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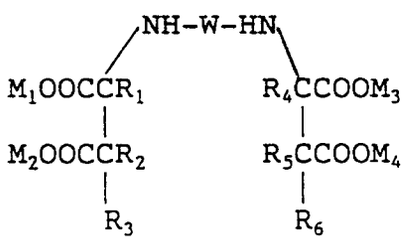
(54) Method for processing silver halide color photographic material.

(57) A method for processing a silver halide color photographic material comprises processing a silver halide color photographic material with a bleaching solution, wherein the bleaching solution contains an iron(III) complex salt of a compound represented by the following formula (I), the silver halide color photographic material has at least one silver halide emulsion layer having a silver iodide content of 1 to 30 mol%, the total coating weight of silver is 2 to 6 g per m^2 of the silver halide color photographic material, and the sum total of the dry thicknesses of hydrophilic colloid layers exclusive of back layers is 12 to 20 μm:



(I)

wherein R_1 to R_6 each represents a hydrogen atom, an aliphatic group, an aromatic group or a hydroxyl group; W represents a bonding group; and M_1 to M_4 each represents a hydrogen atom or a cation.

EP 0 595 102 A1

FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic material (hereinafter referred to simply as color photographic material).

BACKGROUND OF THE INVENTION

Generally, the basic steps for processing color photographic materials include a color development step and a desilverization step. In the color development step of the processing of a color photographic material, the exposed silver halide is reduced by a color developing agent to silver, and at the same time, the oxidized color developing agent is reacted with a color former (coupler) to form a dye image. In the desilverization step subsequent to the color development step, silver formed in the color development step is oxidized by the action of an oxidizing agent (commonly called a bleaching agent), and then dissolved by a complexing agent of silver ion (commonly called a fixing agent) to thereby remove it. Accordingly, only a dye image is formed on the color photographic material processed by these steps. The practical processing steps of a color photographic material optionally include auxiliary steps in addition to the above two basic steps of color development and desilverization to maintain the photographic and physical quality of the image or to improve the preservability of the image. Examples of such auxiliary steps include a hardening bath for preventing the light-sensitive layers from being excessively softened during processing, a stop bath for effectively stopping the development reaction, an image stabilizing bath for stabilizing the image, and a back layer removing bath for removing the backing layer of the support.

Further, the above-described desilverization step sometimes includes two steps where the bleaching bath and the fixing bath are provided separately, or sometimes includes only one step composed of a bleaching-fixing bath containing both the bleaching agent and the fixing agent in one bath to carry out rapid processing and to simplify the processing step from the standpoint of labor savings.

Conventionally, iron(III) complex salts (e.g., the iron(III) complex salts of aminopolycarboxylic acids, particularly ethylenediaminetetraacetato ferrates) are mainly used as bleaching agents in the processing of the color photographic materials.

The demand for the prevention of environmental pollution has increased in recent years. It has been demanded to provide photographic reagents capable of reducing environmental pollution in the field of color photographic materials. From this point of view, it is demanded to identify and use as conventional bleaching agents iron(III) complex salts which have a low environmental impact and do not pollute the environment. To meet this goal, it has been proposed that a compound having a better biodegradability be used in place of the ethylenediaminetetraacetic acid (hereinafter abbreviated to EDTA) conventionally used in the formation of the iron(III) complex salts. For example, EP430000A1 proposes the use of nitrilomonopropionic acid diacetic acid (hereinafter abbreviated to NMP) and nitrilotriacetic acid (hereinafter abbreviated to NTA) as chelating agents which have a good biodegradability in comparison with EDTA.

However, when the iron(III) complex salt of NMP or NTA is used as the bleaching agent, the cyan density in the unexposed area is increased in the processing of iodide-containing color photographic materials for photographing such as color negative photographic materials and reversal color photographic materials. Namely, there is caused a problem that cyan stain is formed.

Accordingly, it has been demanded to develop a method for processing a color photographic material for photographing which can prevent cyan stain from being formed and which gives an image having excellent photographic characteristics even when there is used a bleaching agent formed from a compound having a good biodegradability in comparison with EDTA.

SUMMARY OF THE INVENTION

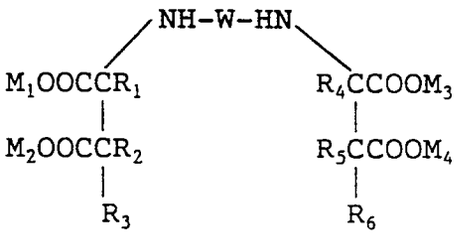
Accordingly, an object of the present invention is to provide a method for processing a color photographic material which can reduce environmental pollution.

Another object of the present invention is to provide a method for processing a color photographic material which can prevent cyan stain from being formed and which provides an image having excellent photographic characteristics.

The above-described objects of the present invention have been achieved by providing a method for processing a color photographic material as described below.

The present invention provides a method for processing a silver halide color photographic material which comprises processing a silver halide color photographic material with a bleaching solution, wherein the bleaching solution contains an iron(III) complex salt of a compound represented by formula (I), the silver

halide color photographic material has at least one silver halide emulsion layer having a silver iodide content of 1 to 30 mol%, the total coating weight of silver coated in the silver halide color photographic material is 2 to 6 g per m^2 of the silver halide color photographic material, and the sum total of the dry thicknesses of hydrophilic colloid layers exclusive of back layers is 12 to 20 μm:



(I)

wherein R_1, R_2, R_3, R_4, R_5 and R_6 each represents a hydrogen atom, an aliphatic group, an aromatic group or a hydroxyl group; W represents a bonding group represented by formula (W); and M_1, M_2, M_3 and M_4 each represents a hydrogen atom or a cation;

$$-(W_1 - Z)_n - W_2 - \qquad (W)$$

wherein W_1 represents an alkylene group or a single bond; W_2 represents an alkylene group or -CO-; Z represents a single bond, -O-, -S-, -CO- or -N(Rw)- (wherein Rw represents a hydrogen atom or an alkyl group which may be substituted) provided that there is no case where Z and W_1 are simultaneously a single bond; and n represents an integer of 1 to 3.

DETAILED DESCRIPTION OF THE INVENTION

Now, the present invention will be described in greater detail below.

Cyan stain is formed in color photographic materials when a bleaching agent having a good biodegradability is used for a bleaching solution, but cyan stain can be effectively prevented from being formed when a silver halide containing color photographic material, wherein the total coating weight of silver coated is 2 to 6 g per m^2 of the color photographic material and the sum total of the dry thicknesses of the hydrophilic colloid layers exclusive of back layers is 12 to 20 μm, is used in combination with a bleaching solution containing an iron(III) complex salt of a compound of formula (I) according to the present invention which has a good biodegradability. Thus, the chelating compounds of formula (I) which have a good biodegradability in comparison with EDTA can be put to practical use.

The total coating weight of silver is more preferably 2 to 4 g, particularly preferably 2 to 3 g per m^2 of the color photographic material. The sum total of the dry thicknesses of the hydrophilic layers exclusive of the back layers is more preferably 12 to 18 μm, particularly preferably 12 to 17 μm.

"Total coating weight" as referred to in the present invention represents the total weight of all coated silver such as a light-sensitive silver halide, a light-insensitive silver halide, a black colloidal silver and a yellow colloidal silver.

When the total coating weight of silver is less than 2 g per m^2 of the photographic material, sensitivity is insufficient and a good color photographic material can not be obtained. Further, when the sum total of the dry thicknesses of the hydrophilic colloid layers exclusive of the back layers is less than 12 μm, the coating of the hydrophilic colloid layers is impossible.

The layer thickness of the photographic material can be measured in the following manner. The photographic material is stored at 25 °C and 50% RH for 7 days after the preparation thereof. Then, the total thickness of the photographic material is measured. Subsequently, the coated layers on the support are removed, and the thickness of the support is measured. The difference in the thickness therebetween is referred to as the thickness of the entire coated layers exclusive of the support. The thickness can be measured, for example, by using a contact type layer thickness measuring device with a piezo-electric transducing element (K-402B Stand, manufactured by Anritsu Electric Co., Ltd.). The coated layers on the support can be removed by using an aqueous solution of sodium hypochlorite. Further, the total thickness on the support can be measured by taking a photograph of the cross section of the photographic material (a photograph at 3,000 × magnification or more) with a scanning type electron microscope.

The compounds of formula (I) used in the present invention will be described in greater detail below.

The aliphatic group represented by R_1, R_2, R_3, R_4, R_5 and R_6 is a straight-chain, branched or cyclic alkyl, alkenyl or alkynyl group and preferably has 1 to 10 carbon atoms. The aliphatic group is more preferably an alkyl group, still more preferably an alkyl group having 1 to 4 carbon atoms, and a methyl group and an ethyl group are particularly preferred.

The aromatic group represented by R_1, R_2, R_3, R_4, R_5 and R_6 is a monocyclic or bicyclic aryl group. Examples thereof include a phenyl group and a naphthyl group. A phenyl group is more preferred.

The aliphatic group and the aromatic group represented by R_1, R_2, R_3, R_4, R_5 and R_6 may optionally have one or more substituent groups. Examples of the substituent groups include an alkyl group (e.g., methyl, ethyl), an aralkyl group (e.g., phenylmethyl), an alkenyl group (e.g., allyl), an alkynyl group, an alkoxy group (e.g., methoxy, ethoxy), an aryl group (e.g., phenyl, p-methylphenyl), an amino group (e.g., dimethylamino), an acylamino group (e.g., acetylamino), a sulfonylamino group (e.g., methane sulfonylamino), a ureido group, a urethane group, an aryloxy group (e.g., phenyloxy), a sulfamoyl group (e.g., methylsulfamoyl), a carbamoyl group (e.g., carbamoyl, methylcarbamoyl), an alkylthio group (e.g., methylthio), an arylthio group (e.g., phenylthio), a sulfonyl group (e.g., methanesulfonyl), a sulfinyl group (e.g., methanesulfinyl), a hydroxy group, a halogen atom (e.g., chlorine atom, bromine atom, fluorine atom), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an aryloxycarbonyl group (e.g., phenyloxycarbonyl), an acyl group (e.g., acetyl, benzoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), an acyloxy group (e.g., acetoxy), a carbonamido group, a sulfonamido group, a nitro group and a hydroxamic acid group. These groups may be in the form of a dissociated form or a salt, if possible.

When the above substituent groups have a carbon chain, the number of carbon atoms is preferably 1 to 4.

Preferably, R_1, R_2, R_3, R_4, R_5 and R_6 are each a hydrogen atom or a hydroxyl group, with a hydrogen atom being more preferred.

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

$$-(W_1 - Z)_n - W_2 - \qquad (W)$$

W_1 is an alkylene group or a single bond. The alkylene group represented by W_1 is preferably a straight-chain or branched alkylene group having 1 to 8 carbon atoms (e.g., methylene, ethylene, propylene) or a cycloalkylene having 5 to 10 carbon atoms (e.g., 1,2-cyclohexylene).

W_2 is an alkylene group or -CO-. The alkylene group represented by W_2 has the same meaning as the alkylene group represented by W_1.

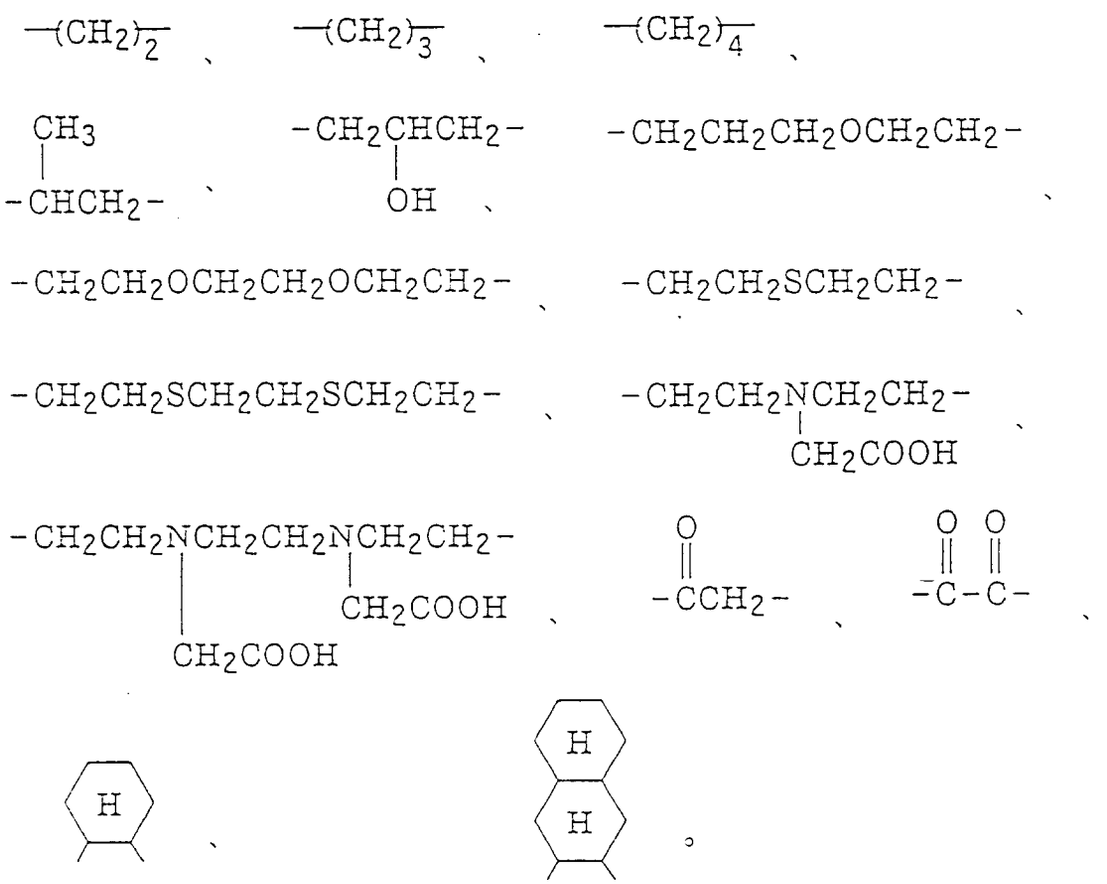
The alkylene groups represented by W_1 and W_2 may be the same or different, or may be substituted. Examples of substituent groups include those already described above in the definition of the substituent groups for R_1. Preferred examples of the substituent groups include an alkyl group, a hydroxyl group and a carboxyl group.

More preferably, W_1 and W_2 are each an alkylene group having 1 to 3 carbon atoms, and a methylene group and an ethylene group are particularly preferred.

Z is a single bond, -O-, -S-, -CO- or -N(Rw)-; Rw is a hydrogen atom or an alkyl group which may be substituted. Examples of substituent groups include those already described above in the definition of the substituent groups for R_1. Preferred examples of the substituent groups include a carboxyl group, a phosphono group, a sulfo group, a hydroxyl group and an amino group. Preferably, Z is a single bond.

Preferably, n is 1 or 2, more preferably 1.

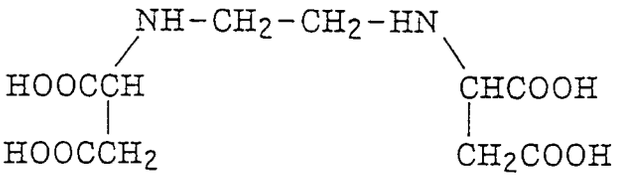
Specific examples of the bonding group represented by W include the following groups:



Examples of the cation represented by M_1, M_2, M_3 and M_4 include alkali metal (e.g., lithium, sodium, potassium) ions, ammonium (e.g., ammonium, tetraethylammonium) ions and pyridinium ions, preferably alkali metal ions, more preferably sodium ion.

Specific examples of compounds of formula (I) which can be used in the present invention include, but are not limited to, the following compounds:

I-1.



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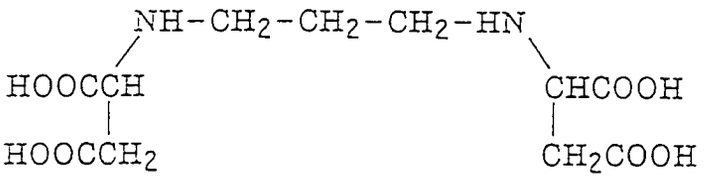

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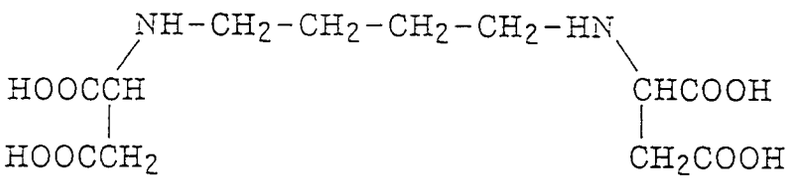

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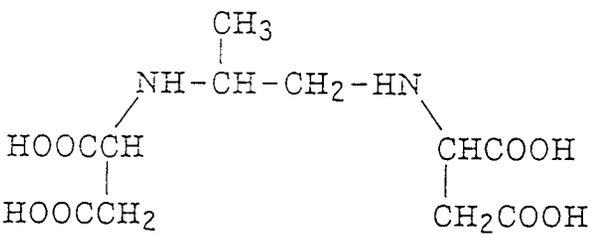
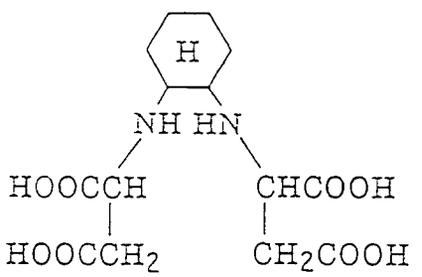
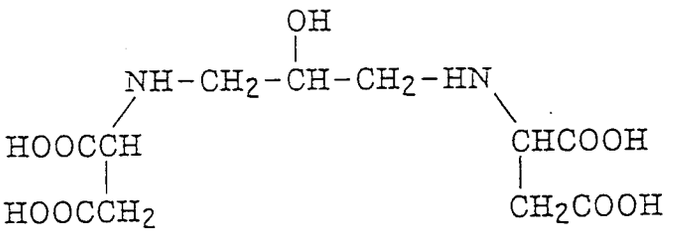


I-5.



I-6.



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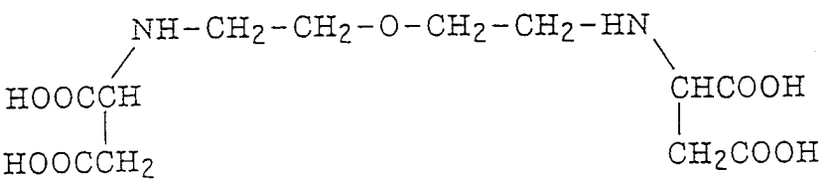

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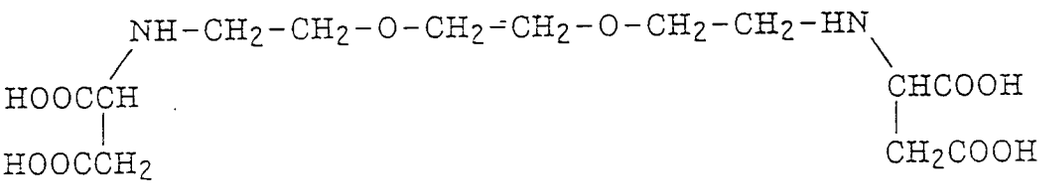

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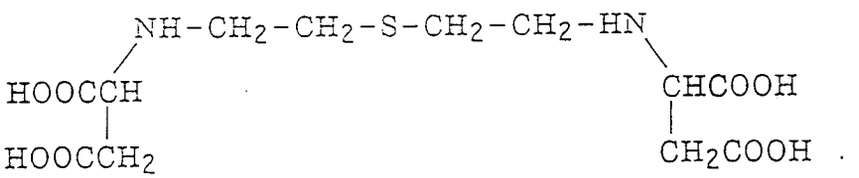

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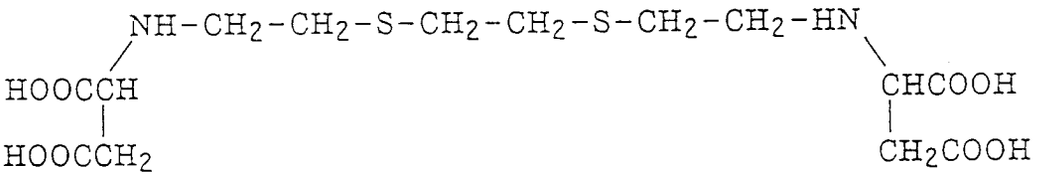
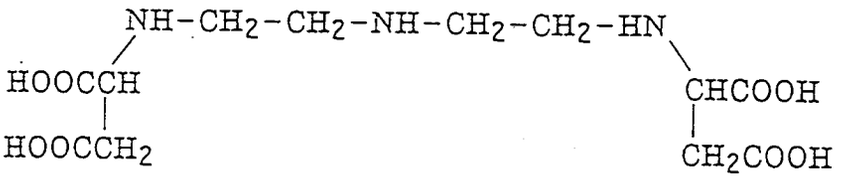


I-11.



