^2 in the bleaching solution, and 100 cm^2 in the other processing solutions.

[0177] The compositions of the processing solutions are shown below:

Color developing solution	Tank solution	Replenishing solution
Diethylenetriaminepentaacetic acid	2.2 g	2.2 g
Di-sodium catechol-3,5-disulfonate	0.3 g	0.3 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g	2.0 g
Sodium sulfite	3.9 g	5.5 g
Potassium carbonate	37.5 g	39.0 g
Disodium N,N-bis(2-sulfoethyl)-hydroxylamine	2.0 g	2.0 g
Potassium bromide	1.4 g	-
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.4 g	3.6 g
2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline sulfate	4.5 g	6.8 g
Water was added to	1.0 l	1.0 l
pH	10.05	10.21
(adjusted with potassium hydroxide and sulfuric acid)		

Bleaching solution	Tank solution	Replenishing solution
Chelate compound used in the present invention, Exemplified Compound 1	0.26 mol	0.39 mol
Ferric nitrate nonahydrate	0.24 mol	0.36 mol
Ammonium bromide	70 g	105 g
Glutaric acid	93 g	140 g
Water was added to	1.0 l	1.0 l
pH	4.6	4.2
(adjusted with aqueous ammonia)		

Fixing (1) tank solution

[0178] A mixed solution of the above bleaching tank solution and the following fixing tank solution in 7 to 93 (volume ratio) (pH: 7.0).

Fixing solution	Tank solution	Replenishing solution
Ammonium sulfite	19 g	57 g
Ammonium thiosulfate aqueous solution (700 g/liter)	280 ml	840 ml
Imidazole	15 g	45 g
Ammonium methanethiosulfonate	40 g	120 g
Ethylenediaminetetraacetic acid	15 g	45 g
Water was added to	1.0 l	1.0 l
pH	7.4	7.45
(adjusted with aqueous ammonia and acetic acid)		

Rinsing water

[0179] The same as that in Example 1.

Stabilizing solution

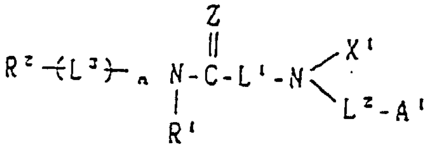
[0180] The same as that in Example 1.

[0181] After the running processing described above, the residual silver amount at the maximum density part was measured in the same manner as that in Example 1 to find that it was 4.0 mg/cm^2 and a desilvering performance was good.

[0182] The metal chelate compound used in the present invention in the embodiment of the present invention is a compound having a biodegradability and contributes to an environmental protection. The processing composition used in the present invention using it enables a rapid processing providing an excellent desilvering performance and has less fluctuation in a processing performance before and after running.

Claims

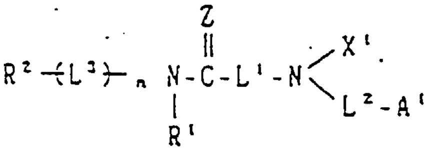
1. Use of at least one compound selected from Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III), and Ce (IV) chelate compounds of a compound represented by formula (I) or a salt thereof:



$$R^2\text{-}\!\left(L^3\right)_n N(R^1)\text{-}\overset{\overset{\displaystyle Z}{\|}}{C}\text{-}L^1\text{-}N\!\left\langle\begin{array}{l}X^1\\ L^2\text{-}A^1\end{array}\right. \qquad (I)$$

wherein R^1 represents a hydrogen atom, an aliphatic group or an aromatic group; R^2 represents an aromatic group; L^3 represents a divalent aliphatic group; n represents 0 or 1; X^1 represents a hydrogen atom or $-L^4-A^2$; L^1, L^2 and L^4 each represents a divalent aliphatic group, a divalent aromatic group, or a divalent linkage group consisting of a combination thereof; A^1 and A^2 each represent a carboxy group; and Z represents an oxygen atom or a sulfur atom, for processing a silver halide photographic material.

