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(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
**210 Nakanuma**
**Minami Ashigara-shi**
**Kanagawa 250-01(JP)**

(72) Inventor: **Ishikawa, Takatoshi, c/o Fuji Photo Film Co., Ltd.**
**No. 210, Nakanuma**
**Minami Ashigara-shi, Kanagawa(JP)**
Inventor: **Seki, Hiroyuki, c/o Fuji Photo Film Co., Ltd.**
**No. 210, Nakanuma**
**Minami Ashigara-shi, Kanagawa(JP)**

(74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**
**Maximilianstrasse 58**
**D-80538 München (DE)**

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

(57) A method for processing a silver halide color photographic material, which greatly improves properties with regard to color stain, fading by heat and color restorability is provided, the method comprising processing a silver halide color photographic material containing a cyan coupler of formula (I) with a bath having a bleaching ability and containing an iron (III) complex of a compound of formula (II) after color development.

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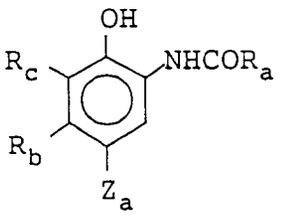
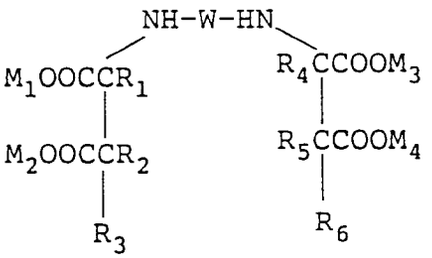


(I)



(II)

## FIELD OF THE INVENTION

This invention relates to a method for processing a silver halide color photographic material, and more particularly to a method for processing a silver halide color photographic material, which enables color restorability (dye reciprocity) to be greatly improved even through rapidly processed, and moreover which markedly prevents dyes from being faded by heat and prevents color stain.

## BACKGROUND OF THE INVENTION

Color developing solutions containing aromatic primary amine color developing agents have been conventionally used to form a color image, and play a leading role in color image formation. However, the color developing solutions have a problem in that they are easily oxidized by air and metals. It is well known that when a color image is formed by using the oxidized developing solutions, fog is increased and sensitivity and gradation are fluctuated, and hence desired photographic characteristics can not be obtained.

Nowadays, the fluctuation in photographic characteristics during continuous processing of the photographic materials tends to increase with shortening of the processing time in particular, and a serious problem with regard to color stain sometimes occurs. This problem is liable to occur particularly when a desilverization stage or a rinsing stage after color development are shortened.

Such a fluctuation in photographic characteristics during continuous processing and color stain as described above are considered to be due to the following matters.

A. The color developing solutions are deteriorated with time, and photographic characteristics are fluctuated, and at the same time, the oxidation products of the developing agents are deposited on the photographic materials, thereby forming color stain.

B. The color developing agents are brought into bleaching solutions and bleaching-fixing solutions and are oxidized, whereby fogging and staining occur.

C. Materials dissolved out from the photographic materials are accumulated in the color developing solutions and deposited on the photographic materials, whereby color stain occurs.

D. Dyes and sensitizing dyes contained in the photographic materials are insufficiently washed off, and as a result, coloration of the photographic materials occurs.

E. Processing solutions in the desilverization stage or solutions in the stabilizing stage subsequent thereto are deteriorated with time, and hence color stain occurs.

F. Bleaching agents remain in the photographic materials after processing, thereby causing color stain.

With regard to E and F among the above-described matters, an improvement in the problem of color stain greatly depends on the types of the bleaching agents, and it is required that fogging is not caused with time even when the stability of rinsing solutions is improved and bleaching components remain in the photographic materials. Further, the improvement in the problem of color stain greatly depends on the types of couplers used.

Rapid processing, i.e., shortening of the processing time, has been highly desired in the art in recent years, and it is particularly desired to shorten the processing time of the desilverization stage which accounts for about half of the entire processing time.

The bleaching step in the desilverization stage includes so-called a color restoration stage wherein not only silver is oxidized, but also leuco ion dye is oxidized, thereby forming a cyan dye. However, when the bleaching time is shortened, oxidation proceeds insufficiently so that lowering of the maximum density of cyan color, that is, a failure in color restoration is caused.

To solve the problem, addition of various bleaching accelerators in the bleaching bath, the bleaching-fixing bath or a prebath thereof has been proposed for enhancing the bleaching power, such as ammonium bromide described in JP-A-51-87036 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), water-soluble iodides described in U.K. Patent 926,569 and halides described in JP-B-53-11854 (the term "JP-B" as used herein means an "examined Japanese patent publication").

When bleaching with bleaching solutions or bleaching-fixing solutions containing iron complex salts of ethylenediaminetetraacetic acid (EDTA) etc. is carried out immediately after processing using reducing agents such as color development, there is caused a problem that the reducing agents are carried on the photographic materials and brought into the subsequent bath having a bleaching ability, so that the failure in the restoration of cyan color is liable to occur.

Couplers described in JP-B-49-11572 and JP-A-59-166956 are known as cyan couplers capable of inhibiting color fading. Some of these couplers are expected to improve color restorability. However, the

effect is not sufficient.

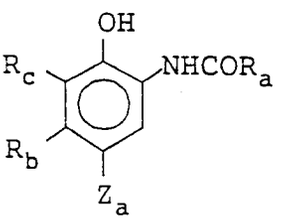
When the above-described methods are applied independently, color stain, color fading by heat or color restorability can be improved to some extents, but still insufficient.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for processing a silver halide color photographic material, which greatly improves the problems of color stain, color fading by heat and color restorability.