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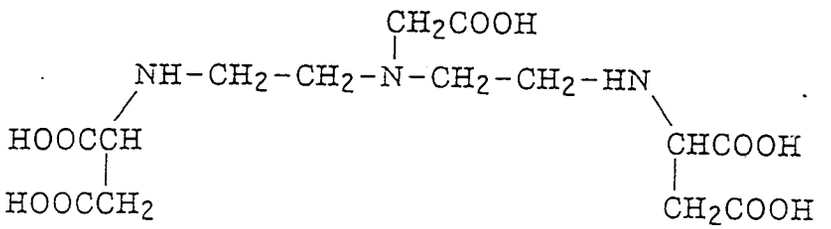

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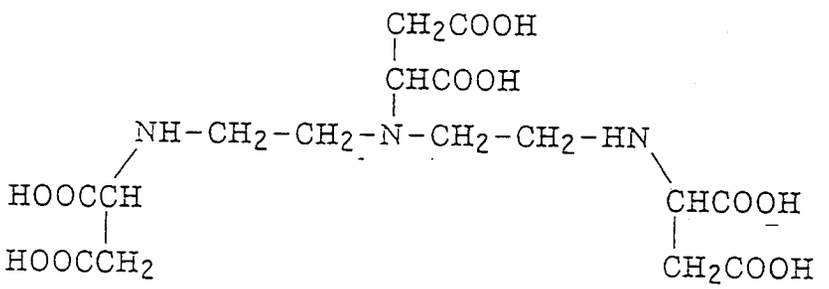

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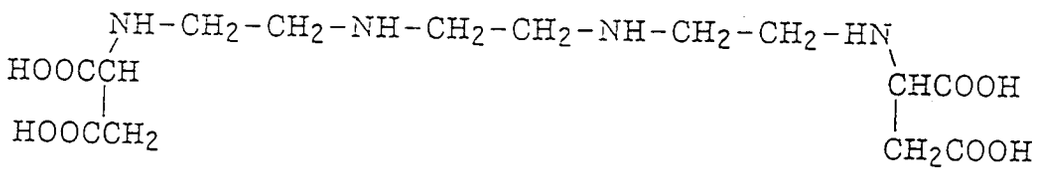

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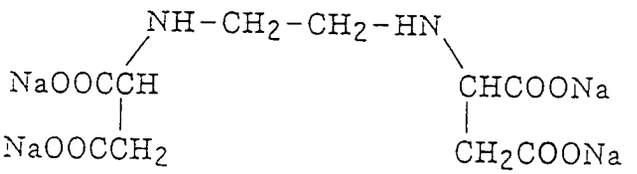

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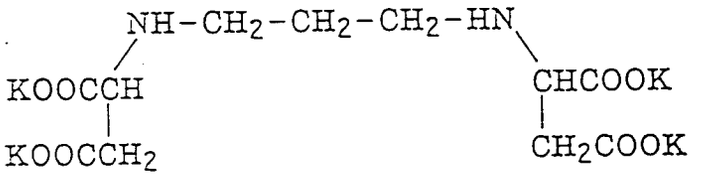

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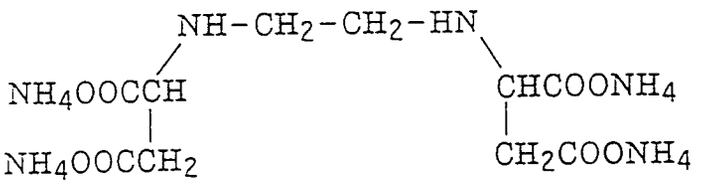

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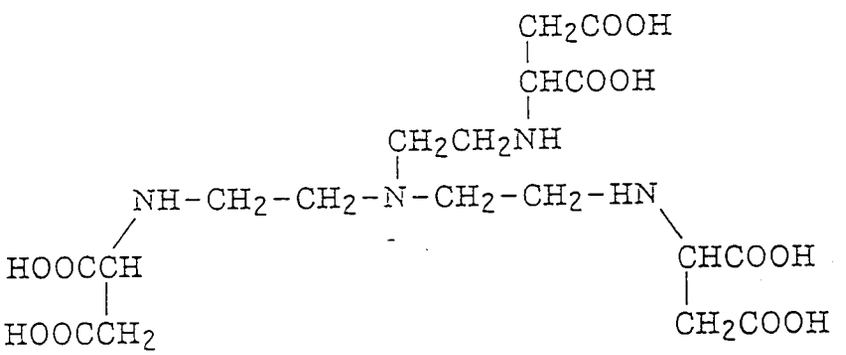

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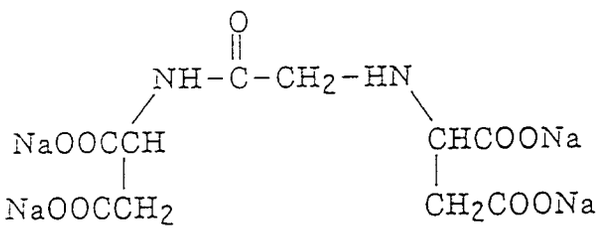

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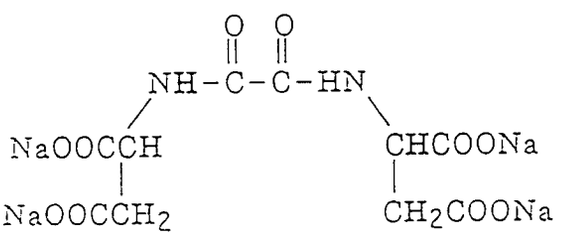

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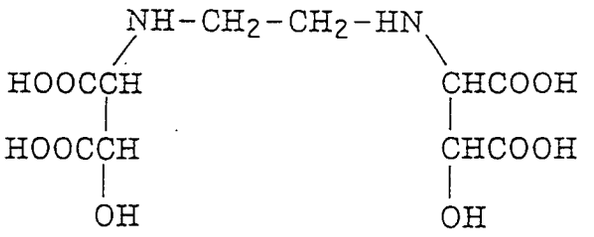

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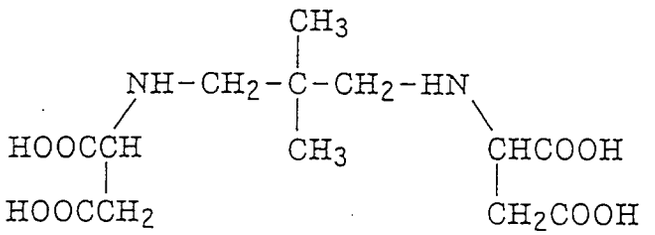

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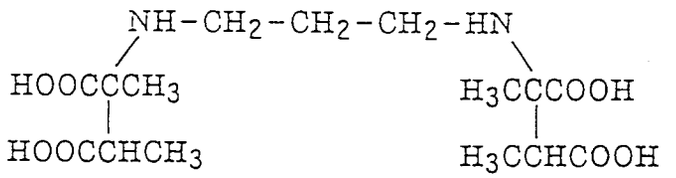

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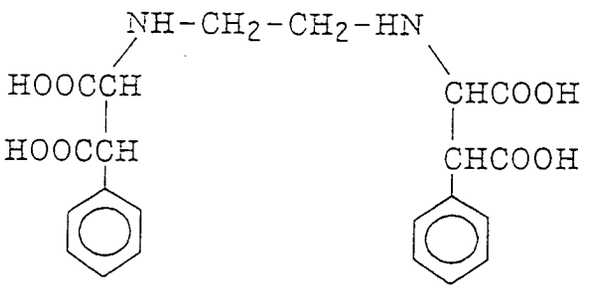
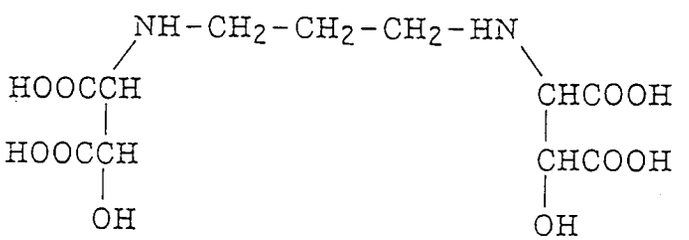


I-25.



Of these compounds, compounds I-1, I-2, I-3, I-15, I-16 and I-17 are preferred.

The compounds of formula (I) can be synthesized by referring to the methods described in JP-A-63-199295 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-3-173857. As described in these patent specifications, the compounds of formula (I) used in the present invention can exist in optically isomeric forms ([R,R], [S,S], [S,R], [R,S]). For example, the

compound (I-1) of formula (I) can exist in three optically isomeric forms ([R,R], [S,S], [S,R]). The compound can be synthesized in individual isomeric form an well as in a mixture of these isomeric forms. All such isomeric forms of the compounds and the mixtures of these isomeric forms thereof are included within the scope of the present invention.

In the present invention, the selective use of a [S,S] isomer of optical isomeric forms is preferable for prevention of cyan stain from being formed as well as from the standpoint of biodegradability.

The term "selective" used herein means that a [S,S] isomer exists in the mixture of optical isomeric forms in the range of from 70 to 100%, preferably from 90 to 100%.

These compounds can be synthesized by referring to the methods described in Springer and Kopekka, Chem. Zvesti., 20(6): 414 to 422 (1966) and JP-A-3-173857.

[S,S] isomers can be selectively synthesized by referring to the methods described in Umezawa et al., THE JOURNAL OF ANTIBIOTICS, Vol. XXXVII, No. 4, pp. 426 (Apr. 1984).

The iron(III) complex salts of the compounds of formula (I) according to the present invention can be prepared by mixing a compound of formula (I) with a ferric salt (e.g., ferric chloride, ferric nitrate or ferric acetate). The resulting iron(III) complex salt may be isolated and used. Alternatively, the complex salt can be isolated in the form of an ammonium salt, a sodium salt or a potassium salt.

The iron(III) complex salts of the compounds of formula (I) according to the present invention are used in an amount of about 0.02 to 1.0 mol, preferably about 0.04 to 0.5 mol, per liter of the bleaching solution. It is preferred that an excess (about 5 to 20 mol% excess) of the compound in the free form be present in addition to the iron(III) complex salt.

The compounds of formula (I) have a good biodegradability, and hence they are preferred from the standpoint of the preservation of the environment. For example, the compound I-1 among the compounds of formula (I) is used as a component of laundry detergent compositions (liquid detergents or powder detergents) in JP-A-63-199295. JP-A-63-199295 discloses that the compound I-1 has an effect of removing stain formed by grape juice, etc. and has a good biodegradability in comparison with EDTA.

Generally, Compound I-1 is present as a 1:1:1:1 mixture of the [R,R], [R,S], [S,R] and [S,S] isomers. However, the present invention have found out that the [S,S] isomer above which is selectively synthesized has a superior biodegradability to the mixture of the [R,R], [R,S], [S,R] and [S,S] isomers, which provides about 70% biolysis by the biodegration test in accordance with "OECD Chemical Test Guide Line" 302B Revised Zahn-Wellens Method.

The iron(III) complex salts of the compounds of formula (I) (bleaching agents) may be used together with conventional bleaching agents. Examples of conventional bleaching agents which can be used together with the iron(III) complex salts of the compounds of formula (I) include the following compounds:

K-(1) Diethylenetriaminepentaacetato Ferrate
K-(2) 1,3-Diaminopropanetetraacetato Ferrate
K-(3) 1,2-Diaminopropanetetraacetato Ferrate
K-(4) 1,2-Cyclohexanediaminetetraacetato Ferrate
K-(5) Glycol Ether Diaminetetraacetato Ferrate
K-(6) Iminodiacetato Ferrate
K-(7) N-Methyliminodiacetato Ferrate
K-(8) 1,4-Diaminobutanetetraacetato Ferrate
K-(9) 1,5-Diaminopentanetetraacetato Ferrate
K-(10) Ethylenediaminetetraacetato Ferrate
K-(11) Nitrilotriacetato Ferrate
K-(12) Hydroxyethyliminodiacetato Ferrate
K-(13) β-Alaninediacetate Ferrate
K-(14) N-(2-Carboxyphenyl)iminodiacetate Ferrate

Of these compounds, K-(2) and K-(11) are preferred.

When two or more bleaching agents are used in combination, it is preferred that the amount of the bleaching agent of the present invention account for at least 40 to 90 mol%, preferably 50 to 90 mol%, of the entire amount of the bleaching agents.

In the present invention, the total amount of the bleaching agent is in the range of 0.05 to 1 mol, preferably 0.1 mol to 0.5 mol per liter of the bleaching solution.

The bleaching agents of the present invention may be used in the form of the complex salts. Alternatively, a ferric salt such as ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate or ferric phosphate and a compound of formula (I) may be added to the bleaching solution to form the iron(III) complex salt in the solution. When the compounds are used in the form of the complex salts, the complex salts may be used either alone or in combinations of two or more thereof. When the iron(III) salt and the

compound of formula (I) are added to form the complex salt in the solution, one or more ferric salts may be used, and one or more members of the compounds of formula (I) may be used. In any case, it is preferred that an excess of the compound of formula (I) be used.

It is preferred that the iron(III) complex salts of the compounds of formula (I) are usually used in the form of an alkali metal salt (e.g., sodium salt or potassium salt) or an ammonium salt. Particularly, an ammonium salt is preferred from the standpoint of solubility.

The bleaching solution containing the above iron(III) ion complex may contain other metal ion complex salts such as cobalt or copper complex salts in addition to the iron complex salt.

These bleaching accelerators may be added to a prebath of the bleaching bath of the present invention.

Examples of the bleach accelerator for use in the present invention includes mercapto- or disulfide-containing compounds as disclosed in U.S. patent 3,893,858, West German Patent 1,290,812, JP-A-53-95630, and Research Disclosure No. 17129 (1978), thiazolidine derivatives as disclosed in JP-A-50-140129, thiourea derivatives as disclosed in U.S. Patent 3,706,561, iodides as disclosed in JP-A-58-16235, polyethylene oxides as disclosed in West German Patent 2,748,430, polyamine compounds as disclosed in JP-B-45-8836, and imidazole compounds. Particularly preferred among these bleach accelerators are mercapto- or disulfide-containing compounds from the standpoint of an accelerating effect. Particularly, compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are preferred. Further, compounds disclosed in U.S. Patent 4,552,836 are preferred. These bleach accelerators may be added to a light-sensitive material.

The bleaching solution used in the present invention may contain rehalogenating agents such as bromides (e.g., potassium bromide, sodium bromide, ammonium bromide) or chlorides (e.g., potassium chloride, sodium chloride, ammonium chloride) in addition to bleaching agents and the above compounds. The rehalogenating agents are used in an amount of 0.1 to 5 mol, preferably 0.5 to 3 mol per liter of the bleaching solution.

Further, the bleaching solution used in the present invention may contain one or more of conventional additives such as inorganic acids and organic acids having pH buffer action such as nitrates (e.g., sodium nitrate, ammonium nitrate), boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorus acid, phosphoric acid, sodium phosphate, glycolic acid, citric acid, sodium citrate and tartaric acid.

The pH value of the bleaching solution of the present invention is in the range of from 3 to 7, preferably from 3.5 to 6.5. The pH range of from 3.5 to 5.0 is most preferable from the standpoint of desilvering characteristics.

To adjust the pH value to the above range, a known acid having pH buffer action as mentioned above can be used.

To attain the objects of the present invention, acids having a pKa value of 2.0 to 5.0 is preferably used. pKa represents a logarithm value of a reciprocal of an acid dissociation constant under an ion strength of 0.1 at 25 °C.

The acid having a pKa value of 2.0 to 5.0 may be an inorganic acid (e.g., phosphoric acid) or an organic acid (e.g., acetic acid, maleic acid and citric acid). Of them, an organic acid is preferable. An organic acid having a carboxyl group is most preferred.

The organic acid having a pKa value of 2.0 to 5.0 may be a monobasic or polybasic organic acid. The metal salt (e.g., sodium salt and potassium salt) or ammonium salt of the polybasic organic acid can be used if the pKa value is in the range of from 2.0 to 5.0. The organic acid having a pKa value of 2.0 to 5.0 can be used in combinations of two or more thereof proviso these organic acids is not an aminopolycarboxylic acid or the ferrate thereof.

Preferred examples of the organic acid having a pKa value of 2.0 to 5.0 according to the present invention include aliphatic monobasic organic acids such as formic acid, acetic acid, monochloroacetic acid, monobromoacetic acid, glycolic acid, propionic acid, monochloropropionic acid, lactic acid, pyruvic acid, acrylic acid, butyric acid, isobutyric acid, pivalic acid, aminobutyric acid, valeric acid and isovaleric acid; amino acid compounds such as aspartic acid, alanine, arginine, ethionine, glycine, glutamine, cysteine, serine, methionine and leucine; aromatic monobasic organic acid such as benzoic acid, mono-substituted benzoic acid (e.g., chloro and hydroxy) and nicotinic acid; aliphatic dibasic organic acid such as oxalic acid, malonic acid, succinic acid, tartaric acid, malic acid, maleic acid, fumaric acid, oxaloacetic acid, glutaric acid, cystine and ascorbic acid; aromatic dibasic organic acid such as phthalic acid and terephthalic acid; and tribasic organic acid such as citric acid. Of them, polybasic organic acids are preferred from the standpoint of the effects of the present invention, bleaching fog, desilvering characteristics and odor. Dibasic organic dicarboxylic acids such as maleic acid, glutaric acid, malic acid, tartaric acid, glutamic acid, fumaric acid and maleic acid are more preferred.

The acid having a pKa value of 2.0 to 5.0 according to the present invention is used in an amount of 0.01 to 4 mol/ℓ, preferably 0.1 to 2 mol/ℓ, and more preferably 0.4 to 1.8 mol/ℓ of the bleaching solution.

When the bleaching solution contains an iron(III) complex salt of a compound of formula (I) and a bleaching accelerator, there is a possibility that the surface of the photographic material may be stained. However, it has been found that stain can be prevented from being formed by adjusting the pH of the bleaching solution.

The processing temperature with the bleaching solution is preferably 35 to 50 °C, more preferably 38 to 45 °C.

The replenishment rate of the bleaching solution is preferably 50 to 500 ml, more preferably 100 to 200 ml per m^2 of the photographic material.

It is preferred that the processing time in the bleaching process be as short as possible, so long as desilverization can be effected. Particularly preferably, the processing time is 30 to 80 sec.

It is preferred that stirring be vigorously conducted from the standpoint of rapid processing. Stirring with a jet stream as described in JP-A-63-183640 is preferred.

Generally, the photographic material is processed with a processing solution having an ability of fixing after the bleaching step. Examples of the processing solution having an ability of fixing include fixing solutions and bleach-fixing (hereinafter referred to as blix) solutions as described in JP-A-61-75352.

Examples of the bleaching agent used for the blix solution include bleaching agents which can be used for the above described bleaching solution.

In the present invention, the bleaching agents are used in an amount of 0.05 to 0.5 mol, preferably 0.1 to 0.4 mol per liter of the blix solution.

Further, the blix solution may contain, as the fixing agents, thiosulfates such as sodium thiosulfate, ammonium thiosulfate, sodium ammonium thiosulfate and potassium thiosulfate, thiocyanates such as sodium thiocyanate, ammonium thiocyanate and potassium thiocyanate, thiourea and thioethers. These fixing agents are used in an amount of 0.3 to 3 mol, preferably 0.5 to 2 mol per liter of the blix solution.

In addition to the bleaching agent and the fixing agent, the blix solution may contain the above-described compounds which may be contained in the bleaching solution.

Furthermore, the blix solution may contain, as preservatives, sulfites such as sodium sulfite, potassium sulfite and ammonium sulfite, hydroxylamines, hydrazines, aldehyde-bisulfite adducts such as acetaldehyde sodium bisulfite adduct, and sulfinic acid compounds such as sodium p-toluenesulfinate.

The blix solution may contain, as a chelating agent, aminopolycarboxylic acid chelating agents (e.g., ethylenediaminetetraacetic acid, 1,3-diaminopropanetetraacetic acid and diethylenetriaminepentaacetic acid) or phosphonic acid chelating agent (e.g., 1-hydroxyethylidene-1,1-diphosphonic acid, N,N,N',N'-ethylenediaminetetramethylenephosphonic acid). The amount of the chelating agent according to the present invention is 0.005 to 2 mol/ℓ, preferably 0.01 to 1 mol/ℓ.

Further, the blix solution may contain various fluorescent brighteners, antifoaming agents, surfactants, polyvinyl pyrrolidone, and organic solvents such as methanol.

The pH of the blix solution is in the range of 4.0 to 9.0, preferably 4.5 to 8.0, more preferably 5.0 to 7.5.

The preferred processing temperature range of the blix solution is the same as in the bleaching solution.

The replenishment rate of the blix solution is preferably 30 to 3,000 ml, more preferably 100 to 1,000 ml per m^2 of the photographic material.

The processing time with the blix solution is 20 sec to 10 min, preferably 30 sec to 4 min.

In the processing method of the present invention, the fixing solution can contain all of the compounds except for the bleaching agents which can be contained in the blix solution.

The pH of the fixing solution is in the range of 3.0 to 9.0, preferably 5.0 to 8.0. The preferred ranges of the concentration, the temperature, the replenishment rate and the processing time of the fixing agent contained in the fixing solution are the same as for the blix solution.

When a rinsing or stabilization step is conducted immediately after the bleaching, blix or fixing step, it is preferred that a part or all of the overflow solution from these steps be introduced into the processing solution such as the bleaching solution, the blix solution or the fixing solution.

The present invention is effective in any processing combined the bleaching bath with the blix bath or the fixing bath, etc., as a desilverization step. Examples of the desilverization step include, but are not limited to, the following combinations:

No. 1 Bleaching-Fixing
No. 2 Bleaching-Rinsing-Fixing
No. 3 Bleaching-Blix
No. 4 Bleaching-Blix-Fixing

Usually, the desilverization step is carried out after the development step. However, water-washing, rinse and development accelerating baths may be optionally provided therebetween.

Further, it is preferred that each stage be carried out by a direct flow or counter-current multi-stage processing system. Particularly, a two-stage or three-stage countercurrent system is preferred.

The color developing solutions used in the present invention contain conventional aromatic primary amine color developing agents. Preferred compounds are p-phenylene derivatives. Typical examples thereof include, but are not limited to, the following compounds:

D-1 N,N-Diethyl-p-phenylenediamine
D-2 2-Amino-5-diethylaminotoluene
D-3 2-Amino-5-(N-ethyl-N-laurylamino)toluene
D-4 4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-5 2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-6 4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline
D-7 N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamide
D-8 N,N-Dimethyl-p-phenylenediamine
D-9 4-Amino-3-methyl-n-methoxyethylaniline
D-10 4-Amino-3-methyl-N-ethyl-N-β-ethoxyethylaniline
D-11 4-Amino-3-methyl-N-ethyl-N-β-butoxyethylaniline

Further, compounds described in European Patent Laid-Open No. 419,450 and JP-A-4-11255 can be preferably used.

Of these p-phenylenediamine derivatives, compound D-5 is particularly preferred.

These p-phenylenediamine derivatives may be in the form of a salt such as a sulfate, hydrochloride, sulfite or p-toluenesulfonate. The aromatic primary amine developing agents are used in an amount of about 0.01 g to about 20 g, more preferably about 0.5 to about 10 g per liter of the developing solution.

The color developing solutions may optionally contain sulfites such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite and potassium metabisulfite and carbonyl sulfite adducts as the preservatives. However, it is preferred that the color developing solutions be substantially free from sulfite ion to improve color formability. The term "substantially free from sulfite ion" as used herein means that the amount of sulfite ion is 0.5 g or less, preferably 0.2 g or less (in terms of sodium sulfite) per liter of the color developing solution. More preferably, the color developing solution is completely free from sulfite ion.