2. A method for processing a silver halide photographic material which comprises processing an imagewise exposed silver halide photographic material with a processing solution comprising 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) or a salt thereof:



$$R^2\text{-}\!\left(L^3\right)_n N(R^1)\text{-}\overset{\overset{\displaystyle Z}{\|}}{C}\text{-}L^1\text{-}N\!\left\langle\begin{array}{l}X^1\\ L^2\text{-}A^1\end{array}\right. \qquad (I)$$

wherein R^1 represents a hydrogen atom, an aliphatic group or an aromatic group; R^2 represents an aromatic group; L^3 represents a divalent aliphatic group; n represents 0 or 1; X^1 represents a hydrogen atom or $-L^4-A^2$; L^1, L^2 and L^4 each represents a divalent aliphatic group, a divalent aromatic group, or a divalent linkage group consisting of a combination thereof; A^1 and A^2 each represent a carboxy group; and Z represents an oxygen atom or a sulfur atom.

3. The method for processing a silver halide photographic material as claimed in claim 2, wherein R^1 is a hydrogen atom.

4. The method for processing a silver halide photographic material as claimed in claim 2, wherein n is 0.

5. The method for processing a silver halide photographic material as claimed in claim 2, wherein L^1, L^2 and L^4 each represents an alkylene having 1 to 6 carbon atoms or a 1,2-phenylene groups.

6. The method for processing a silver halide photographic material as claimed in claim 2, wherein L^1, L^2 and L^4 each represents a methylene group.

7. The method for processing a silver halide photographic material as claimed in claim 2, wherein X^1 is $-L^4-A^2$.

8. The method for processing a silver halide photographic material as claimed in claim 2, wherein Z is an oxygen atom.

9. The method for processing a silver halide photographic material as claimed in claim 2, wherein a metal salt constituting said chelate compound is a Fe(III) salt.

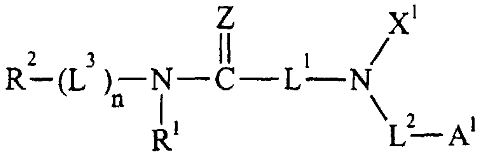
10. The method for processing a silver halide photographic material as claimed in claim 2, wherein said chelate compound is used in an amount of 0.005 to 1 mole per litre of said processing solution.

11. The use according to claim 1, wherein a composition containing the chelate compound has a bleaching ability for a silver halide color photographic material.

12. A method according to claim 2, wherein the photographic material is a color photographic material and the processing solution has a bleaching ability and contains the at least one chelate compound as a bleaching agent.

Patentansprüche

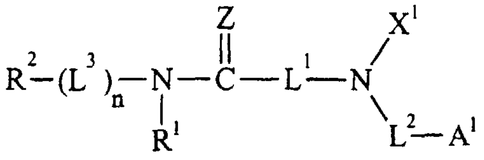
1. Verwendung mindestens einer Verbindung, ausgewählt aus Fe(III)-, Mn(III)-, Co(III)-, Rh(II)-, Rh(III)-, Au(II)-, Au (III)- und Ce(IV)-Chelatverbindungen einer durch die Formel (I) wiedergegebenen Verbindung oder eines Salzes davon:



$$R^2\text{—}(L^3)_n\text{—}\underset{\displaystyle R^1}{\underset{|}{N}}\text{—}\overset{\displaystyle Z}{\overset{\|}{C}}\text{—}L^1\text{—}N\begin{matrix}\diagup X^1\\ \diagdown L^2\text{—}A^1\end{matrix}\qquad (I)$$

worin R^1 ein Wasserstoffatom, eine aliphatische Gruppe oder eine aromatische Gruppe bedeutet; R^2 eine aromatische Gruppe bedeutet; L^3 eine divalente aliphatische Gruppe bedeutet; n 0 oder 1 bedeutet; X^1 ein Wasserstoffatom oder $-L^4-A^2$ bedeutet; L^1, L^2 und L^4 jeweils eine divalente aliphatische Gruppe, eine divalente aromatische Gruppe oder eine divalente Bindungsgruppe bestehend aus einer Kombination davon bedeuten; A^1 und A^2 jeweils eine Carboxygruppe bedeuten; und Z ein Sauerstoffatom oder ein Schwefelatom bedeutet, zum Verarbeiten eines photographischen Silberhalogenidmaterials.