Examples of compounds which can directly preserve the color developing agents include various hydroxylamines; hydroxamic acids as described in JP-A-63-43138; hydrazines and hydrazides as described in JP-A-63-146041; phenols as described in JP-A-63-44657 and JP-A-63-58443; α-hydroxyketones and α-aminoketones as described in JP-A-63-44656; and various saccharides as described in JP-A-63-36244. It is preferred that in combination with the above-described compounds, there are used monoamines as described in JP-A-63-4235, JP-A-63-24254, JP-A-63-21647, JP-A-63-146040, JP-A-63-27841 and JP-A-63-25654; diamines as described in JP-A-63-30845, JP-A-63-146040 and JP-A-63-43139; polyamines as described in JP-A-63-21647, JP-A-63-26655 and JP-A-63-44655; nitroxy radicals as described in JP-A-63-53551; alcohols as described in JP-A-63-43140 and JP-A-63-53549; oximes as described in JP-A-63-56654; and tertiary amines as described in JP-A-63-239447.

Examples of other preservatives which can be used include various metals as described in JP-A-57-44148 and JP-A-57-53749; salicylic acids as described in JP-A-59-180558; alkanolamines as described in JP-A-54-3532; polyethyleneimines as described in JP-A-56-94349; and aromatic polyhydroxy compounds as described in U.S. Patent 3,746,544. Particularly, the addition of the aromatic polyhydroxy compounds is preferred.

The color developing solutions used in the present invention have a pH of preferably 9 to 12, more preferably 9 to 11.0. The color developing solutions may contain conventional additives for the developing solutions.

It is preferred that buffering agents be used to maintain the pH.

Specific examples of buffering agents include, but are not limited to, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium tertiary phosphate, potassium tertiary phosphate, disodium hydrogen phosphate, dipotassium hydrogenphosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate) and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate).

The buffering agents are used in an amount of preferably at least 0.1 mol, particularly preferably 0.1 to 0.4 mol per liter of the color developing solution.

Further, the color developing solutions may contain various chelating agents as suspending agents for calcium and magnesium or to improve the stability of the color developing solutions.

Preferred chelating agents are organic compounds such as aminopolycarboxylic acids, organic phosphoric acids and phosphonocarboxylic acids. Specific examples thereof include, but are not limited to, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, trans-cyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, hydroxyethyliminodiacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine-o-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid.

These chelating agents may be used in combinations of two or more thereof.

These chelating agents may be used in an amount sufficient to sequester metal ions, and are used in an amount of, for example, about 0.1 to 10 g per liter of the color developing solution.

The color developing solutions may optionally contain development accelerators. However, it is preferred that the color developing solutions be substantially free from benzyl alcohol, which is known as a development accelerator, from the standpoint of environmental pollution, the preparation of the solutions and the prevention of color contamination. The term "substantially free from benzyl alcohol" as used herein means that the developing solutions contain 2 ml or less of benzyl alcohol per liter, and preferably are completely free from benzyl alcohol.

Examples of development accelerators include thioether compounds as described in JP-B-37-16088 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-37-5987, JP-B-38-7826, JP-B-44-12380, JP-B-45-9019 and U.S. Patent 3,813,247; p-phenylenediamine compounds as described in JP-A-52-49829 and JP-A-50-15554; quaternary ammonium salts as described in JP-A-50-137726, JP-B-44-30074, JP-A-56-156826 and JP-A-52-43429; amine compounds as described in U.S. Patents 2,494,903, 3,128,182, 4,230,796 and 3,253,919, JP-B-41-11431, and U.S. Patents 2,482,546, 2,596,926 and 3,582,346; polyalkylene oxides as described in JP-B-37-16088, JP-B-42-25201, U.S. Patent 3,128,183, JP-B-41-11431, JP-B-42-23883 and U.S. Patent 3,532,501; and 1-phenyl-3-pyrazolidones and imidazoles.

In the present invention, anti-fogging agents may be added. The anti-fogging agents include alkali metal halides such as sodium chloride, potassium bromide and potassium iodide and organic anti-fogging agents. Typical examples of organic anti-fogging agents include nitrogen-containing heterocyclic compounds such as benztriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenztriazole, 5-nitrobenztriazole, 5-chlorobenztriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolizine and adenine.

The color developing solutions used in the present invention may contain fluorescent brighteners. Preferred fluorescent brighteners are 4,4'-diamino-2,2'-disulfostilbene compounds. The compounds are used in an amount of 0 to 5 g, preferably 0.1 to 4 g/liter.

If desired, surfactants such as alkylsulfonic acids, arylsulfonic acids, aliphatic carboxylic acids and aromatic carboxylic acids may be added.

The processing temperature with the color developing solutions is 20 to 50 °C, preferably 30 to 45 °C. The processing time is 20 sec to 5 min, preferably 30 sec to 3 min. It is preferred that the replenishment rate of the color developing solutions be as small as possible. The replenishment rate thereof is generally 100 to 1500 ml, preferably 100 to 800 ml, still more preferably 100 to 400 ml per m^2 of the photographic material.

The development bath may be optionally composed of two or more baths, and the first bath or the final bath is replenished with the replenisher of the color developing solution to thereby shorten the development time or to reduce the replenishment rate.

The processing method of the present invention can be applied to reversal color processing. Black and white first developing solutions conventionally used in the reversal processing of color photographic materials and developing solutions conventionally used in the processing of black and white photographic materials can be used as black and white developing solutions in the above reversal color processing when the processing of the present invention is applied thereto. Further, various additives conventionally added to the black and white developing solutions can be used. Typical examples of the additives include developing agents such as 1-phenyl-3-pyrazolidone, metol and hydroquinone, preservatives such as sulfites, accelerators composed of an alkali such as sodium hydroxide, sodium carbonate or potassium carbonate, inorganic or organic inhibitors such as potassium bromide, 2-methylbenzimidazole and methylbenzthiazole, water softeners such as polyphosphates, and restrainers composed of a very small amount of an iodide or a mercapto compound.

The processing method of the present invention comprises the above-described processing steps such as the color development step, desilvering step, etc. Generally, the rinsing step and the stabilization step are conducted after the desilvering step. However, a simple processing method wherein only the stabilization step is conducted without substantially rinsing after the desilvering step can be used.

Rinsing water used in the rinsing stage may optionally contain conventional additives. Examples of such additives include water softeners such as inorganic phosphoric acid, aminopolycarboxylic acids and organic phosphoric acids, microbicides for preventing the growth of bacteria and algae, antifungal agents (e.g., isothiazolone, organochlorine microbicides, benztriazole), and surfactants for preventing unevenness in drying from occurring. Further, compounds described in L.E. West, "Water Quality Criteria", Phot. Sci. and Eng., vol. 9, No. 6, page 344 to 359 (1965) can be used.

Processing solutions which can stabilize the dye image can be used as stabilizing solutions used in the stabilizing step. Examples of the stabilizing solutions include solutions having a buffer action at a pH of 3 to 6, and solutions containing an aldehyde (e.g., formalin), a formaldehyde releasing compound as described in JP-A-4-270344, N-methylol compound as described in JP-A-5-34889 or an azolylmethylamine compound as described in European Patent Laid-Open No. 0,504,909A2. The stabilizing solutions may contain azoles such as pyrazole and 1,2,4-triazole, ammonium compounds, metal (e.g., Bi, Al) compounds, fluorescent brighteners, chelating agents (e.g., 1-hydroxyethylidene-1,1-diphosphonic acid), microbicides, antifungal agents, hardening agents and surfactants.

The rinsing stage and the stabilization stage are carried out by a multi-stage countercurrent system. The number of stages is preferably 2 to 4. The replenishment rate per unit area is 1 to 50 times, preferably 2 to 30 times, more preferably 2 to 15 times the amount bought over from the prebath.

Water used in the rinsing stage and the stabilization stage may be tap water. However, deionized water (obtained by passing water through ion exchange resins to reduce the concentration of each of Ca ion and Mg ion to 5 mg/ℓ or lower) and sterilized water (obtained by sterilizing water by halogen or an ultraviolet light germicidal lamp) are preferred.

When processing is carried out continuously by using automatic processors in the above-described processing steps of the photographic materials, there is a possibility that the processing solutions may be concentrated by evaporation. This phenomenon is particularly remarkable when the amount of the photographic materials to be processed is small, or the opening area of the processing solutions is large. It is preferred that an appropriate amount of water or a correcting solution be added to correct the concentrations of the processing solutions.

Any suitable processing system can be used in carrying out the processing method of the present invention. Specific examples thereof include batch processing (the details thereof are described in Shashin Kogyo, page 98, November 1974), drum processing (the details thereof are described in Shashin Kogyo, page 45, December 1974) and hanger processing (the details thereof are described in Shashin Kogyo, page 80, January 1975). Further, there can be used continuous processing wherein processing is carried out continuously while the replenishment of the processing solutions is made in proportion to the amount of the photographic materials processed.

Development processing is usually carried out by using automatic processors. Specific examples of automatic processors include roller automatic processors (the details thereof are described in Shashin Kogyo, page 71, February 1975), cine system automatic processors (the details thereof are described in Shashin Kogyo, page 70, March 1975 and ibid., page 40, April 1975), leader belt system automatic processors (the details thereof are described in Shashin Kogyo, page 36, May 1975), and roller convey type automatic processors (the details thereof are described in Shashin Kogyo, page 41, June 1975).

Important factors for automatically feeding the processing solutions to the photographic materials in the functions of the automatic processor are stirring for physically diffusing processing reagents and temperature control for expediting chemical reactions. The details thereof are described in Shashin Kogyo, page 82, October 1974 and ibid., page 41, July 1975.

The essential factors of the automatic processor before the introduction of the photographic materials into the processing baths are photographic material-receiving containers (e.g., magazine, cassette, patrone, packaging material, etc.), photographic material-joining means, cutting means (e.g., splicer, cutter), an exposure device, a reader for information such as DX code and a detector (e.g., broken perforation detection).

After the photographic materials leave the processing baths, an essential factor is drying. The details of drying are described in Drying Device edited by Ryozo Kiriei (published by Nikkan Kogyo Shinbun Sha) and Shashin Kogyo, page 41, July 1975.

From another point of view, important factors of the processor are the interfacial area (S) between the processing solution and air and the opening ratio (degree) ($K = S/V$) thereof to the capacity (V) of the

processing solution. These factors are described in JP-A-53-57835 and JP-A-61-153645.

In automatic processors having a small tank capacity (V), the exchange ratio of the processing solution is relatively increased, and hence the use of automatic processors having a small opening ratio (K) and a small tank capacity (V) is preferred when the frequency of processing is not that frequent. In this case, the methods described in JP-A-63-131138 and JP-A-63-216050 can be used.

With regard to the interrelation between the parts of the processor and the processing solution, the important factors are such that the processor parts are not rusted by the processing solutions, ingredients which cause photographic deterioration are not dissolved out, and the processor parts are not physically deteriorated. These matters are partly described in JP-A-2-186342 and JP-A-2-186344. The forms of the processing baths include multi-chamber processing baths as described in JP-A-1-267648 and JP-A-2-67554, electroprocessing baths as described in JP-A-3-209471, JP-A-3-273237 and JP-A-3-293661, and processing capsule processing using slits (0.2 mm level) as described in EP 0,456,210A2.

An example of an automatic processor which can be preferably used in the present invention will be illustrated below.

In the present invention, the time during which the photographic material is in the air while being transferred from one bath to another bath, that is, the cross-over time, is preferably as short as possible. The cross-over time is preferably not longer than 10 seconds, more preferably not longer than 7 seconds, still more preferably not longer than 5 seconds.

To achieve the above short cross-over time, it is preferred that a cine type automatic processor be used in the present invention. A leader convey system is particularly preferred. The automatic processor FP-550B manufactured by Fuji Photo Film Co., Ltd. uses this system. It is preferred that the linear velocity in the conveying of the photographic material be higher as opposed to lower. In the leader system, the linear velocity is generally 30 cm to 2 m/min, preferably 50 cm to 1.5 m/min.

The belt conveying systems described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259 are preferred as the leader and the conveying means of the photographic materials. Particularly, the systems described in JP-A-3-126944, JP-A-3-127062 and JP-A-3-127061 are preferred as the conveying mechanism.

The preferred structures of cross-over racks are those having a mixing-preventing plate as described in JP-A-3-126943 to shorten the cross-over time and at the same time, to prevent the processing solutions from being mixed with each other.

It is preferred that the stirring of each processing solution be intensified as much as possible from the standpoint of effectively displaying the effect of the present invention.

Specific examples of methods for increasing the intensity of stirring include a method described in JP-A-62-183460 and JP-A-62-183461, that is, a method wherein a jet stream of the processing solution is allowed to collide with the emulsion layer surface of the photographic material as applied to color negative film processor FP-230B manufactured by Fuji Photo Film Co., Ltd.; a method wherein a rotary means is used to increase the stirring effect as described in JP-A-62-183461; a method wherein while a wire bar blade provided in the processing solution is brought into contact with the emulsion layer surface of the photographic material, the photographic material (film) is transferred to thereby form a turbulent flow on the emulsion layer surface, thus improving the stirring effect; and a method wherein the circulating flow rate of the entire processing solutions is increased. Among them, the method wherein a jet stream of the processing solution is allowed to collide with the emulsion layer surface is most preferred. It is preferred that this method be applied to all of the processing baths.

The effect of the present invention can be greatly improved by allowing the jet stream to collide with the emulsion layer surface within preferably 15 seconds, more preferably 10 seconds, still more preferably 5 seconds after the photographic material is brought into contact with the processing solution having an ability of fixing in processing the photographic material with the processing solution having an ability of fixing.

The reasons for this unexpected effect so far are not known. However, it is believed that when stirring is weak or inefficient immediately after the photographic material is brought into contact with the processing solution having an ability of fixing, such weak or inefficient stirring results in the formation of a residual color, but when the jet stream is allowed to intensively collide with the emulsion layer surface, the factor which forms the residual color can be removed.

More specifically, a system where a processing solution pressure-fed by means of a pump is discharged through a nozzle provided opposite to the emulsion layer surface as described in an Example of JP-A-62-183460 (right lower column of page 3 to right lower column of page 4) is preferred as the method wherein the jet stream is allowed to collide with the emulsion layer surface. Examples of the pump which can be used in the system include magnet pumps MD-10, MD-15 and MD-20 (manufactured by Iwaki KK).

The pore size (diameter) of the nozzle is 0.5 to 2 mm, preferably 0.8 to 1.5 mm. It is preferred that the nozzle be provided in the direction perpendicular to the chamber plate and the film surface. It is also preferred that the nozzle open in the form of a circle. The nozzle is provided at an angle of 60 to 120 degrees to the conveying direction and may be in the form of a rectangle or a slit. The number of nozzles is 1 to 50, preferably 10 to 30 per liter of the tank capacity. When the jet stream is not even and strikes only a part of the film, development blurs and unevenness in the residual color may occur. Accordingly, it is preferred that the positions of the nozzles be directed such that the jet stream does not strike only the same part of the film. For example, the nozzles are preferably arranged so that 4 to 8 holes are provided in the direction perpendicular to the conveying direction and are directed to strike the film at appropriate intervals. When the distance between the nozzle and the film is too short, the above-described blurs and unevenness are liable to occur, while when the distance is too long, the stirring effect is reduced. Accordingly, the distance between the nozzles and the film is preferably 1 to 12 mm, more preferably 3 to 9 mm.

The flow rate of the processing solution discharged from each nozzle should be in the optimum range, and is preferably 0.5 to 5 m/sec, particularly preferably 1 to 3 m/sec.

The circulation of the entire amount of each processing solution may be conducted only through the nozzles. Alternatively, a circulating means may be separately provided. The entire circulating flow rate of each processing solution is 0.2 to 5 ℓ, preferably 0.5 to 4 ℓ/min/liter of each tank capacity. However, it is preferred that the circulating flow rate in the desilverization step of each of the bleaching step, the blix step and the fixing step be relatively large and be in the range of preferably 1.5 to 4 ℓ.

It is preferred that the automatic processors used in the processing of the present invention be provided with a device for aerating the bleaching solution. When aeration is conducted, a lowering in the bleaching rate caused by the formation of an iron(II) complex salt during continuous processing or the formation of a cyan leuco dye called a failure in color restoration can be prevented from occurring.

It is preferred that aeration be carried out by feeding air at a flow rate of at least 0.01 ℓ per liter of the processing bath through porous nozzles having a pore size of 300 μm or smaller as described in JP-A-2-176746 and JP-A-2-176747.

Processing where the photographic materials are continuously or intermittently processed while the replenishers are fed, is called running processing. The bleaching solution during running processing is apt to be made very foamy by the surfactant dissolved out from the photographic materials processed. Hence, when aeration is conducted, many foams are formed, and often run over the processing bath. It is preferred that an anti-foaming means be provided to prevent excess foam from being formed. Specifically, the methods described in JP-A-4-3057, JP-A-4-56853 and JP-A-4-56854 are effective.

It is preferred that the concentration of the processing solutions caused by evaporation during running processing be corrected. The most preferred correcting method is such that an amount of water corresponding to the amount of water evaporated be estimated and added, and an amount of water calculated from a coefficient previously determined on the basis of information on the working time, stop time and temperature controlling time of the automatic processor as described in JP-A-4-1756 be added. Further, the correcting methods using a solution level sensor as described in JP-A-3-248155, JP-A-3-249644, JP-A-3-249645, JP-A-3-249646 and JP-A-4-14042 are preferred.

The amount of water evaporated can be reduced by decreasing the opening area or controlling the air flow rate of an exhaust fan.

For example, the preferred opening ratio of the color developing solution is as described above, and it is preferred that the opening areas of other processing solutions be reduced.

The exhaust fan is provided to prevent dew condensation from occurring during temperature controlling, and the exhaust rate is preferably 0.1 to 1 m^3/min, particularly preferably 0.2 to 0.4 m^3/min.

The evaporation of the processing solutions is affected by the drying conditions of the photographic materials. Drying systems using a ceramic heater which generates hot air are preferred. The flow rate of hot air is preferably 4 to 20 m^3/min, particularly preferably 6 to 10 m^3/min.

The thermostat for preventing overheating with which the ceramic heater which generates hot air is provided, is preferably one which is operated by heat transfer. The position of the thermostat to be set is allowed to lie windward or leeward through heat dissipation fins or a heat transfer part.

It is preferred that the drying temperature be controlled depending on the water content of the photographic materials to be processed. The optimum drying temperature of the films of 35 mm in width is 45 to 55 °C, and that of Blowny film is 55 to 65 °C.

Replenishing pumps are used in the replenishment of the processing solutions, and bellows system replenishing pumps are preferred.

As a method for improving replenishment accuracy, it is effective that the diameter of the solution feed tube to the replenishment nozzles be decreased to prevent back flow from occurring during the stop of the operation of the pump. The inner diameter of the tube is preferably 1 to 8 mm, particularly preferably 2 to 5 mm.

Various mechanical parts and materials are used in the production of the automatic processors. Preferred materials will be illustrated below.

Modified PPO (modified polyphenylene oxide), and modified PPE (modified polyphenylene ether) are preferred as materials for tanks such as the processing tanks and the temperature controlling tanks and as materials for processing racks and guides to be contacted with the solutions. An example of modified PPO is Nolyl (a product of Nippon G.E. Plastic). Examples of modified PPE include Zailon (a product of Asahi Chemical Co., Ltd.) and Upiace (a product of Mitsubishi Gas Kagaku KK). These materials have excellent chemical resistance to the developing solution, the fixing solution and the blix solution and are suitable for use in injection molding. Further, these materials have advantages in that low expansion molding, press molding and various blow molding techniques such as gas counter pressure molding can be conducted. When these molding methods are used, the integral molding of the processing rack and the temperature controlling tank and the integral molding of guides having a complicated structure and racks can be made possible. Further, thick-wall molded articles and other thick-wall members such as blocks can be produced. Large-size housing components such as covers for the automatic processors can be produced by engineering blow molding. Since these materials have a heat-resistant temperature higher than that of general-purpose ABS resin, they can be used as materials for the drying zone of the automatic processors. Further, when heat resistance and rigidity are required, glass fiber-reinforced materials or filler-loaded materials can be used.

ABS resins (acrylonitrile/butadiene/styrene resins) have chemical resistance to the processing solutions (e.g., the color developing solution, the bleaching solution, the fixing solution, the blix solution), and hence ABS resins can be used as a material for parts of the tanks and racks. Examples of ABS resins which can be used include Denka (a product of Denki Kagaku Kogyo KK), Saicolac (a product of Ube Industries, Ltd.) and ABS resins manufactured by Mitsubishi Monsanto KK and Nippon Gosei Gomu KK. It is preferred that ABS resins be used in an atmosphere at 80 °C or lower. ABS resins have good injection moldability and give molded articles having less sink marks and a good surface profile, and hence ABS resins are materials suitable for use in the production of the housings of the automatic processors, and are also suitable for use in the production of the feed parts of the processors and cassettes.

Further, olefin resins such as PE (polyethylene) and PP (polypropylene) have generally high chemical resistance to the processing solutions (e.g., the color developing solution, the bleaching solution, the fixing solution, the stabilizing solution). Examples of PE include the products of Showa Denko KK and Ube Industries, Ltd. Examples of PP include the products of Ube Industries, Ltd., Chisso Corporation, Mitsui Toatsu Chemicals, Inc. and Asahi Chemical Industry Co., Ltd. PE and PP are used as materials for the replenishment tanks and waste solution tanks of the automatic processors. These materials are inexpensive and can be easily molded into large-size tanks by blow molding. Accordingly, these materials can be preferably used in the production of parts which do not require high dimensional accuracy.

PVC (polyvinyl chloride resin) has excellent chemical resistance, is inexpensive, can be easily welded and has excellent processability. Many types of PVC resins are produced by Denki Kagaku Kogyo KK, Riken Vinyl Industry Co. and other molding makers. Plate materials produced by extrusion, such as Takiron Plate (a product of Takiron Chemical Co., Ltd.) and Hishi Plate (a product of Mitsubishi Plastics Industries Co., Ltd.) are commercially available. Various modified PVC resins are also commercially available. Examples of commercially available acrylic-modified PVC resins include Kaidak (a product of Tsutsunaka Plastic) and the product of Sun Arrow Kagaku KK. The acrylic-modified PVC resins provide molded articles having a smooth surface and good water repellency. Accordingly, when the tanks are produced therefrom, ingredients do not tend to precipitate from the processing solutions (e.g., the deposition of the developing agent from the color developing solution does not tend to occur). Hence, the acrylic-modified PVC resins are materials suitable for use in the production of the tanks. The surfaces of extruded or injection molded articles can be smoothed by using soybean oil modified PVC resins in addition to the use of the acrylic-modified PVC resins, since when PVC is modified with soybean oil, fluidity during molding can be improved. The addition of soybean oil (preferably modified soybean oil) to the PVC resins has such an effect that the surfaces of the resins can be smoothened, the quality of the photographic materials is not damaged by scratching, and fluidity during molding can be improved.

Crystalline polymers can be used as materials for the guides of the processing tanks and the processing zones to prevent the developing agent from being deposited and to improve the conveyability of the photographic materials. PBT (polybutylene terephthalate), HDPE (ultra-high-density polyethylene resin),

PTFE (polytetrafluoroethylene resin), PFA (tetrafluoroethylene/perfluoroalkoxyethylene resin) and PVDF (polyvinylidene fluoride resin) are suitable for use in the production of the guides contacted with the photographic materials and parts where the ingredients are apt to be deposited from the processing solutions (e.g., the color developing solution). The above-described fluorides may be coated on other materials such as PPE.

Thermoplastic resins such as PVC (polyvinyl chloride resin), PP (polypropylene), PE (polyethylene), UHMPE (ultra-high molecular-weight polyethylene), PMP (polymethylpentene), PPS (polyphenylene sulfide), modified PPO (modified polyphenylene oxide) and modified PPE (modified polyphenylene ether) are suitable as materials for rollers in the processing parts. Olefin resins such as PP, PE and PMP can be injection molded into rollers having a smooth surface and have a low specific gravity. Accordingly, since rotary load can be reduced, the emulsion layer surface sides of the photographic materials conveyed are hardly marred. These resins are widely used in the production of drum rollers used in turning parts. Materials such as UHMPE and PTFE (including PFA and PVDF) are suitable for use in the parts where the photographic materials are slid and the parts where the processing solutions must be repelled. The rollers prepared therefrom have an effect of preventing the photographic materials from being marred by the solidified materials of deposits from the processing solutions. Rollers provided with a surface layer composed of UHMPE or PTFE (or rollers coated therewith) are suitable for use as rollers positioned at the interface where the rollers are brought into contact with the processing solutions, and as squeeze rollers. PVC resins are suitable for use in the production of rollers because the resins can be easily processed into the rollers by extrusion. Rollers having a low-hardness non-rigid resin part on the surface thereof can be easily produced therefrom by double extrusion. The rollers are brought into soft contact with the photographic materials. Modified PPO resins, modified PPE resins and modified PPS resins in addition to PVC resins are suitable for use in the production of conveying rollers because these resins have rigidity and can withstand high rotating torque. It is preferred that these resins be reinforced with reinforcing materials such as glass fiber or minerals (e.g., mica, talc, potassium titanate) to further increase rigidity. When the resins are reinforced, the flexural modulus of rollers can be improved, the rollers can be prevented from being distorted by creep with the passage of time, and conveyability can be stably ensured over a long period of time without bending. Further, inorganic materials may be added to the resins. When the resins containing the inorganic materials are molded, the surfaces of the resulting rollers are satin-tough-finished by inorganic particles which appear on the surfaces of the rollers, whereby the photographic materials conveyed can be prevented from being slipped. Roughness on the surfaces of the rollers can be controlled by adjusting the particle size and amount of the inorganic materials added.

Thermosetting resins are suitable for use in the production of conveying rollers having a small diameter and rollers having a long length for conveying photographic materials having a large width. Examples of thermosetting resins which can be preferably used include PF (phenolic resins), thermosetting urethane resins and unsaturated polyester resins. Epoxy resins are suitable for use in the production of the rollers brought into contact with some processing solutions exclusive of alkaline processing solutions. Resol resins are preferred as PF, and OR-85 (a product of Mitsui Toatsu Chemicals, Inc.) is particularly suitable. It is preferred that the resins be reinforced with graphite. Since the diameters of rollers produced from these resins can be made smaller (e.g., an outer diameter of 8 mm), processing racks can be smaller-sized. Examples of suitable thermosetting urethane resins include Unilon (a product of Nippon Unipolymer), Pandex (a product of Dainippon Ink & Chemicals Inc.) and Takenate (a product of Takeda Chemical Industries, Ltd.).

Rollers coated with fluororesins can be preferably used to prevent the rollers from being stained by the developing solution. Specific examples of fluororesins include the resins described in JP-A-4-161955.

Elastomers can be used in the production of non-rigid rollers such as nip rollers. Examples of the elastomers which can be preferably used include olefin elastomers, styrene elastomers, urethane elastomers and vinyl chloride elastomers.

Thermoplastic crystalline resins such as PA (polyamide), PBT (polybutylene terephthalate), UHMPE (ultra-high molecular-weight polyethylene), PPS (polyphenylene sulfide), LCP (wholly aromatic polyester, liquid crystal polymer) and PEEK (polyether ether ketone) are suitable for use in the production of gears and sprockets in the processing zones.

Examples of PA include polyamide resins such as nylon 66, nylon 6 and nylon 12, aromatic polyamides having aromatic rings in the molecular chain and modified polyamides. Examples of suitable nylon 66 and nylon 6 include Zaitel (a product of Toray Industries, Inc. and du Pont). Examples of suitable nylon 12 include Lilusun (a product of Toray Industries, Inc.) and Diamide (a product of Daicel Huls). An example of suitable aromatic polyamide includes Reny polyamide MXD 6 (a product of Mitsubishi Gas Kagaku KK). An example of suitable modified polyamide include Arlene modified polyamide 6T (a product of Mitsui

Petrochemical Industries, Ltd.). Since PA has a high water absorption ratio, PA is apt to be swollen in the processing solutions. Accordingly, glass fiber-reinforced PA and carbon fiber-reinforced PA are preferred. The aromatic polyamides have a relatively low water absorption ratio, and hence the aromatic polyamides are hardly swollen and give articles with high dimensional accuracy. High-molecular products such as MC nylon obtained by completion molding can have a sufficient performance without being reinforced with fiber. Further, oil-containing nylon resins such as polyslider can be used.

Unlike PA, PBT has a very low water absorption ratio, and hence PBT has high chemical resistance to the processing solutions. PBT products of Toray Industries, Inc. and Dainippon Ink & Chemicals Inc. and Barox (a product of Nippon G.E. Plastic KK) can be used. Glass fiber-reinforced PBT and non-reinforced PBT can be used depending on the parts to be required. It is preferred that glass fiber-reinforced PBT be used in combination with non-reinforced PBT to improve the intermesh of gears.

It is preferred that UHMPE not be reinforced. Examples of suitable UHMPE include Rubmer and Hyzex Million (products of Mitsui Petrochemical Industries, Ltd.), New Light (a product of Sakushin Kogyo KK), Sunfine (a product of Asahi Chemical Industry Co., Ltd.) and ultra-high-molecular weight polyethylene UHMW (a product of Dai Nippon Printing Co., Ltd.).

It is preferred that PPS be reinforced with glass fiber or carbon fiber.

Examples of usable LCP include Victrex (a product of ICI Japan), Econol (a product of Sumitomo Chemical Co., Ltd.), Zaider (a product of Nippon Oil Co., Ltd.) and Vectra (a product of Polyplastics).

PEEK has very good chemical resistance to any of the processing solutions used in the processors and good durability. Even when PEEK is not reinforced, PEEK can display a good performance. Hence, PEEK is a preferred material.

Ultra-high-molecular-weight polyethylene is preferred as a material for bearings.

Usually, stainless steel (SUS 316) and titanium are used as materials for springs used in the processing solutions in the automatic processors. When the springs can not be appropriately made of titanium, plastic springs can be used.

When deformation under a load is small (the critical strain of Hook's law is 1.6% or below), PBT (e.g., Barox 310 manufactured by Nippon G.E. Plastics), PP (e.g., M-1500 manufactured by Asahi Chemical Industry Co., Ltd.), modified PPO (e.g., Nolyl manufactured by Nippon G.E. Plastics) and modified PPE (e.g., Zailon manufactured by Asahi Chemical Industry Co., Ltd.) are used. When spring force is insufficient, glass fiber reinforced materials are effective.

PSF (polysulfone), PAR (polyarylate), PES (polyether sulfone), PEI (polyether imide) and PAI (polyamide-imide) are suitable to impart a stable nip force to the springs over a long period of time. Particularly, super-enplane noncrystalline resins are superior. PSF, PES and PEI are particularly preferred. An example of usable PSF include Uther P1700 (a product of Armco). An example of usable PES include Victrex (a product of ICI Japan). An example of usable PEI include Ultem (a product of Nippon G.E. Plastics).

When the springs are used under a heavy load over a long period of time, crystalline resins such as PEEK, PPS and LCP are used. The noncrystalline resins are low in creep and excellent in dimensional accuracy during molding, and hence the resins are very suitable for use as materials for the springs used under a light load. When a high fatigue threshold stress is required, the crystalline resins are suitable. A typical example of PEEK is Victrex 450G (a product of ICI Japan). A typical example of PPS is Lighton. A typical example of LCP I type is Econol E2000 (a product of Sumitomo Chemical Co., Ltd.). A typical example of LCP II type is Vectra A950 (a product of Polyplastic).

Expanded vinyl chloride resins, expanded silicone resins and expanded urethane resins are suitable for use as non-rigid materials for squeeze rollers, etc. An example of the expanded urethane resins is Rubicel (a product of Toyo Polymer KK).

EPDM rubber, silicone rubber, biton rubber, olefin elastomers, styrene elastomers, urethane elastomers and vinyl chloride elastomers are preferred as rubber materials and elastomers for use in the production of pipes, joints for pipes and joints for agitation jet pipes, and as sealing materials. Specific examples of these rubbers and elastomers include Sumiflex (a product of Sumitomo Bakelite Co., Ltd.), Millastomer (olefin elastomer) (a product of Mitsui Petrochemical Industries, Ltd.), Thermolan (rubber-filled olefin elastomer) and Rubberlon (products of Mitsubishi Petrochemical Co., Ltd.), Santoprene (a product of Nippon Monsanto KK or A.E.S. Japan), Sunprene (a product of Mitsubishi Kasei Vinyl KK), and silicone rubber and biton rubber as described in JP-A-198052.

Ultra-high-strength polyethylene resin fiber (e.g., those described in JP-A-4-6554), polyvinylidene fluoride resin fiber (e.g., those described in JP-A-4-16941) and aramid fiber (e.g., Kepula, a product of Toray Du Pont KK) can be used as the core materials of belts such as conveying belts.

The above-described materials such as plastic materials used in the production of various members of the processing tanks, etc. of the processors can be easily chosen, for example, from Plastic Molding Material Commercial Transaction Handbook - Characteristic Data Base (edition of 1991) (published by Gosei Jushi Kogyo Shinbun Sha).

Any material of paper, plastics and metals can be used as materials for replenishing cartridges. Particularly, plastic materials having a coefficient of permeation of 50 $ml/m^2 \cdot atm \cdot day$ or below are preferred. The coefficient of oxygen permeation can be measured by the method described in O_2 Permeation of Plastic Container, Modern Packing, N.J. Calyan (December 1968), pp. 143-145.

Specific examples of the plastic materials which can be used include polyvinylidene chloride (PVDC), nylon (NY), polyethylene (PE), polypropylene (PP), polyester (PES), ethylene-vinyl acetate copolymer(EVA), ethylenevinyl alcohol copolymer (EVAL), polyacrylonitrile (PAN), polyvinyl alcohol (PVA) and polyethylene terephthalate (PET). It is preferred from the standpoint of reducing oxygen permeability that PVDC, NY, PE, EVA, EVAL and PET be used.

These materials alone may be used and may be molded. These materials may be molded into a film, and a laminate of two or more films (so-called composite film) may be used. These materials may be processed into a container such as a bottle type, a cubic type or a pillow type. However, cubic type containers which are flexible and easy to handle and allow the volume thereof to be reduced after use and containers having a similar structure thereto are particularly preferred.

Examples of the composite film which can be preferably used include, but are not limited to, the following laminates:

PE/EVAL/PE
PE/aluminum foil/PE
NY/PE/NY
NY/PE/EVAL
PE/NY/PE/EVAL/PE
PE/NY/PE/PE/PE/NY/PE
PE/SiO_2 layer/PE
PE/PVDC/PE
PE/NY/aluminum foil/PE
PE/PP/aluminum foil/PE
NY/PE/PVDC/NY
NY/EVAL/PE/EVAL/NY
NY/PE/EVAL/NY
NY/PE/PVDC/NY/EVAL/PE
PP/EVAL/PE
PP/EVAL/PP
NY/EVAL/PE
NY/aluminum foil/PE
Paper/Aluminum foil/PE
Paper/PE/Aluminum foil/PE
PE/PVDC/NY/PE
NY/PE/Aluminum foil/PE
PET/EVAL/PE
PET/Aluminum foil/PE
PET/Aluminum foil/PET/PE

The composite films have a thickness of about 5 to 1500 μm, preferably about 10 to 1000 μm.

The finished containers have an internal volume of about 100 ml to 20 ℓ, preferably about 500 ml to 10 ℓ.

The container (cartridge) may be placed in an outer case, or the container and the outer case may be integrally molded.

Various processing solutions can be charged into the cartridges of the present invention. Examples of the processing solutions include the color developing solution, the black and white developing solution, the bleaching solution, the compensating solution, the reversal solution, the fixing solution, the blix solution and the stabilizing solution. It is preferred that the color developing solution, the black and white developing solution, the fixing solution and the blix solution be put into cartridges having a low coefficient of oxygen permeation.

The present invention can be applied to various color photographic materials. Typical examples of the photographic materials include general-purpose and movie color negative films, color reversal films for

slides or TV, color positive films and color reversal papers.

Silver halide to be contained in the photographic emulsion layers of the photographic materials of the present invention contains a silver iodide such as silver iodobromide, silver iodochloride and silver iodochlorobromide in at least one layer. The silver iodide content is 1 to 30 mol%, preferably 2 to 25 mol%.

Silver halide grains contained in the photographic emulsions may have a regular crystal form such as a cubic, octahedral or tetradecahedral form, an irregular crystal form such as a spherical or plate-like form, a crystal form having a defect such as a twinning plane, or a composite form thereof.

With regard to the grain size of the silver halide grains, the grains may range from fine grains having a grain size of about 0.2 μm or below to larger-size grains having a grain size of about 10 μm (the diameter of the grain is defined as the diameter of a circle having an area equal to the projected area of the grain). Any of a polydisperse emulsion and a monodisperse emulsion may be used.

The silver halide photographic emulsions used in the present invention can be prepared, for example, by the methods disclosed in Research Disclosure (RD), No. 17643 (December 1978), pp. 22-23, "I. Emulsion Preparation and Types"; ibid., No. 18716 (November 1979) page 648; P. Glafkides, Chimie et Physique Photographique (Paul Montel 1967); G.F. Duffin, Photographic Emulsion Chemistry (Focal Press 1966); and V.L. Zelikman et al., Making and Coating Photographic Emulsion (Focal Press 1964).

Monodisperse emulsions as described in U.S. Patent 3,574,628 and 3,655,394 and U.K. Patent 1,413,748 can be preferably used. Further, tabular grains having an aspect ratio of about 5 or more can be used in the present invention. The tabular grains can be prepared by the methods described in Gutoff, Photographic Science and Engineering, Vol. 14, pp. 248-257 (1970), U.S. Patents 4,434,226 4,414,310, 4,430,048, and 4,439,520 and U.K. Patent 2,112,157.

In order to attain the effects of the present invention, it is preferable to use tabular grains having an average aspect ratio of 5 to 30. In particular, tabular grains having an average aspect ratio of 5 to 15 are preferably used to attain better effects of the present invention.

The monodisperse emulsion which can be preferably used in the present invention is an emulsion of silver halide grains which are observed on its electron microphotograph to be uniform in shape and grain size and exhibit a S/r ratio of 0.20 or more, preferably 0.02 to 0.15, more preferably 0.03 to 0.10 wherein S is the standard deviation of grain diameter distribution and r is the average grain diameter. The standard deviation S of grain diameter distribution can be determined by the following equation:

$$S = \sqrt{\frac{\Sigma (r - r_i)^2 n_i}{\Sigma n_i}}$$

The average grain diameter r as defined herein indicates the average of the diameter values of silver halide grains if they are spherical or the average of the diameter
values of circles having the same area as the projected area of silver halide grains if they are otherwise, e.g., cubic. Assuming that the diameter of individual grains is r_i and the number of grains is n_i, the average grain diameter r is defined by the following equation:

$$r = \frac{\Sigma n_i r_i}{\Sigma n_i}$$

The foregoing grain diameter can be measured by various methods commonly used in the art for the foregoing purpose. Typical examples of these measuring methods are described in Rabrand (phonetic), "Analytical Table of Grain Diameter", A. S. T. M. Symposium on Light Microscopy, 1955, pp. 94 - 122, and Meas and James, "The Theory of Photographic Process", 3rd edition, Macmillan, 1966, Chapter 2. The grain diameter can be determined from the projected area of grain or approximation to the diameter of grain. If grains are substantially uniform in shape, the grain diameter distribution can be fairly exactly

represented by diameter or projected area.

The relationship of grain diameter distribution with other factors can be determined by the method described in Tribeli & Smith, "Empirical Relationship between Sensitometry Distribution and Grain Diameter Distribution in Photographic Emulsion", The Photographic Journal, vol. IXXIX, 1940, pp. 330 - 338

The crystal structure of the grain may be uniform or different in the halogen composition between the interior of the grain and the surface layer thereof or may have a laminar structure. The grain may be joined to silver halide having a different composition by epitaxial growth, or may be joined to a compound other than silver halide, such as silver rhodanide or lead oxide.

A mixture of grains having various crystal forms may be used.

Usually, the silver halide emulsions are subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives used in these steps are described in Research Disclosure No. 17643 (December 1978), Research Disclosure No. 18716 (November 1979) and Research Disclosure No. 307105 (November 1989). The places where the additives are described are listed below.

Conventional photographic additives which can be used in the present invention are also described in the above three Research Disclosures, and the places are shown in the following Table.

	Additive	RD17643	RD18716	RD307105
1	Chemical Sensitizing Agent	page 23	right column of page 648	page 866
2	Sensitivity Increaser		right column of page 648	
3	Spectral Sensitizing Agent, Supersensitizing agent	pages 23 to 24	right column of page 648 to right column of page 649	pages 866 to 868
4	Brightening Agent	page 24	right column of page 647	page 868
5	Anti-fogging Agent, Stabilizer	pages 24 to 25	right column of page 649	pages 868 to 870
6	Light Absorber, Filter Dye, UV light Absorber	pages 25 to 26	right column of page 649 to left column of page 650	page 873
7	Stain Inhibitor	right column of page 25	left column to right column of page 650	page 872
8	Dye Image Stabilizer	page 25	left column of page 650	page 872
9	Hardening Agent	page 26	left column of page 651	pages 874 to 875
10	Binder	page 26	left column of page 651	pages 873 to 874
11	Plasticizer, Lubricant	page 27	right column of page 650	page 876
12	Coating Aid, Surfactant	pages 26 to 27	right column of page 650	pages 875 to 876
13	Antistatic Agent	page 27	right column of page 650	pages 876 to 877
14	Matting Agent			pages 878 to 879

Various color couplers can be used in the present invention. Typical examples thereof are described in the patent specifications cited in the aforesaid RD No. 17643, VII-C to G and RD No. 307105, VII-C to D.

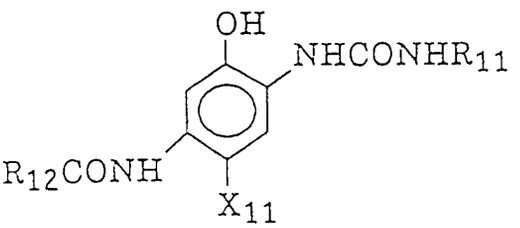
Examples of yellow couplers which can be preferably used include those described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,792, and 4,248,961, JP-B-58-10739, U.K. Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023 and 4,511,649, EP249,473A, JP-A-3-211548, JP-A-4-277741,

JP-A-4-309945, JP-A-4-355751, U.S. Patent 5,118,599, JP-A-4-218042 and European Patent Laid-Open No. 501,306.

Magenta couplers which can be preferably used include 5-pyrazolone compounds and pyrazoloazole compounds. Specific examples of the magenta couplers which can be preferably used include those described in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,064, RD No. 24220 (June 1984), JP-A-60-33552, RD No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, and 4,556,630 and WO(PCT) 88/04795.

Cyan couplers include phenol couplers and naphthol couplers. Examples of cyan couplers which can be preferably used include those 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 Laid-Open No. 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,753,871, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, JP-A-61-42658 and European Patents 484,909, 456,226, 491,197 and 488,248.

In the present invention, the photographic light-sensitive material may preferably comprise a cyan coupler represented by formula (CI) to inhibit the rise in yellow stain with time after processing:



(CI)

wherein R_{11} represents an aryl group; R_{12} represents an alkyl or an aryl group; and X_{11} represents a hydrogen atom or a group capable of splitting off by a coupling reaction with an oxidation product of an aromatic primary amine developing agent.

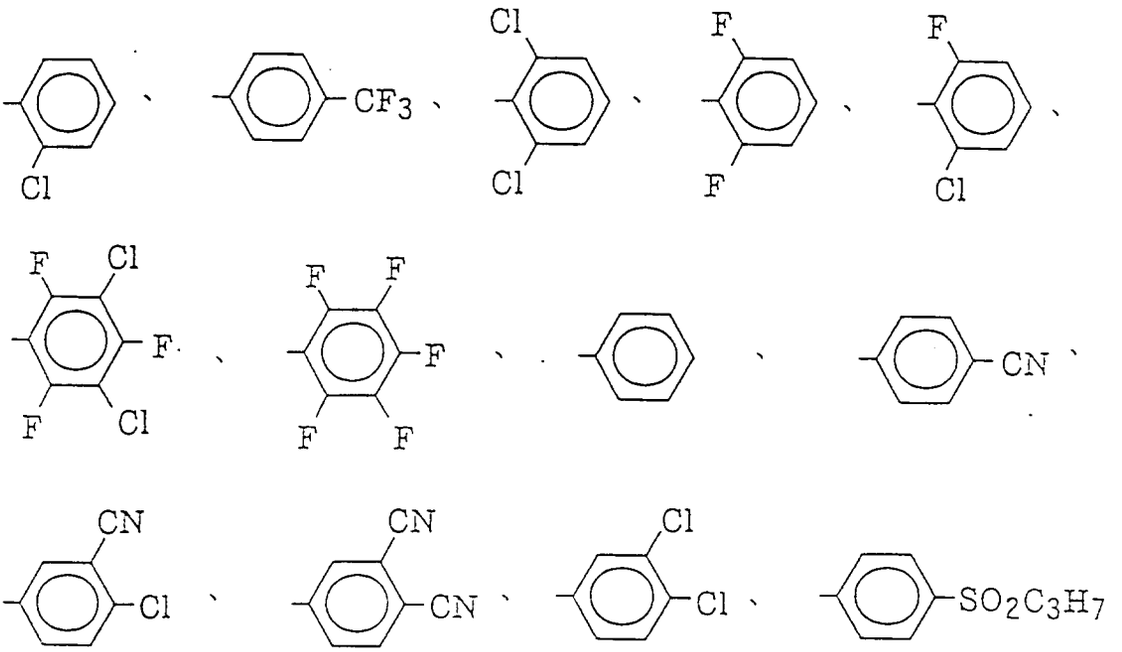
In formula (CI), R_{11} represents a C_{6-36}, preferably C_{6-24} aryl group which may be substituted. Examples of substituents which may be contained in the aryl group represented by R_{11} include halogen atom, cyano group, nitro group, carboxyl group, sulfo group, alkyl group, aryl group, heterocyclic group, alkoxy group, aryloxy group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, aryloxycarbonyl group, acyl group, sulfonyl group, acylamino group, sulfonamide group, carbamoyl group, sulfamoyl group, ureide group, alkoxycarbonylamino group, and sulfamoylamino group (These substituents are referred to as "substituent group A"). Preferred among these substituents are halogen atom (e.g., F, Cl, Br, I), cyano group, alkyl group, aryloxy group, alkylsulfonyl group, arylsulfonyl group, acylamino group, and sulfonamide group.