2. Verfahren zum Verarbeiten eines photographischen Silberhalogenidmaterials, umfassend das Verarbeiten des bildweise belichteten photograpischen Silberhalogenidmaterials mit einer Verarbeitungslösung, enthaltend mindestens eine von Fe(III)-, Mn(III)-, Co(III)-, Rh(II)-, Rh(III)-, Au(II)-, Au(III)- und Ce(IV)-Chelatverbindungen einer durch die Formel (I) wiedergegebenen Verbindung oder eines Salzes davon:



$$R^2\text{—}(L^3)_n\text{—}\underset{\displaystyle R^1}{\underset{|}{N}}\text{—}\overset{\displaystyle Z}{\overset{\|}{C}}\text{—}L^1\text{—}N\begin{matrix}\diagup X^1\\ \diagdown L^2\text{—}A^1\end{matrix}\qquad (I)$$

worin R^1 ein Wasserstoffatom, eine aliphatische Gruppe oder eine aromatische Gruppe bedeutet; R^2 eine aromatische Gruppe bedeutet; L^3 eine divalente aliphatische Gruppe bedeutet; n 0 oder 1 bedeutet; X^1 ein Wasserstoffatom oder $-L^4-A^2$ bedeutet; L^1, L^2 und L^4 jeweils eine divalente aliphatische Gruppe, eine divalente aromatische Gruppe oder eine divalente Bindungsgruppe bestehend aus einer Kombination davon bedeuten; A^1 und A^2 jeweils eine Carboxygruppe bedeuten; und Z ein Sauerstoffatom oder ein Schwefelatom bedeutet.

3. Verfahren zum Verarbeiten eines photographischen Silbemalogenidmaterials wie in Anspruch 2 beansprucht, worin R^1 ein Wasserstoffatom ist.

4. Verfahren zum Verarbeiten eines photographischen Silberhalogenidmaterials wie in Anspruch 2 beansprucht, worin n 0 ist.

5. Verfahren zum Verarbeiten eines photographischen Silbemalogenidmaterials wie in Anspruch 2 beansprucht, worin L^1, L^2 und L^4 jeweils eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen oder eine 1,2-Phenylengruppe bedeutet.

6. Verfahren zum Verarbeiten eines photographischen Silbemalogenidmaterials wie in Anspruch 2 beansprucht, worin L^1, L^2 und L^4 jeweils eine Methylengruppe bedeuten.

7. Verfahren zum Verarbeiten eines photographischen Silbemalogenidmaterials wie in Anspruch 2 beansprucht, worin X^1 -L^4-A^2 ist.

8. Verfahren zum Verarbeiten eines photographischen Silberhalogenidmaterials wie in Anspruch 2 beansprucht, worin Z ein Sauerstoffatom ist.

9. Verfahren zum Verarbeiten eines photographischen Silberhalogenidmaterials wie in Anspruch 2 beansprucht, worin ein die Chelatverbindung aufbauendes Metallsalz ein Fe(III)-Salz ist.

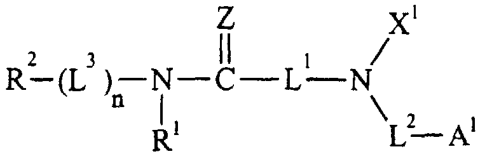
10. Verfahren zum Verarbeiten eines photographischen Silbemalogenidmaterials wie in Anspruch 2 beansprucht, worin die Chelatverbindung in einer Menge von 0,005 bis 1 mol pro Liter der Verarbeitungslösung verwendet wird.

11. Verwendung nach Anspruch 1, worin eine die Chelatverbindung enthaltende Zusammensetzung eine Bleichfähigkeit für ein farbphotographisches Silberhalogenidmaterial hat.

12. Verfahren nach Anspruch 2, worin das photographische Material ein farbphotographisches Material ist und die Verarbeitungslösung eine Bleichfähigkeit hat und mindestens eine Chelatverbindung als Bleichmittel enthält.