R_{12} represents a C_{1-36}, preferably C_{1-24} straight-chain, branched or cyclic alkyl group which may be substituted or a C_{6-36}, preferably C_{6-24} aryl group which may be substituted. Examples of substituents which may be contained in the alkyl or aryl group represented by R_{12} include the foregoing substituent group A. R_{12} is preferably an alkyl group, particularly an alkyl group which is substituted by an aryloxy group, sulfonyl group, arylthio group, heterocyclic group or the like in the 1-position.

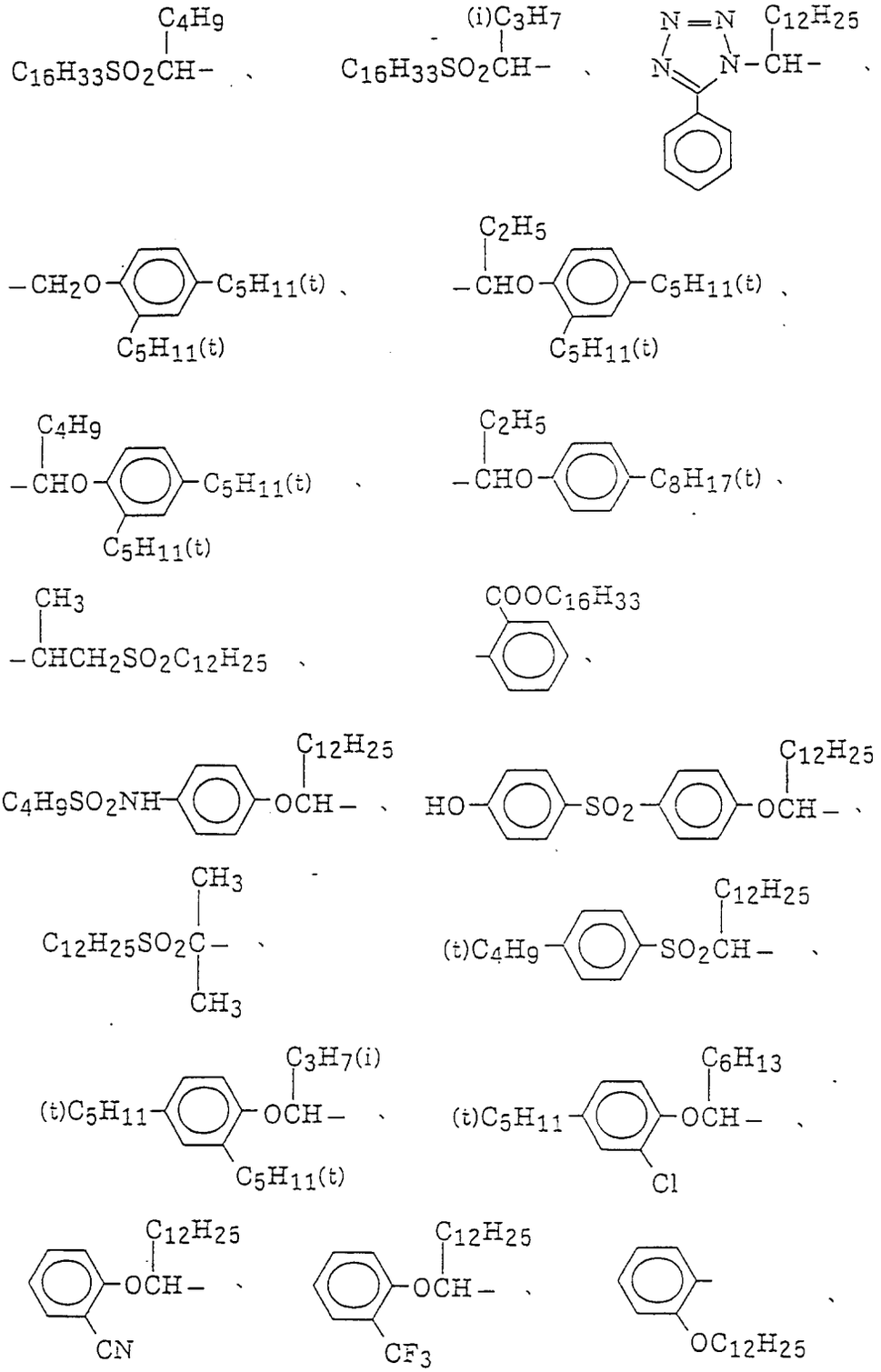
X_{11} represents a hydrogen atom or a coupling-separatable group capable of splitting off by a coupling reaction with an oxidation product of an aromatic primary amine developing agent. Examples of such a coupling-separatable group include halogen atom (e.g., F, Cl, Br, I), sulfo group, C_{1-36}, preferably C_{1-24} alkoxy group, C_{6-36}, preferably C_{6-24} aryloxy group, C_{2-36}, preferably C_{2-24} acyloxy group, C_{1-36}, preferably C_{1-24} alkyl or arylsulfonyloxy group, C_{1-36}, preferably C_{1-24} alkylthio group, C_{6-36}, preferably C_{6-24} arylthio group, C_{4-36}, preferably C_{4-24} imido group, C_{1-36}, preferably C_{1-24} carbamoyloxy group, and C_{1-36}, preferably C_{2-24} heterocyclic group connected to the coupling active position via a nitrogen atom (e.g., tetrazole-5-yl, pyrazolyl, imidazolyl, 1,2,4-triazole-1-yl). The alkoxy group or the groups mentioned thereafter may be substituted by groups selected from the foregoing substituent group A. X_{11} is preferably a hydrogen atom, fluorine atom, chlorine atom, sulfo group, alkoxy group or aryloxy group, particularly hydrogen atom or chlorine atom.

Examples of the various substituents in formula (CI) will be given below.

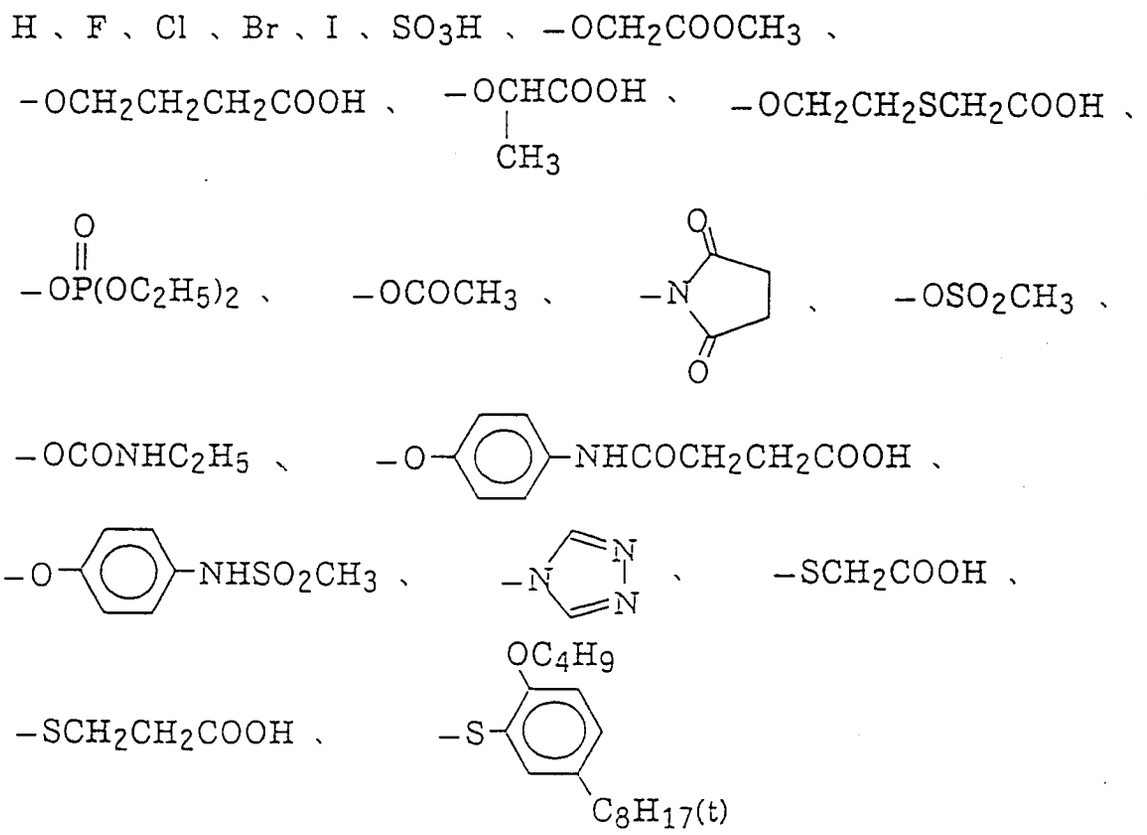
Examples of R_{11}:



Examples of R_{12}:

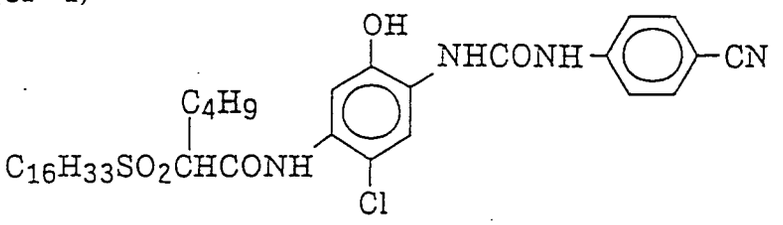


Examples of X_{11}:

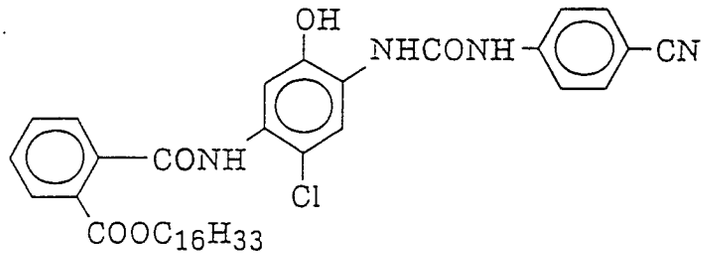


Specific examples of the cyan coupler represented by formula (CI) will be given below.

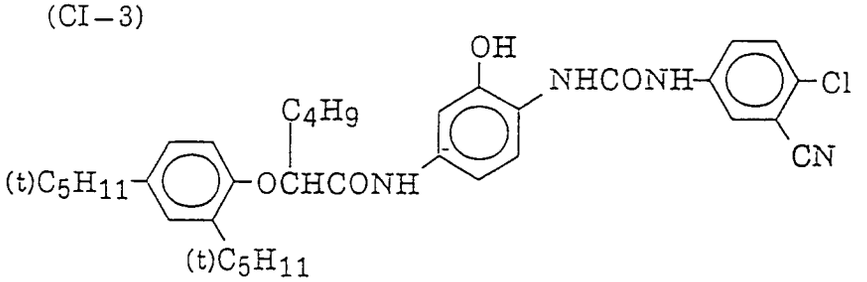
(CI-1)



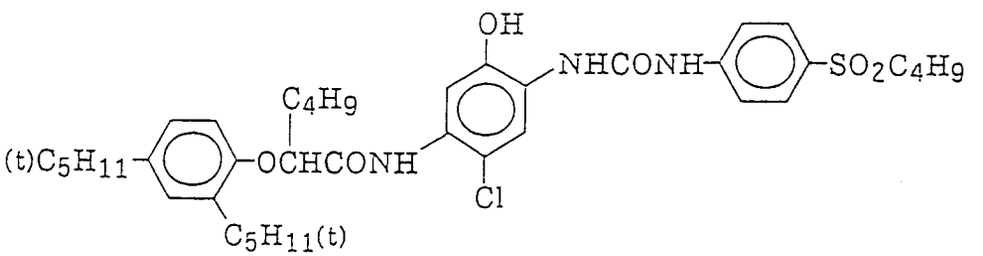
(CI-2)



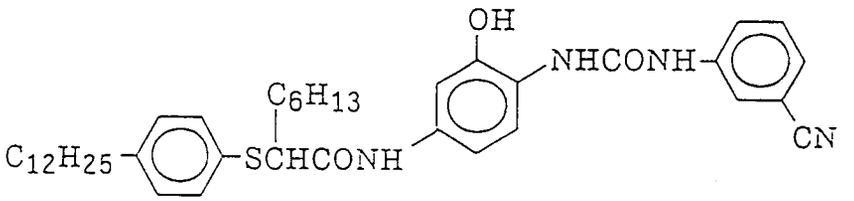
(CI-3)



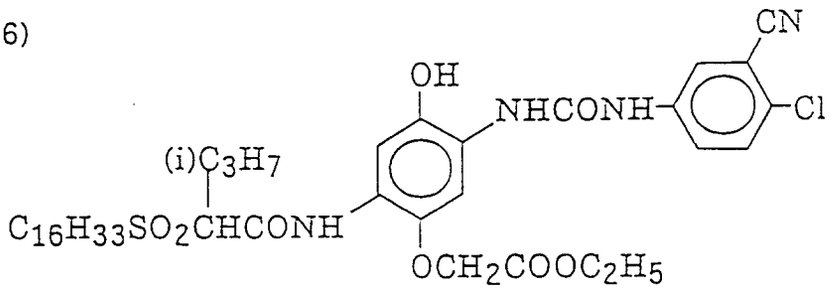
(CI-4)



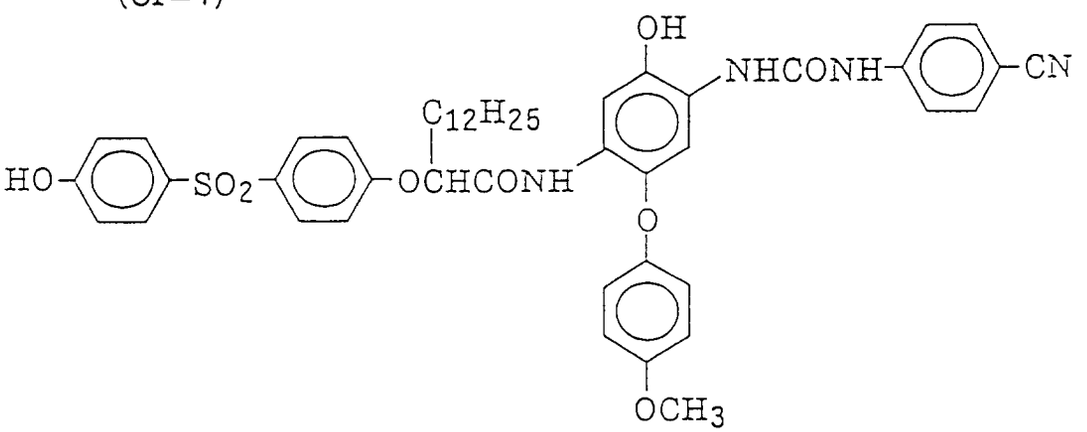
(CI-5)



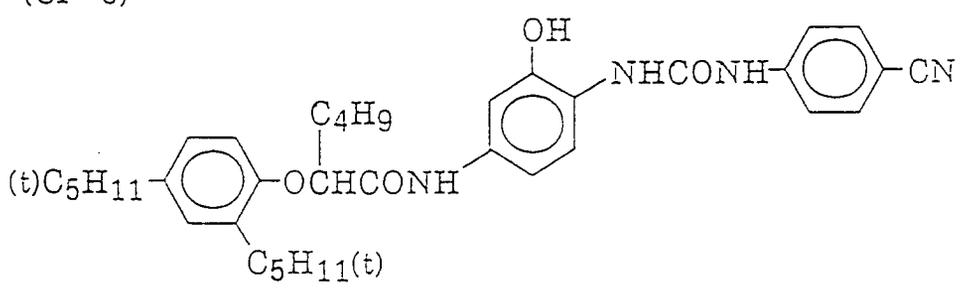
(CI-6)



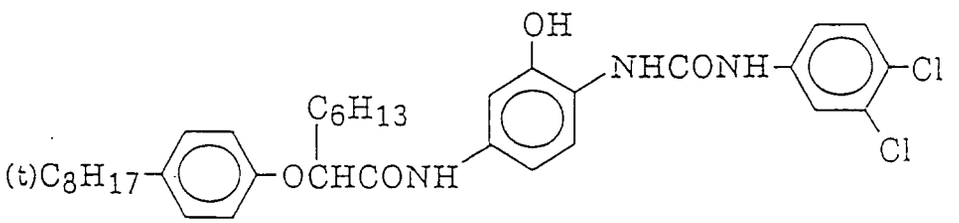
(CI-7)



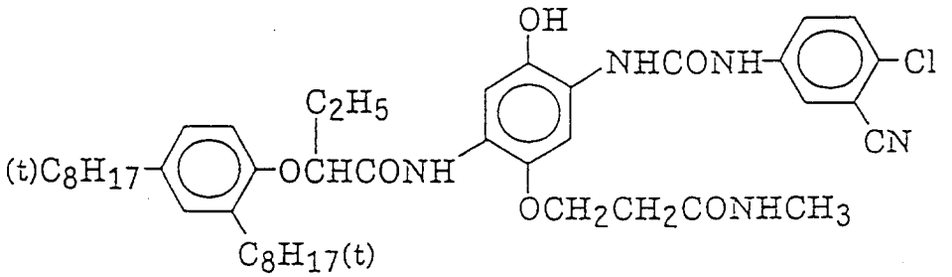
(CI-8)



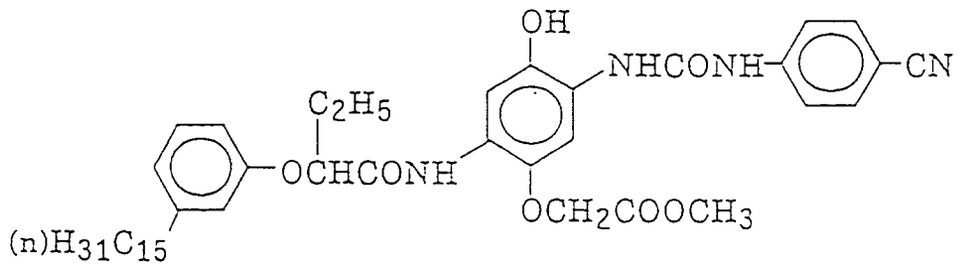
(CI-9)



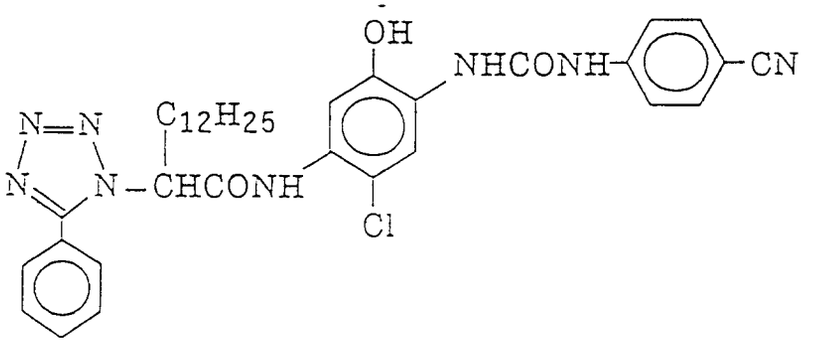
(CI-10)



(CI-11)



(CI-12)



Of them, (CI-3) or (CI-8) is preferable.

Specific examples of compounds other than described above and methods for the synthesis of these couplers are disclosed in U.S. Patents 2,772,162, 2,895,826, 4,327,173, 4,333,999, 4,334,011, 4,430,423, 4,500,635, 4,518,687, 4,564,586, 4,609,619, and 4,746,602, and JP-A-59-164555.

The coupler represented by formula (CI) of the present invention is preferably incorporated in the silver halide emulsion layer. The total amount of these couplers to be used is in the range of 2 to 2 x 10^{-3} mol, preferably 1 to 5 x 10^{-3} mol, more preferably 5 x 10^{-1} to 1 x 10^{-2} mol per mol of silver halide contained in the same layer.

The coupler represented by formula (CI) of the present invention can be incorporated in the photographic light-sensitive material in the same manner as ordinary couplers as described later

Preferred examples of colored couplers for correcting undesired absorptions of developed dyes include those described in RD No. 17643, Item VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, U.K. Patent 1,146,368, JP-A-3-251843 and JP-A-4-212149. Couplers which release a fluorescent dye during coupling to correct undesired absorptions of developed dyes as described in U.S. Patent 4,774,181 and couplers having, as an eliminable group, a dye precursor group capable of reacting with a developing agent to form a dye as described in U.S. Patent 4,777,120 can also be preferably used.

Preferred examples of couplers whose developed dye has appropriate diffusibility include the compounds described in U.S. Patent 4,366,237, U.K. Patent 2,125,570, European Patent 96,570 and West German Patent Laid-Open No. 3,234,533.

Typical examples of polymer couplers include the compounds described in U.S. Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320 and 4,576,910 and U.K. Patent 2,102,173.

Couplers which release a photographically useful group with coupling can be preferably used. Preferred examples of couplers which release imagewise a nucleating agent or a development accelerator include those described in U.K. Patents 2,097,140 and 2,131,188, JP-A-59-157638, JP-A-59-170840 and JP-A-4-211248.

Examples of other couplers which can be used in the photographic materials of the present invention include competitive couplers as described in U.S. Patent 4,130,427; couplers which release a dye whose color is restored to the original one after elimination as described in European Patent 173,302A; couplers which release a bleaching accelerator as described in RD No. 11449, RD No. 24241 and JP-A-61-201247; couplers which release a ligand as described in U.S. Patent 4,553,477; couplers which release a leuco dye as described in JP-A-61-75747; and couplers which release a fluorescent dye as described in U.S. Patent 4,774,181.

The couplers used in the present invention can be introduced into the photographic materials by various conventional dispersion methods.

Examples of high-boiling solvents which can be used in oil-in-water dispersion methods are described in U.S. Patent 2,322,027. Specific examples of high-boiling organic solvents having a boiling point of not lower than 175 °C under atmospheric pressure which can be used in the oil-in-water dispersion methods include phthalic esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate); phosphoric or phosphonic esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, di-2-ethylhexyl phenyl phosphonate); benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl p-hydroxybenzoate); amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, N-tetradecylpyrrolidone); alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-t-amyl alcohol); aliphatic carboxylic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrate, isostearyl lactate, trioctyl citrate); aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline); and hydrocarbons (e.g., paraffin, dodecylbenzene, diisopropylnaphthalene). Organic solvents having a boiling point of about 30 °C or higher, preferably not lower than 50 °C, but not higher than about 160 °C can be used as co-solvents. Typical examples of the organic solvents include acetic esters such as butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

Specific examples of the steps and effects of latex dispersion methods and impregnating latex are described in U.S. Patent 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The couplers are impregnated with loadable latex polymers (e.g., those described in U.S. Patent 4,203,716) in the presence or absence of the aforesaid high-boiling organic solvents or are dissolved in a water-insoluble, but organic solvent-soluble polymer and can be emulsified and dispersed in an aqueous solution of hydrophilic colloid. Homopolymers or copolymers described in WO(PCT) 88/00723 (pages 12 to 30) can be preferably used. Particularly, acrylamide polymers are preferred from the standpoint of stabilizing dye images.

Suitable supports which can be used in the present invention are described in the aforesaid RD No. 17643 (page 28) and RD No. 18716 (right column of page 647 to left column of page 648).

It is preferred that the supports for the color negative films used in the present invention be those having an electrically conductive layer and a transparent magnetic layer on one side thereof as described in JP-A-4-62543, those having a magnetic recording layer as described in Fig. 1A of WO(PCT) 90/04205, and those having a striped magnetic recording layer and a transparent magnetic recording layer adjacent to the striped magnetic recording layer as described in JP-A-4-124628. It is preferred that a protective layer as described in JP-A-4-73737 be provided on these magnetic layers.

The supports have a thickness of preferably 70 to 120 μm. Various plastic films described in JP-A-4-124636 (the first line of right upper column of page 5 to the 5th line of right upper column of page 6) can be used as the support materials. Examples of supports which can be preferably used include films of cellulose derivatives (e.g., diacetyl-, triacetyl-, propionyl-, butanoyl-, acetylpropionyl-acetate) and films of polyesters (e.g., polyethylene terephthalate, poly-1,4-cyclohexanedimethylene terephthalate, polyethylene naphthalate). The polyester films are preferred as the supports used in the present invention from the

standpoint of obtaining a higher effect of removing water.

Any of the conventional patrones can be used as the containers in which the color negative films of the present invention are put.

Particularly, the containers described in Fig. 1G to Fig. 3 of U.S. Patent 4,834,306 and Fig. 1 to Fig. 3 of U.S. Patent 4,846,418 are preferred.

It is preferred that the color negative films used in the present invention have the structures described in JP-A-4-125558 (the first line of left upper column of page 14 to the 11th line of left lower column of page 18).

The present invention will now be illustrated in greater detail by reference to the following examples which, however, are not to be construed as limiting the invention in any way.

EXAMPLE 1

The following layers having the following compositions were coated on a cellulose triacetate film support having a subbing layer to prepare a multi-layer photographic material designated as Sample C.

Composition of Light-Sensitive Layer

The following abbreviations are used for the following principal ingredients:

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

The amounts of the silver halide emulsions and colloidal silver are represented by coating weights in g/m^2 in terms of silver. The amounts of the couplers, the additives and gelatin are represented by coating weights in g/m^2. The amounts of the sensitizing dyes are represented by moles per one mole of silver halide in the same layer.

First layer (antihalation layer)	
Black colloidal silver	0.10
Gelatin	1.90
ExM-1	2.0×10^{-2}
HBS-1	3.0×10^{-2}

Second layer (interlayer)	
Gelatin	2.10
UV-1	3.0×10^{-2}
UV-2	6.0×10^{-2}
UV-3	7.0×10^{-2}
ExF-1	4.0×10^{-3}
HBS-2	7.0×10^{-2}

Third layer (low-sensitivity red-sensitive emulsion layer)	
Emulsion A (in terms of silver)	0.15
Emulsion B (in terms of silver)	0.25
Gelatin	1.50
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-1	0.11
ExC-3	0.11
ExC-4	3.0×10^{-2}
ExC-7	1.0×10^{-2}
HBS-1	7.0×10^{-3}

Fourth layer (intermediate-sensitivity red-sensitive emulsion layer)	
Emulsion C (in terms of silver)	0.25
Emulsion D (in terms of silver)	0.45
Gelatin	2.00
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-1	0.16
ExC-2	8.0×10^{-2}
ExC-3	0.17
ExC-7	1.5×10^{-2}
ExY-1	2.0×10^{-2}
ExY-2	1.0×10^{-2}
Cpd-10	1.0×10^{-4}
HBS-1	0.10

Fifth layer (high-sensitivity red-sensitive emulsion layer)	
Emulsion E (in terms of silver)	0.60
Gelatin	1.60
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-5	7.0×10^{-2}
ExC-6	8.0×10^{-2}
ExC-7	1.5×10^{-2}
HBS-1	0.15
HBS-2	8.0×10^{-2}

Sixth layer (interlayer)	
Gelatin	1.10
P-2	0.17
Cpd-1	0.10
Cpd-4	0.17
HBS-1	5.0×10^{-2}

Seventh layer (low-sensitivity green-sensitive emulsion layer)	
Emulsion F (in terms of silver)	0.10
Emulsion G (in terms of silver)	0.15
Gelatin	0.50
ExS-4	5.0×10^{-4}
ExS-5	2.0×10^{-4}
ExS-6	0.3×10^{-4}
ExM-1	3.0×10^{-2}
ExM-2	0.20
ExY-1	3.0×10^{-2}
Cpd-11	7.0×10^{-3}
HBS-1	0.20

Eighth layer (intermediate-sensitivity green-sensitive emulsion layer)	
Emulsion H (in terms of silver)	0.55
Gelatin	1.00
ExS-4	5.0×10^{-4}
ExS-5	2.0×10^{-4}
ExS-6	3.0×10^{-5}
ExM-1	3.0×10^{-2}
ExM-2	0.25
ExM-3	1.5×10^{-2}
ExY-1	4.0×10^{-2}
Cpd-11	9.0×10^{-3}
HBS-1	0.20

Ninth layer (high-sensitivity green-sensitive emulsion layer)	
Emulsion I (in terms of silver)	0.45
Gelatin	0.90
ExS-4	2.0×10^{-4}
ExS-5	2.0×10^{-4}
ExS-6	2.0×10^{-5}
ExS-7	3.0×10^{-4}
ExM-1	1.0×10^{-2}
ExM-4	3.9×10^{-2}
ExM-5	2.6×10^{-2}
Cpd-2	1.0×10^{-2}
Cpd-9	2.0×10^{-4}
Cpd-10	2.0×10^{-4}
HBS-1	0.20
HBS-2	5.0×10^{-2}

Tenth layer (yellow filter layer)	
Gelatin	0.90
Yellow colloidal silver	5.0×10^{-2}
Cpd-1	0.20
HBS-1	0.15

Eleventh layer (low-sensitivity blue-sensitive emulsion layer)	
Emulsion J (in terms of silver)	0.10
Emulsion K (in terms of silver)	0.20
Gelatin	1.00
ExS-8	2.0×10^{-4}
ExY-1	9.0×10^{-2}
ExY-3	0.90
Cpd-2	1.0×10^{-2}
HBS-1	0.30

Twelfth layer (high-sensitivity blue-sensitive emulsion layer)	
Emulsion L (in terms of silver)	0.40
Gelatin	0.60
ExS-8	1.0×10^{-4}
ExY-3	0.12
Cpd-2	1.0×10^{-3}
HBS-1	4.0×10^{-2}

Thirteenth layer (first protective layer)	
Fine grains of silver iodobromide (average grain size: 0.07 μm, AgI content: 1 mol%) (in terms of silver)	0.20
Gelatin	0.80
UV-2	0.10
UV-3	0.10
UV-4	0.20
HBS-3	4.0×10^{-2}
P-3	9.0×10^{-2}

Fourteenth layer (second protective layer)	
Gelatin	0.90
B-1 (diameter 1.5 μm)	0.10
B-2 (diameter 1.5 μm)	0.10
B-3	2.0×10^{-2}
H-1	0.40

Further, the following Cpd-3, Cpd-5 to Cpd-8, P-1, P-2 and W-1 to W-3 were added to improve preservability, processability, pressure resistance, antifungal and antimicrobial properties, antistatic properties and coatability.

In addition thereto, each layer appropriately contained B-4, F-1 to F-11, an iron salt, a lead salt, a gold salt, a platinum salt, an iridium salt and a rhodium salt.

The emulsions used in the present example are shown in Tables 1 and 2 below.

TABLE 1

Emulsion No.	Average AgI content (%)	Mean Grain size in terms of the average diameter of the corresponding spheres (μm)	Coefficient of Variation in Grain size Distribution (%)	Ratio of Diameter/ Thickness	Grain size in terms of the average diameter of circles corresponding to Projected Areas (μm)	Average Thickness (μm)
Emulsion A	2.0	0.2	12	1	-	-
" B	2.0	0.3	14	1	-	-
" C	4.7	0.3	12	1	-	-
" D	4.7	0.5	8	1	-	-
" E	8.8	0.65	22	6.5	0.16	0.16
" F	2.9	0.15	16	1	-	-
" G	2.9	0.25	18	1	-	-
" H	4.7	0.45	10	1	-	-
" I	8.8	0.60	25	7.2	1.01	0.14
" J	3.0	0.2	30	4.5	0.29	0.064
" K	3.0	0.5	26	7.0	0.84	0.12
" L	9.0	0.85	23	6.5	1.39	0.21

Each of Emulsions A to L was a silver iodobromide emulsion.

TABLE 2

Emulsion No.	Grain Structure (Iodide Structure = Ratio of Amount of silver (AgI content %))		
Emulsion A	Uniform structure	cubic grains	
" B	Uniform structure	cubic grains	
" C	Triple structure = 4/1/5	(1/38/1)	cubic grains
" D	Triple structure = 4/1/5	(1/38/1)	cubic grains
" E	Triple structure = 12/59/29	(0/11/8)	tabular grains
" F	Triple structure = 45/5/50	(1/38/1)	octahedral grains
" G	Triple structure = 45/5/50	(1/38/1)	octahedral grains
" H	Triple structure = 4/1/5	(1/38/1)	octahedral grains
" I	Triple structure = 12/59/29	(0/11/8)	tabular grains
" J	Uniform structure	tabular grains	
" K	Uniform structure	tabular grains	
" L	Triple structure = 8/59/33	(0/11/8)	tabular grains

In Tables 1 and 2 above,

(1) Each emulsion was reduction-sensitized during the preparation of the grains by using thiourea dioxide and thiosulfonic acid according to the Examples of JP-A-2-191938.

(2) Each emulsion was subjected to gold sensitization, sulfur sensitization and selenium sensitization in the presence of sodium thiocyanate and spectral sensitizing dyes according to the Examples of JP-A-3-

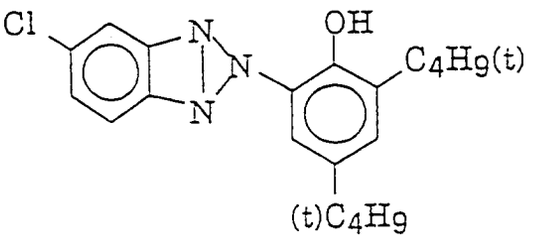
237450.

(3) Tabular grains were prepared by using low-molecular gelatin according to the Examples of JP-A-1-158426.

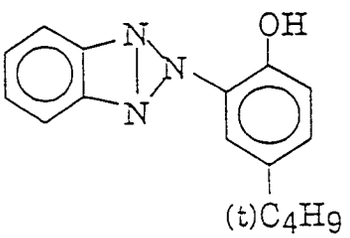
(4) Tabular grains and regular crystal grains showed dislocation lines as described in JP-A-3-237450 under observation through a high-pressure electron microscope.

The chemical structural formulas or chemical names of the compounds used in the present invention are shown below.

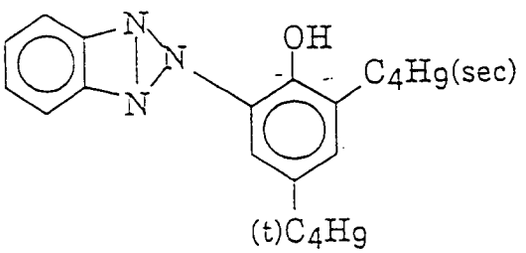
UV-1



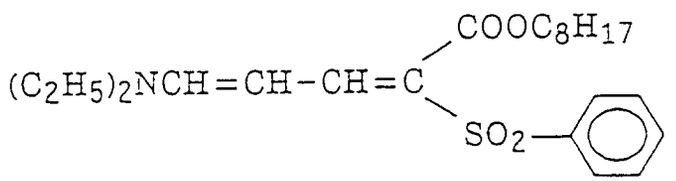
UV-2



UV-3



UV-4

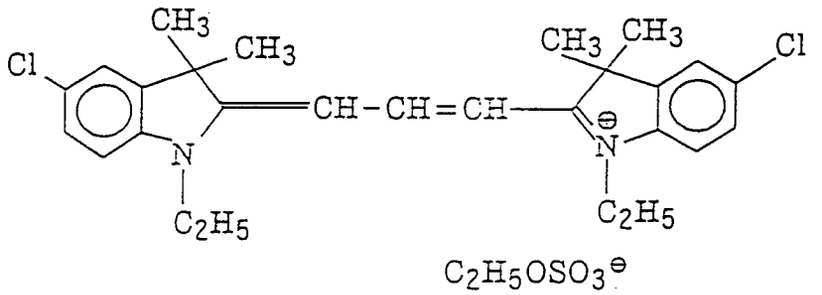


HBS-1 Tricresyl Phosphate

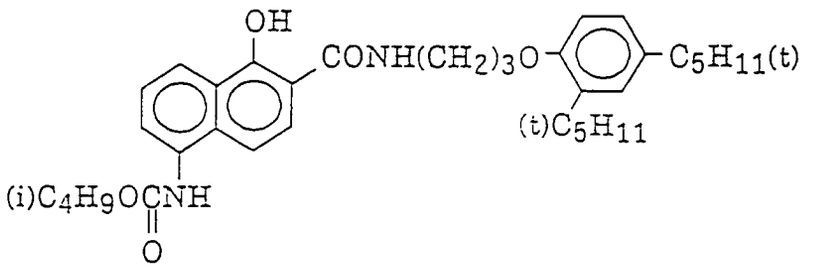
HBS-2 Dibutyl phthalate

HBS-3 Tri(2-ethylhexyl) Phosphate

ExF-1



ExC-1



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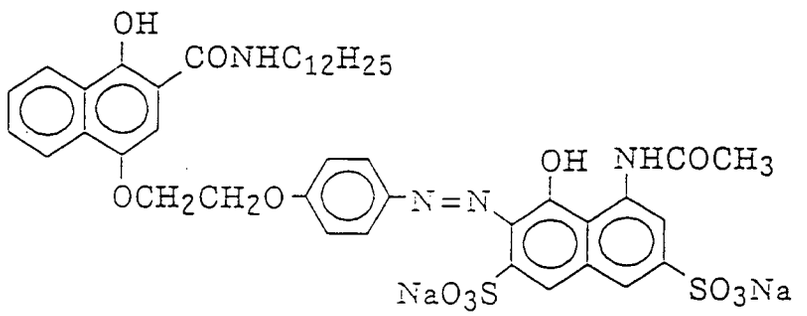

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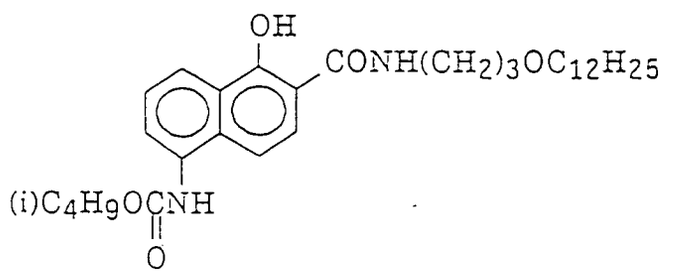

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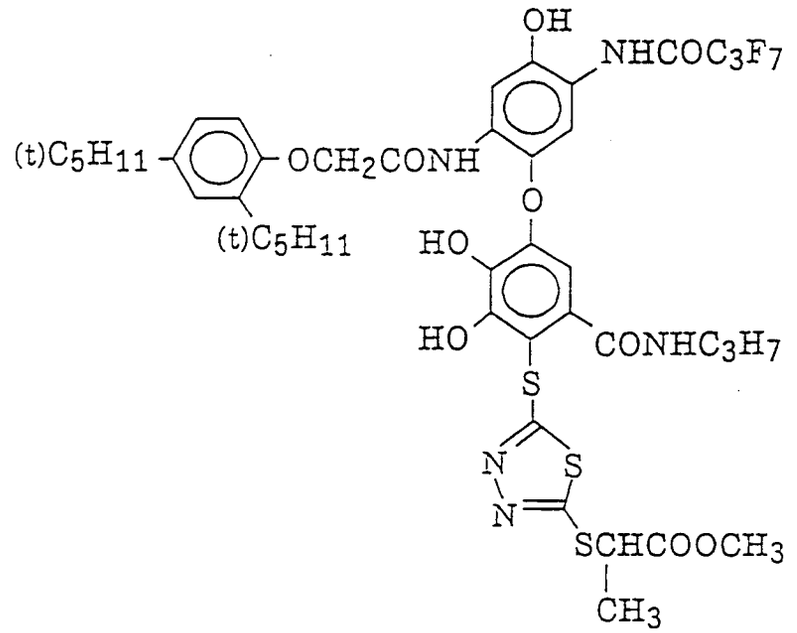

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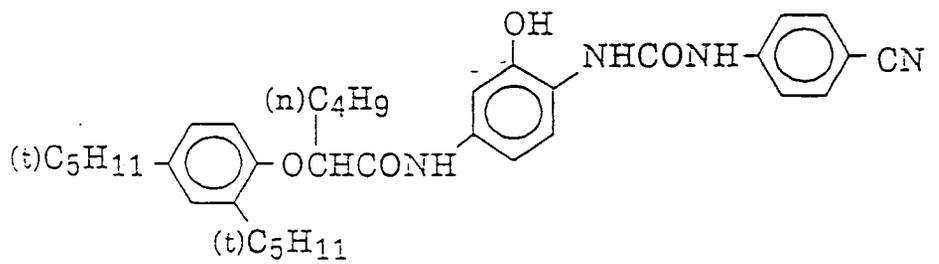
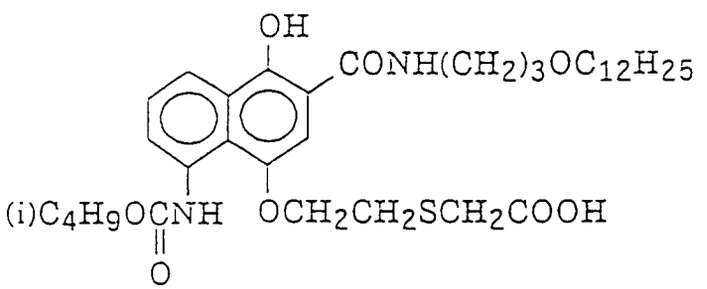
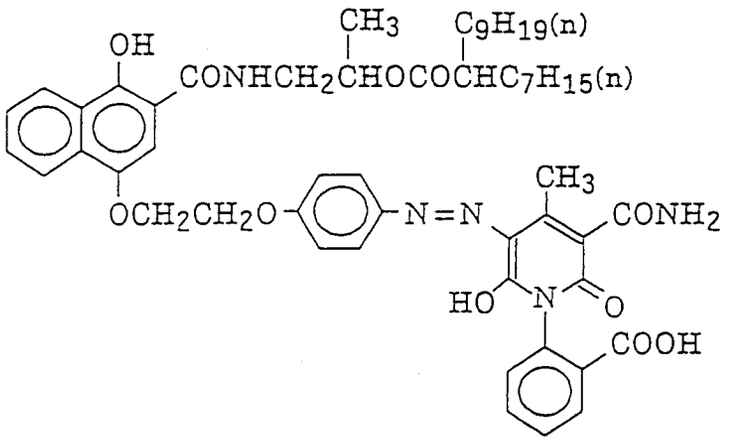