Revendications

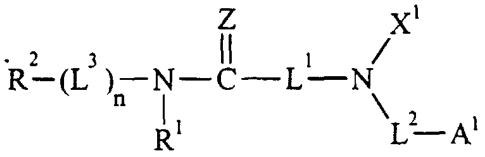
1. Utilisation d'au moins un composé choisi parmi les dérivés chélates de Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) et Ce (IV) d'un composé représenté par la formule (I) ou un de ses sels :



$$R^2\text{—}(L^3)_n\text{—}\underset{\substack{|\\ R^1}}{N}\text{—}\overset{\substack{Z\\ \|}}{C}\text{—}L^1\text{—}N\begin{matrix}\diagup X^1\\ \diagdown L^2\text{—}A^1\end{matrix} \qquad \text{(I)}$$

dans laquelle R^1 représente un atome d'hydrogène, un groupe aliphatique ou un groupe aromatique; R^2 représente un groupe aromatique; L^3 représente un groupe aliphatique divalent; n représente 0 ou 1; X^1 représente un atome d'hydrogène ou -L^4-A^2; L^1, L^2 et L^4 représentent chacun un groupe aliphatique divalent, un groupe aromatique divalent ou un groupe de liaison divalent constitué d'une combinaison de ces groupes; A^1 et A^2 représentent chacun un groupe carboxy; et Z représente un atome d'oxygène ou un atome de soufre, pour le traitement d'un matériau photographique à l'halogénure d'argent.

2. Procédé de traitement d'un matériau photographique à l'halogénure d'argent, qui comprend le traitement d'un matériau photographique à l'halogénure d'argent exposé selon l'image avec une solution de traitement comprenant au moins un des dérivés chélates de Fe (III), Mn (III), Co (III), Rh (II), Rh (III), Au (II), Au (III) et Ce (IV) d'un composé représenté par la formule (I) ou un de ses sels :



$$R^2\text{—}(L^3)_n\text{—}\underset{\substack{|\\ R^1}}{N}\text{—}\overset{\substack{Z\\ \|}}{C}\text{—}L^1\text{—}N\begin{matrix}\diagup X^1\\ \diagdown L^2\text{—}A^1\end{matrix} \qquad \text{(I)}$$

dans laquelle R^1 représente un atome d'hydrogène, un groupe aliphatique ou un groupe aromatique; R^2 représente un groupe aromatique; L^3 représente un groupe aliphatique divalent; n représente 0 ou 1; X' représente un atome d'hydrogène ou $-L^4-A^2$; L^1, L^2 et L^4 représentent chacun un groupe aliphatique divalent, un groupe aromatique divalent ou un groupe de liaison divalent constitué d'une combinaison de ces groupes; A^1 et A^2 représentent chacun un groupe carboxy; et Z représente un atome d'oxygène ou un atome de soufre.

3. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel R^1 est un atome d'hydrogène.

4. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel n est égal à 0.

5. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel L^1, L^2 et L^4 représentent chacun un groupe alkylène ayant de 1 à 6 atomes de carbone ou un groupe 1,2-phénylène.

6. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel L^1, L^2 et L^4 représentent chacun un groupe méthylène.

7. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel X^1 représente $-L^4-A^2$.

8. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel Z est un atome d'oxygène.

9. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel le sel métallique constituant ledit dérivé chélate est un sel de Fe(III).

10. Procédé de traitement d'un matériau photographique à l'halogénure d'argent tel que revendiqué dans la revendication 2, dans lequel ledit dérivé chélate est utilisé en une quantité comprise entre 0,005 et 1 mole par litre de ladite solution de traitement.

11. Utilisation selon la revendication 1, dans laquelle la composition contenant le dérivé chélate possède un pouvoir de blanchiment d'un matériau photographique couleur à l'halogénure d'argent.

12. Procédé selon la revendication 2, dans lequel le matériau photographique est un matériau photographique couleur et la solution de traitement possède un pouvoir de blanchiment et contient, en tant qu'agent de blanchiment, au moins un des dérivés chélates.