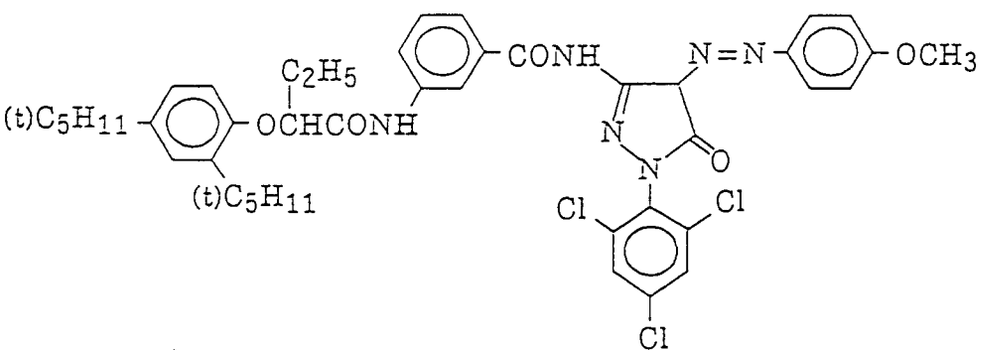
ExC-6



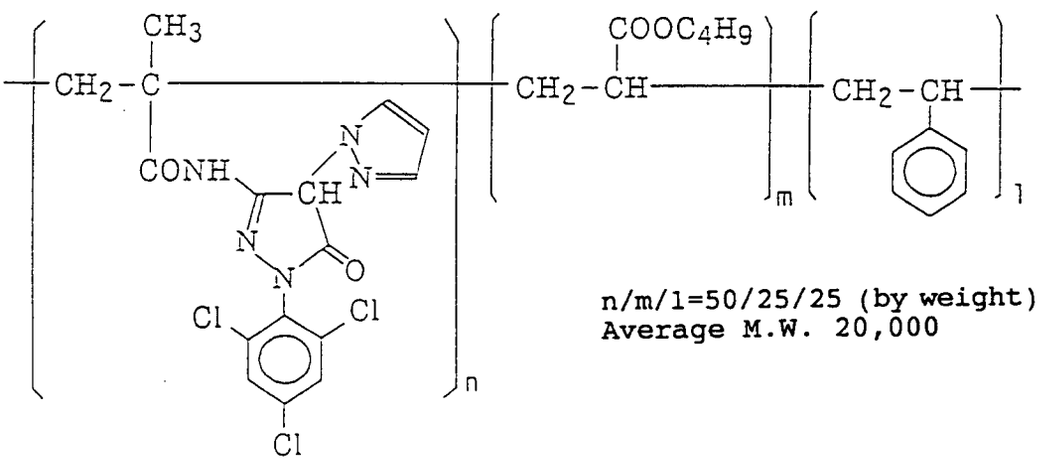
ExC-7



ExM-1

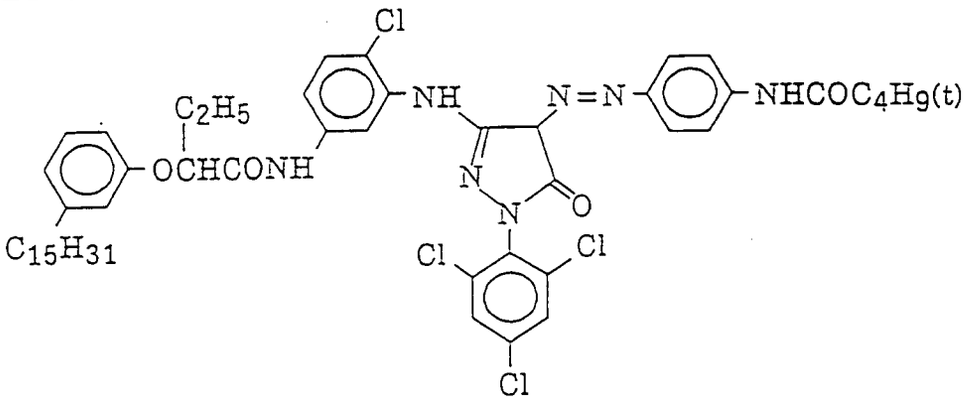


ExM-2

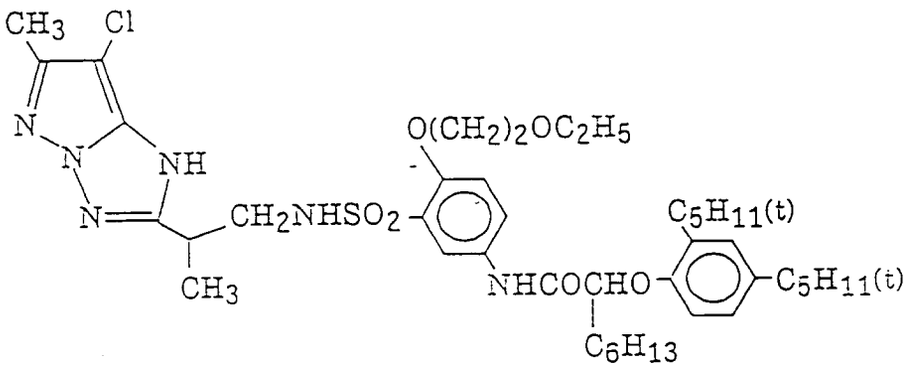


n/m/l=50/25/25 (by weight)
Average M.W. 20,000

ExM-3



ExM-4



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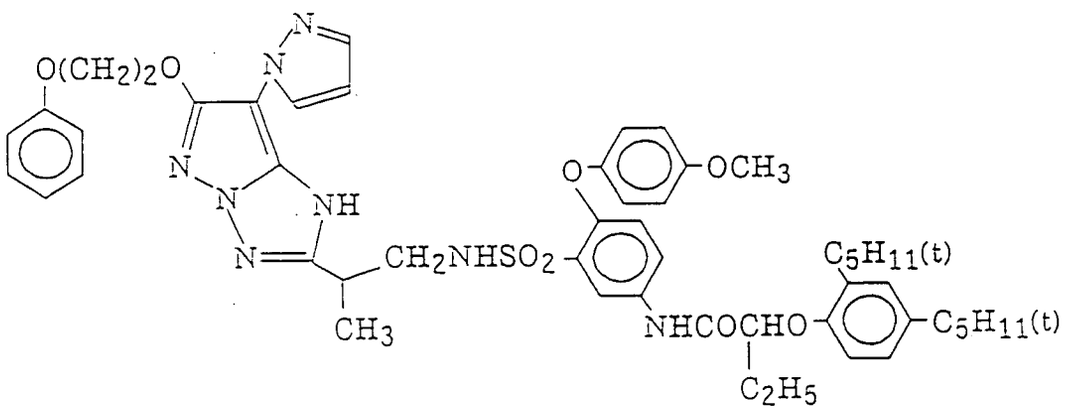
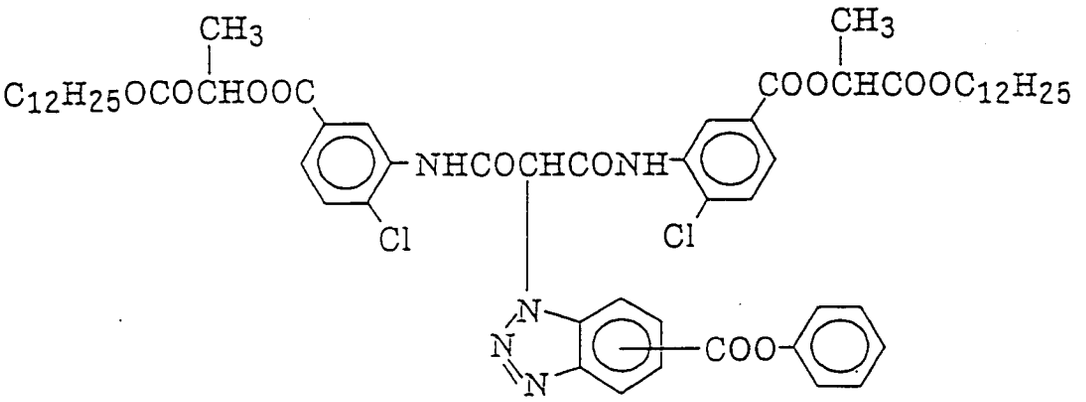


ExY-1



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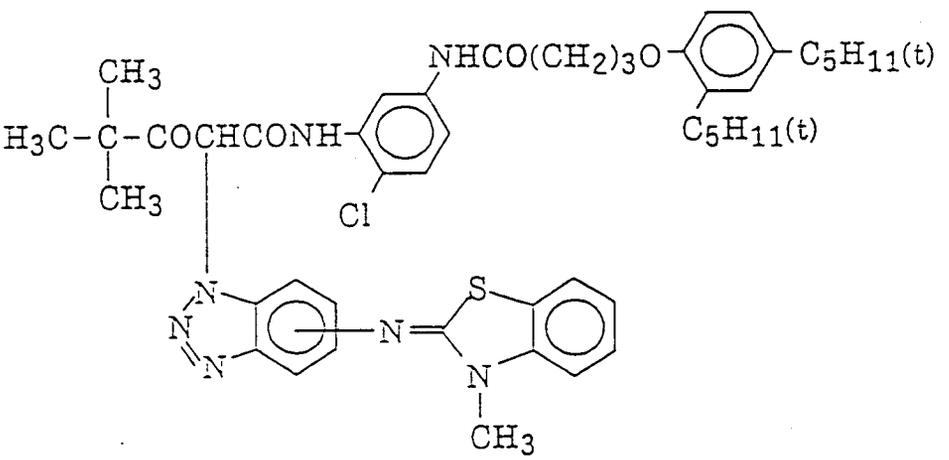
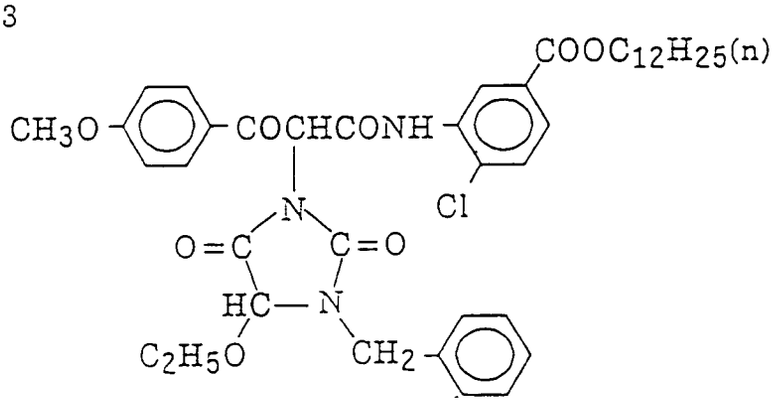
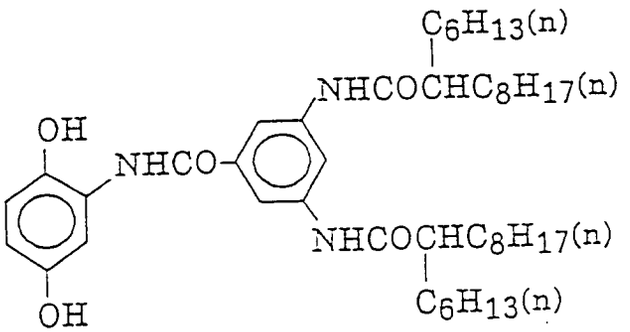


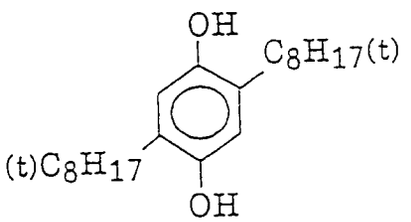
ExY-3



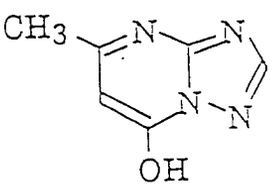
Cpd-1



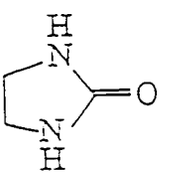
Cpd-2



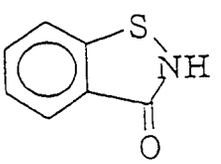
Cpd-3



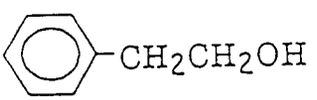
Cpd-4



Cpd-5



Cpd-6



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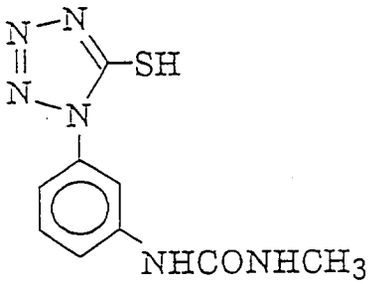
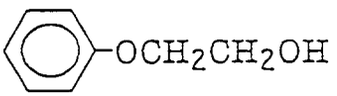
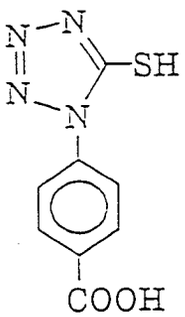


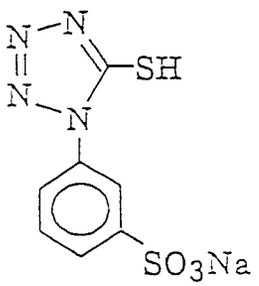
Cpd-8



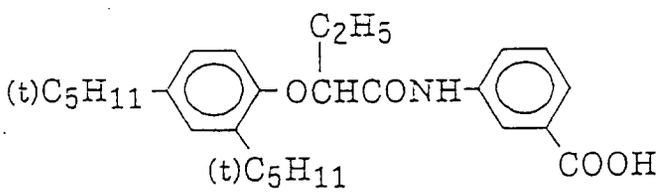
Cpd-9



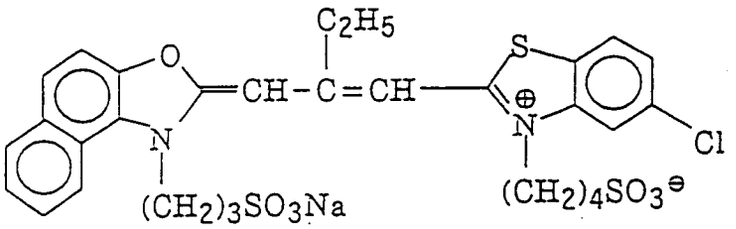
Cpd-10



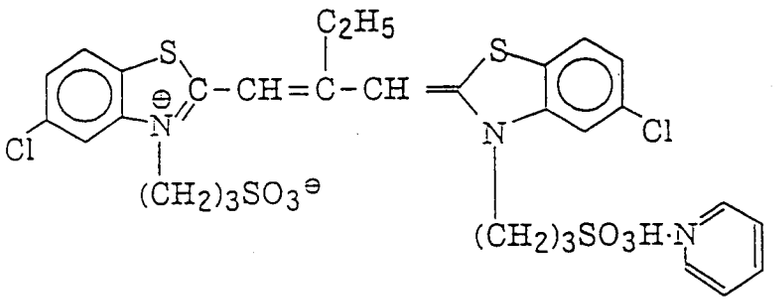
Cpd-11



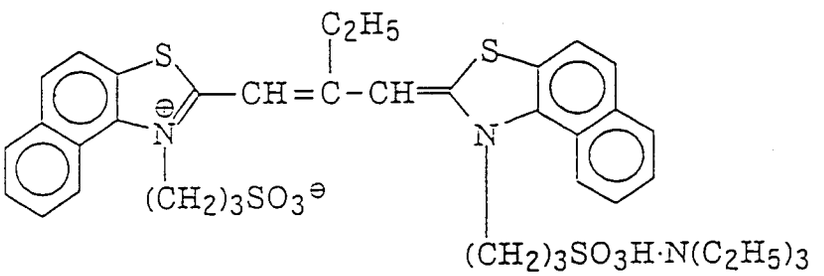
ExS-1



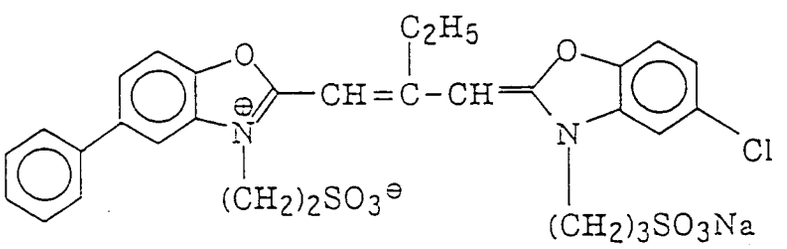
ExS-2



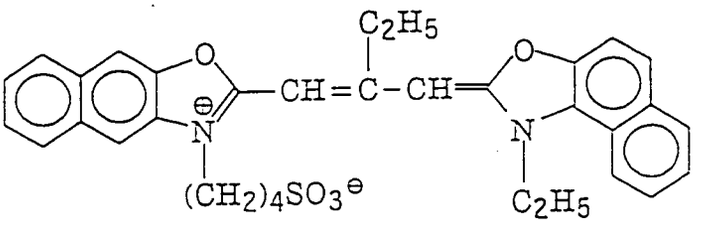
ExS-3



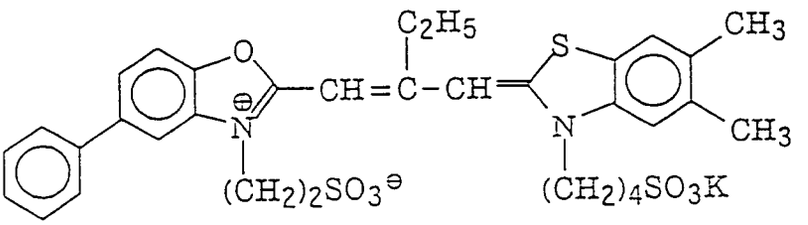
ExS-4



ExS-5



ExS-6



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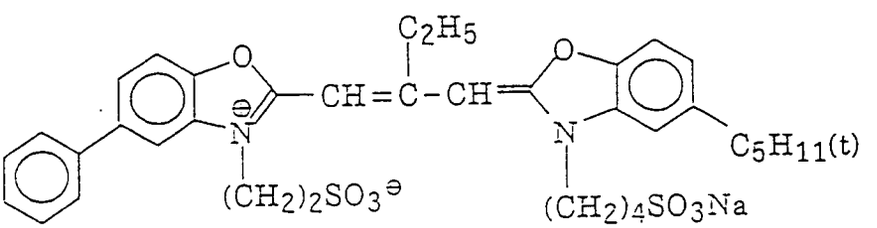
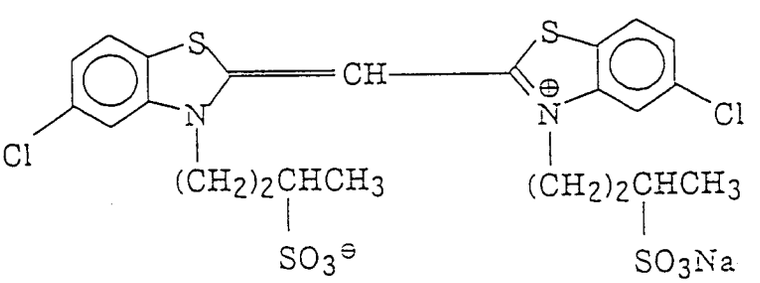
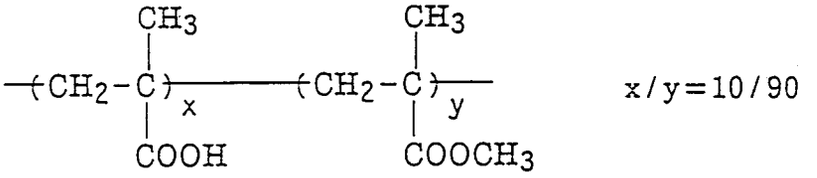


ExS-8

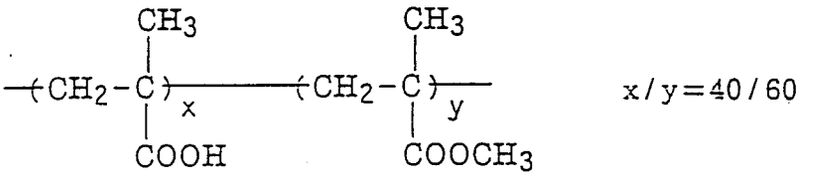


B-1



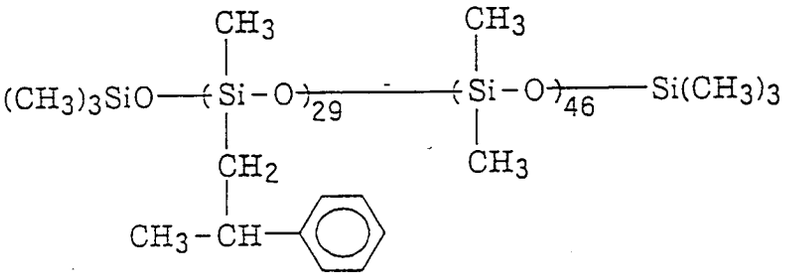
x/y=10/90

B-2

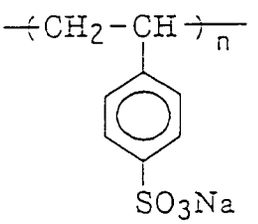


x/y=40/60

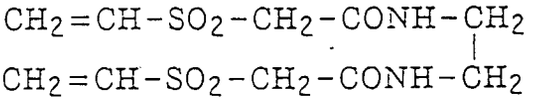
B-3



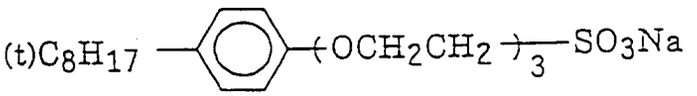
B-4



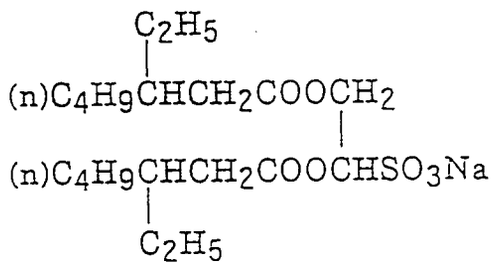
H-1



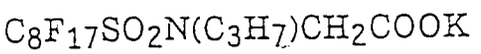
W-1



W-2



W-3

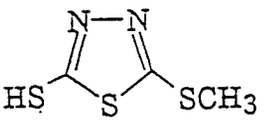


P-1 Copolymer of Vinylpyrrolidone and Vinyl Alcohol (70:30 by weight)

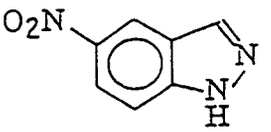
P-2 Polyvinyl Pyrrolidone (average mol. wt. = about 10,000)

P-3 Polyethyl Acrylate

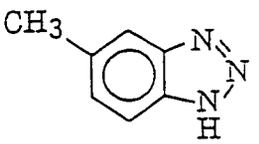
F-1



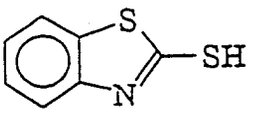
F-2



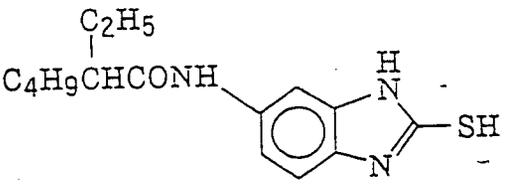
F-3



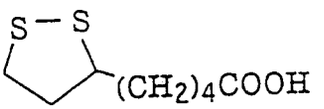
F-4



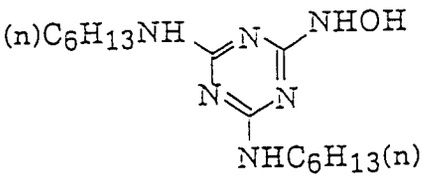
F-5



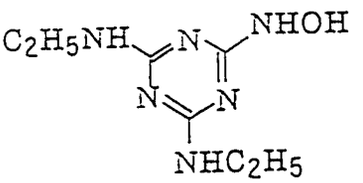
F-6



F-7



F-8



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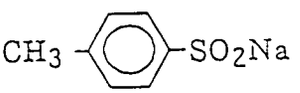

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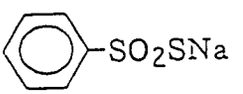

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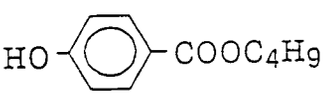

Samples A, B and D were prepared in the same manner as Sample C except that the coating weight of silver was changed as shown below while the ratio of each silver halide was not changed. Further, Samples E, F and G were prepared in the same manner as Sample C except that the layer thickness was changed as shown below by changing the amount of gelatin while the ratio of gelatin in each layer was not changed.

Sample	Coating Weight of Silver (g/m^2)	Layer Thickness (μm)
A	7	17
B	6	17
C	4	17
D	2	17
E	4	22
F	4	19
G	4	14

The color photographic materials were exposed to light, and then processed in the following manner.

(Processing Step)

Step	Processing Time	Processing Temp. (°C)
Color development	3 min 15 sec	38
Bleaching	3 min 00 sec	38
Rinse	30 sec	24
Fixing	3 min 00 sec	38
Rinse (1)	30 sec	24
Rinse (2)	30 sec	24
Stabilization	30 sec	38
Drying	4 min 20 sec	55

The processing solutions had the following compositions:

Color developing solution	Amount (g)
Diethylenetriaminepentaacetic Acid	1.0
1-Hydroxyethylidene-1,1-diphosphonic Acid	2.0
Sodium Sulfite	4.0
Potassium Carbonate	30.0
Potassium Bromide	0.4
Potassium Iodide	1.5 mg
Hydroxylamine Sulfate	2.4
4-[N-Ethyl-N-(β-hydroxyethyl)amino]-2-methylaniline Sulfate	4.5
Water to make	1.0 liter
pH (adjusted with potassium hydroxide and sulfuric acid)	10.05

Bleaching Solution	Amount (g)
Ammonium Ethylenediaminetetraacetato Ferrate	0.25 mol
3-Mercapto-1,2,4-triazole	0.03
Ammonium Bromide	140.0
Ammonium Nitrate	30.0
Ammonia Water (27%)	6.5 ml
Water to make	1.0 liter
pH (adjusted with ammonia water and nitric acid)	6.0

Fixing Solution	Amount (g)
Disodium Ethylenediaminetetraacetate	0.5
Ammonium Sulfite	20.0
Aqueous Solution of Ammonium Thiosulfate (700 g/ℓ)	295.0 ml
Acetic Acid (90%)	3.3
Water to make	1.0 liter
pH (adjusted with ammonia water and acetic acid)	6.7

Stabilizing Solution	Amount (g)
Sodium p-Toluenesulfinate	0.03
Polyoxyethylene p-Monononylphenyl Ether (average degree of polymerization : 10)	0.2
Disodium Ethylenediaminetetraacetate	0.05
1,2,4-Triazole	1.3
1,4-Bis(1,2,4-triazole-1-ylmethyl)piperazine	0.75
Water to make	1.0 liter
pH	8.5

After the samples were processed, the cyan density

$$(D_{min}^{R0})$$

of the unexposed area was measured with a photographic densitometer FSD-103 (manufactured by Fuji Photo Film Co., Ltd.) (standard density). In another experiment, processing was carried out by using the following bleaching solution in place of the above-described bleaching solution. The cyan density

$$(D_{min}^{R1})$$

of the unexposed area was measured. The difference in the density

$$(D_{min}^{R1} - D_{min}^{R0})$$

of each sample between the former processing and the latter processing was determined, and the increase (ΔDc) in cyan stain was evaluated. The results are shown in Table 3 below.

Bleaching Solution	Amount (g)
Compounds shown in Table 3	0.27 mol
Ammonia Water (27%)	56 ml
Ferric Nitrate Nonahydrate	0.25 mol
Ammonium Bromide	140
Acetic Acid	30
Water to make	1.0 liter
pH (adjusted with ammonia water and nitric acid)	4.0

Each compound shown in Table 3 below was reacted with ferric nitrate in the bleaching solution to thereby form ammonium salt of the iron(III) complex salt of the compound shown in Table 3.

TABLE 3

No.	Photographic Material			Compound in Bleaching Solution	ΔDc	Remarks
		Coating Weight of Silver (g/m^2)	Layer Thickness (μm)			
1	A	7	17	NMP	0.10	Comp. Ex.
2	B	6	17	"	0.08	"
3	C	4	17	"	0.08	"
4	D	2	17	"	0.08	"
5	E	4	22	"	0.08	"
6	F	4	19	"	0.08	"
7	G	4	14	"	0.08	"
8	A	7	17	NTA	0.12	"
9	G	4	14	"	0.11	"
10	A	7	17	I-2*	0.09	"
11	B	6	17	"	0.03	Invention
12	C	4	17	"	0.01	"
13	D	2	17	"	0.01	"

TABLE 3 (cont'd)

No.	Photographic Material			Compound in Bleaching Solution	ΔDc	Remarks
		Coating Weight of Silver (g/m^2)	Layer Thickness (μm)			
14	E	4	22	I-2*	0.11	Comp. Ex.
15	F	4	19	"	0.04	Invention
16	G	4	14	"	0.01	"
17	E	4	22	I-3*	0.10	Comp. Ex.
18	G	4	14	"	0.01	Invention
19	E	4	22	I-8*	0.10	Comp. Ex.
20	G	4	14	"	0.02	Invention
21	A	7	17	I-2**	0.09	Comp. Ex.
22	B	6	17	"	0.01	Invention
23	C	4	17	"	0	"
24	D	2	17	"	0	"
25	E	4	22	"	0.11	Comp. Ex.
26	F	4	19	"	0.01	Invention

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TABLE 3 (cont'd)

No.	Photographic Material	Coating Weight of Silver (g/m^2)	Layer Thickness (μm)	Compound in Bleaching Solution	ΔDc	Remarks
27	G	4	14	I-2**	0	Invention
28	E	4	22	I-3**	0.10	Comp. Ex.
29	G	4	14	"	0	Invention
30	E	4	22	I-8**	0.10	Comp. Ex.
31	G	4	14	"	0	Invention

* The mixture compound of the [R,R], [R,S], [S,R] and [S,S] isomer was used.

** The compound comprised 99 to 100% of the [S,S] isomer.

It is apparent from the results shown in Table 3 that when the iron(III) complex salts of nitrilomonopropionic acid diacetic acid (NMP) and nitrilotriacetic acid (NTA) which are described as the compounds having a good biodegradability in JP-A-3-186841 are used, cyan stain is increased and hence the results are not preferred in comparison with the standard processing using the iron(III) complex salt of ethylenediaminetetraacetic acid (EDTA). Further, it can be seen from the results shown in Table 3 that even when the coating weight of silver or the layer thickness of the photographic materials is changed, cyan stain

can not be prevented from being formed.

However, it is apparent from the results shown in Table 3 that cyan stain can be effectively prevented from being formed when the iron(III) complex salts of the compounds of formula (I) which have a good biodegradability according to the present invention are used, and further the coating weight of silver (2 to 6 g/m^2) and the layer thickness (12 to 20 μm) are controlled.

Further, the effect is more remarkable in Sample Nos. 21 to 31 where 99 to 100% of the [S,S] isomer was used.

EXAMPLE 2

The processing Nos. 16, 18 and 20 of Example 1 were repeated except that the concentration of each compound and ferric nitrate nonahydrate in the bleaching solution was reduced to 1/2, an equimolar amount of sodium bromide was used in place of ammonium bromide and an equimolar amount of sodium hydroxide was used in place of ammonia water. The results for each processing showed that the density of cyan stain was lower by 0.01 than the density of cyan stain for the corresponding processing in Example 1.

EXAMPLE 3

A Sample 301 was prepared in the same manner as in Example 1 except that a polyethylene naphthalate support of 100 μm in thickness was used in place of the cellulose triacetate film having a subbing layer used in the preparation of Sample C, and the striped magnetic layer described in Example 1 of JP-A-4-124628 was coated on the back side of the support. The Sample 301 was subjected to the same test as No. 12 of Example 1. It was found that similar effects to those of Example 1 were obtained.

Further, a Sample 302 was prepared in the same manner as in Example 1 except that the same support having a back layer as used in the preparation of Sample No. I-3 of Example 1 of JP-A-4-62543 was used in place of the support used in the preparation of Sample C of Example 1, and further $C_8F_{17}SO_2N(C_3H_7)$-CH_2COOK (15 mg/m^2) was used in the second protective layer. The resulting Sample 302 was processed into the format of Fig. 5 of JP-A-4-62543, and subjected to the same test as No. 12 of Example 1. It was found that effects similar to those of Example 1 were obtained.

EXAMPLE 4

Sample G as prepared in Example 1 was cut into 35-mm wide strips, imagewise exposed to light, and then subjected to continuous processing (running test) by means of an automatic developing machine until the replenishment of the bleach bath reached twice the tank capacity. The running test was conducted with the kind of the bleaching agent contained in the bleaching solution varied as set forth in Table 4.

The processing steps and the composition of the processing solutions will be given below.

(Processing step)

Step	Processing time	Processing temperature	Replenishment rate*	Tank capacity
Color development	3 min. 5 sec.	38.0 °C	23 mℓ	17 ℓ
Bleach	60 sec.	38.0 °C	5 mℓ	5 ℓ
Blix	60 sec.	38.0 °C	--	5 ℓ
Fixing	60 sec.	38.0 °C	16 mℓ	5 ℓ
Rinsing	30 sec.	38.0 °C	34 mℓ	3 ℓ
Stabilization (1)	20 sec.	38.0 °C	--	3 ℓ
Stabilization (2)	20 sec.	38.0 °C	20 mℓ	3 ℓ
Drying	1 min.	60 °C		

* Replenishment rate: per 1.1 m of 35-mm wide photographic light-sensitive material (corresponding to a roll of film with 24 exposures)

The stabilization step was effected in a countercurrent process wherein the processing solution flew backward from the bath (2) to the bath (1). The overflow liquid from the rinsing bath was all introduced into the fixing bath. The replenishment of the blix bath was conducted in such a manner that the liquids overflown through notches on the upper portion of the bleaching bath and the fixing bath in the automatic developing machine by the supply of replenishers to the bleaching bath and the fixing bath were all introduced into the blix bath. The amount of the developer brought over to the bleaching step, the amount of the bleaching solution brought over to the blix step, the amount of the blix solution brought over to the fixing step, and the amount of the fixing solution brought over to the rinsing step were 2.5 mℓ, 2.0 mℓ, 2.0 mℓ, and 2.0 mℓ per 1.1 m of 35-mm wide photographic light-sensitive material, respectively. The time required for the photographic light-sensitive material to cross over from one step to the subsequent step was 6 seconds. This time is included in the processing time for preceding process.

The composition of the various processing solutions will be given below.

Color developer (unit: g)

	Tank solution	Replenisher
Diethylenetriaminepentaacetic acid	2.0	2.0
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.0
Sodium sulfite	3.9	4.5
Potassium carbonate	37.5	38.0
Potassium bromide	1.4	0.7
Potassium iodide	1.3 mg	--
Hydroxylamine sulfate	2.4	4.0
2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline sulfate	4.5	6.0
Water to make	1.0 ℓ	1.0 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	10.05	10.15

Bleaching solution (common to both running solution and replenisher)(unit: g unless otherwise specified)

Ferric ammonium aminopolycarboxylate monohydrate	0.25 mol
Aminopolycarboxylic acid specified above	0.01 mol
Ammonium bromide	80
Ammonium nitrate	15
Hydroxyacetic acid	25
Acetic acid	40
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia)	4.4

Blix bath running solution

A 15 : 85 (volumetric ratio) mixture of the foregoing bleaching solution and the following fixing solution (pH 7.0)

Fixing solution (common to both running solution and replenisher) (unit: g unless otherwise specified)

Ammonium sulfite	19
Aqueous solution of ammonium thiosulfate (700 g/ℓ)	280 mℓ
Imidazole	15
Ethylenediaminetetraacetic acid	15
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	7.4

Rinsing solution

Tap water was passed through a mixed bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B produced by Rohm & Haas) and an OH type strongly basic anion exchange resin (Amberlite IR-400) so that the calcium and magnesium ion concentrations were each reduced to 3 mg/ℓ or less. To the solution were then added 20 mg/ℓ of dichlorinated sodium isocyanurate and 150 mg/ℓ of sodium sulfate. The pH range of the solution was from 6.5 to 7.5.

Stabilizing solution (common to both running solution and replenisher)

Sodium p-toluenesulfonate	0.03
Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10)	0.2
Disodium ethylenediaminetetraacetate	0.05
1,2,4-Triazole	1.3
1,4-Bis(1,2,4-triazole-1-ylmethyl) piperazine	0.75
Water to make	1.0 ℓ
pH	8.5

Sample G was exposed to light through an optical wedge, processed at the beginning or the end of each running test, and then measured for minimum cyan density by means of a Macbeth densitometer.

The results are set forth in Table 4.

Table 4

No.	Aminopolycarboxylic acid	Cyan Density: At the beginning of running test	Cyan Density: At the end of running test	Remarks
41	ethylenediaminetetra-acetic acid	0.30	0.36	Comp. Example
42	1,3-propanediamine-tetraacetic acid	0.34	0.39	"
43	methyliminodiacetic acid	0.33	0.38	"
44	nitrilotriacetic acid	0.30	0.36	"
45	β-alaninediacetic acid	0.31	0.38	"
46	I-1*	0.25	0.27	Invention
47	I-2*	0.25	0.27	"
48	I-3*	0.26	0.28	"
49	I-8*	0.26	0.28	"
50	I-1**	0.23	0.24	"
51	I-2**	0.23	0.23	"
52	I-3**	0.23	0.23	"
53	I-8**	0.23	0.24	"

* The mixture compound of the [R,R], [R,S], [S,R] and [S,S] isomer was used.
** The compound comprised 99 to 100 % of the [S,S] isomer.

Table 4 shows that the samples according to the present invention (No. 46 - No. 53) exhibit a low cyan density when processed at the beginning of running test and an extremely small cyan density rise with the progress of running test.

Further, Sample Nos. 50 - 53, prepared from [S, S] isomers, exhibit an even lower cyan density and provide the most desirable results.

EXAMPLE 5

Processing was effected in the same manner as in No. 12 processing of Example 1 except that Samples H, I, J and K, prepared by replacing the cyan coupler ExC-5 in the 5th layer in Sample C by the cyan couplers set forth in Table 5 in the equimolecular amount, respectively, were used (bleaching agent: I-2*).

The samples thus processed were measured for yellow density on unexposed portion, allowed to stand at a temperature of 60 °C and a relative humidity of 70 % for 15 days, and then again measured for yellow density on unexposed portion to determine a rise in yellow density on unexposed portion with time (ΔD_Y).

The results are set forth in Table 5.

Table 5

Sample	Cyan Coupler	Yellow Density Rise (ΔD_Y)
C	ExC-5 (CI-3)	0.02
H	CI-2	0.02
I	CI-6	0.03
J	C_p-R	0.08
K	ExC-3	0.06

C_p-R

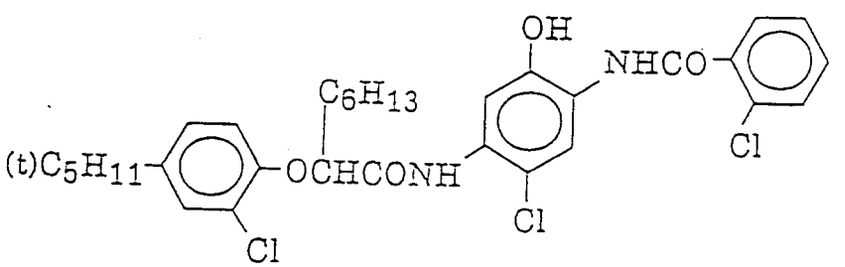


Table 5 shows that the photographic light-sensitive materials comprising cyan couplers represented by formula (CI) advantageously exhibit a small rise in yellow density on unexposed portion with time.

EXAMPLE 6

Processing was effected in the same manner as in No. 15 processing of Example 1 except that acetic acid to be contained in the bleaching solution was replaced by malonic acid or succinic acid in the equimolecular amount. As a result, the rise in the amount of cyan stain (ΔD_c) was reduced to 0.01 in all the cases.

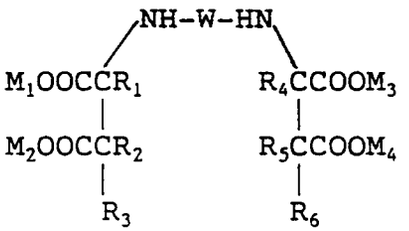
It will be understood from the above disclosure that according to the processing method of the present invention, cyan stain can be effectively prevented from being formed and a color image having excellent

photographic characteristics can be obtained when the iron(III) complex salts of the compounds of formula (I) which have a good biodegradability are used as the bleaching agents, and the total coating weight of silver and the dry thickness of the color photographic material containing silver iodide are controlled.

Further, when the [S,S] isomer of the compound represented by formula (I) is mainly used, cyan stain can be more effectively prevented from being formed.

Claims

1. A method for processing a silver halide color photographic material which comprises processing a silver halide color photographic material with a bleaching solution, wherein the bleaching solution contains an iron(III) complex salt of a compound represented by formula (I), the silver halide color photographic material has at least one silver halide emulsion layer having a silver iodide content of 1 to 30 mol% provided on one surface of a support, has the total weight of coated silver of 2 to 6 g per m^2, and has the total of the dry thicknesses of hydrophilic colloid layers on said one surface of 12 to 20 μm:



(I)

wherein R_1, R_2, R_3, R_4, R_5 and R_6 each represents a hydrogen atom, an aliphatic group, an aromatic group or a hydroxyl group; W represents a bonding group represented by the following formula (W); and M_1, M_2, M_3 and M_4 each represents a hydrogen atom or a cation:

$$-(W_1 - Z)_n - W_2 - \qquad (W)$$

wherein W_1 represents an alkylene group or a single bond; W_2 represents an alkylene group or -CO-; Z represents a single bond, -O-, -S-, -CO- or -N(Rw)-, wherein Rw represents a hydrogen atom or an alkyl group which may be substituted, provided that Z and W_1 are not a single bond at the same time; and n is an integer of 1 to 3.

2. The method of claim 1, wherein the total coating weight of silver is 2 to 4 g per m^2 of the color photographic material.

3. The method of claim 1, wherein the total coating weight of silver is 2 to 3 g per m^2 of the color photographic material.

4. The method of claim 1, wherein the sum total of the dry thickness of the hydrophilic colloid layers exclusive of back layers is 12 to 18 microns.

5. The method of claim 1, wherein the sum total of the dry thickness of the hydrophilic colloid layers exclusive of back layers is 12 to 17 microns.

6. The method of claim 1, wherein R_1, R_2, R_3, R_4, R_5 and R_6 each represents a hydrogen atom, an alkyl group, an aromatic group, or a hydroxyl group.

7. The method of claim 1, wherein R_1, R_2, R_3, R_4, R_5 and R_6 each represents a hydrogen atom or a hydroxyl group.

8. The method of claim 1, wherein R_1, R_2, R_3, R_4, R_5 and R_6 each represents a hydrogen-atom.

9. The method of claim 1, wherein W_1 and W_2 each represents an alkylene group having 1 to 3 carbon atoms.

10. The method of claim 1, wherein Z represents a single bond.

11. The method of claim 1, wherein n is 1.

12. The method of claim 1, wherein a [S,S] isomer of the compound represented by formula (I) is selectively used.

13. The method of claim 1, wherein the iron(III) complex salt of a compound represented by formula (I) is used in an amount of 0.02 to 1.0 mol per liter of the bleaching solution.

14. The method of claim 1, wherein the bleaching solution has a pH of from 3 to 7.

15. The method of claim 14, wherein the bleaching solution has a pH of from 3.5 to 6.5.

16. The method of claim 15, wherein the bleaching solution has a pH of from 3.5 to 5.0.

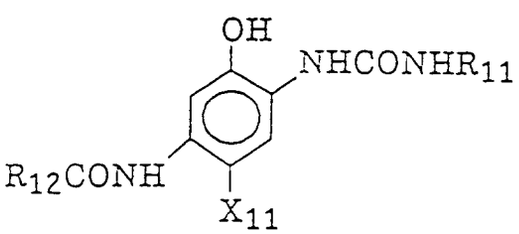
17. The method of claim 1, wherein the bleaching solution contains an acid having a pKa value of 2.0 to 5.0.

18. The method of claim 1, wherein the bleaching solution contains an acid having a pKa value of 2.0 to 5.0 in an amount of 0.01 to 4 mol/l.

19. The method of claim 17, wherein the acid having a pKa value of 2.0 to 5.0 is a polybasic organic acid.

20. The method of claim 1, wherein the silver halide emulsion layers of the silver halide color photographic material has a silver iodide content of 2 to 25 mol%.

21. The method of claim 1, wherein the silver halide photographic material contains at least one cyan coupler represented by formula (CI):



(CI)

wherein R_{11} represents an aryl group, R_{12} represents an alkyl or an aryl group, X_{11} represents a hydrogen atom or a group capable of splitting off by a coupling reaction with an oxidation product of an aromatic primary amine developing agent.

22. The method of claim 21, wherein the coupler represented by formula (CI) is used in the total amount of 2 to 2 x 10^{-3} mol per mol of silver halide contained in the same layer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 11 6452

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 556 782 (KONICA CORPORATION) 25 August 1993 * Example 5 *	1-22	G03C7/42 G03C7/30
P,X	EP-A-0 553 569 (KONICA CORPORATION) 4 August 1993 * example 2 *	1-22	
P,X	EP-A-0 532 003 (KONICA CORPORATION) 17 March 1993 * Example 2 *	1-22	
D,A	EP-A-0 430 000 (AGFA-GEVAERT AG) 5 June 1991 * See claim 1 *	1-22	
A	US-A-4 983 315 (PROCTER AND GAMBLE CO.) 8 January 1991 * whole document * & JP-A-3 173 857 (D,A)	1-22	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	28 FEBRUARY 1994	GUILLEMOIS F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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