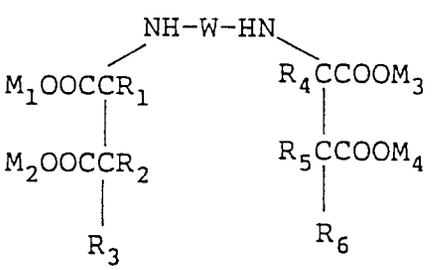
As a result of extensive studies on compounds capable of being used as bleaching agents, the present inventors have found compounds having an excellent effect as bleaching agent which have not been used in the field of photography. The processing method providing an excellent effect on color stain, etc. has been accomplished on based on the above discovery.

Namely, the above-described object of the present invention has been achieved by the method for processing a silver halide color photographic material which comprises processing a silver halide color photographic material containing at least one cyan coupler represented by formula (I) with a bath having a bleaching ability and containing at least one iron (III) complex of compounds represented by formula (II) after color development:



(I)

wherein $R_a$ represents an alkyl group, a cycloalkyl group, an aryl group, an amino group or a heterocyclic group; $R_b$ represents an acylamino group or an alkyl group having at least 2 carbon atoms; $R_c$ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; or $R_c$ and $R_b$ may be combined together to form a ring; $Z_a$ represents a hydrogen atom, a halogen atom or a group which is eliminated by the reaction with an oxidation product of aromatic primary amine developing agents,



(II)

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:

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

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 $-N(R_W)-$ (wherein $R_W$ is a hydrogen atom or an alkyl group which may be substituted) provided that Z and $W_1$ are not simultaneously a single bond; and n represents an integer of 1 to 3.

## DETAILED DESCRIPTION OF THE INVENTION

The cyan couplers of formula (I) will be illustrated in greater detail below.

In formula (I), the alkyl group represented by $R_a$ is preferably an alkyl group having 1 to 32 carbon atoms. Examples of the alkyl group include methyl group, butyl group, tridecyl group, cyclohexyl group and allyl group. Examples of the aryl group represented by $R_a$ include phenyl group and naphthyl group. A typical example of the heterocyclic group represented by $R_a$ includes 2-pyridyl group. When $R_a$ is an amino group, a phenyl-substituted amino group is particularly preferred and the phenyl moiety thereof may be substituted.

The groups represented by $R_a$ may be substituted by one or more substituents selected from the group consisting of an alkyl group, an aryl group, an alkyl-or aryloxy group (e.g., methoxy, dodecyloxy, methoxyethoxy, phenyloxy, 2,4-di-t-amylphenoxy, 3-t-buty-4-hydroxyphenyloxy, and naphthyloxy), a carboxy group, an alkyl- or arylcarbonyl group (e.g., methoxycarbonyl, and phenoxycarbonyl), an acyloxy group (e.g., acetyl, and benzoyloxy), a sulfamoyl group (e.g., N-ethylsulfamoyl, and N-octadecylsulfamoyl), a carbamoyl group (e.g., N-ethylcarbamoyl, and N-methyldodecylcarbamoyl), a sulfonamido group (e.g., methanesulfonamido, and benzenesulfonamido), an acylamino group (e.g., acetylamino, benzamido, ethoxycarbonylamino, and phenylaminocarbonylamino), an imido group (e.g., succinimido, and hydantoinyl), a sulfonyl group (e.g., methanesulfonyl), a hydroxyl group, a cyano group, a nitro group and a halogen atom.

In formula (I), $Z_a$ is a hydrogen atom, a halogen atom or a group which is eliminated by the reaction with an oxidation product of the aromatic primary amine color developing agents (an eliminable group). The eliminable group and the halogen atom are collectively referred to as "coupling-eliminable group" (which is eliminated upon the coupling reaction with the oxidation product). Examples of the coupling-eliminable group include a halogen atom (e.g., fluorine atom, chlorine atom, and bromine atom), an alkoxy group (e.g., dodecyloxy, methoxycarbamoylmethoxy, carboxypropyloxy, and methylsulfonylethoxy), an aryloxy group (e.g., 4-chlorophenoxy, and 4-methoxyphenoxy), an acyloxy group (e.g., acetoxy, tetradecanoyloxy, and benzoyloxy), a sulfonyloxy group (e.g., methanesulfonyloxy, and toluenesulfonyloxy), an amido group (e.g., dichloroacetylamino, methanesulfonylamino, toluenesulfonylamino), an alkoxycarbonyloxy group (e.g., ethoxycarbonyloxy, and benzyloxycarbonyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), an aliphatic or aromatic thio group (e.g., phenylthio, and tetrazolylthio), an imido group (e.g., succinimido, and hydantoinyl), an N-heterocyclic group (e.g., 1-pyrazolyl, and 1-benztriazolyl) and an aromatic azo group (e.g., phenylazo). These eliminable groups may contain a photographic useful group.

In formula (I), $R_b$ is an acylamino group or an alkyl group having at least 2 carbon atoms (e.g., ethyl, propyl, and t-butyl), and $R_c$ is a hydrogen atom, a halogen atom (e.g., fluorine atom, chlorine atom, and bromine atom), an alkyl group (e.g., methyl, ethyl, and propyl) or an alkoxy group (e.g., methoxy, and ethoxy), or $R_b$ and $R_c$ may be combined together to form a ring.

Specific examples of the cyan couplers of formula (I) include the following compounds, but the present invention is not limited thereto.

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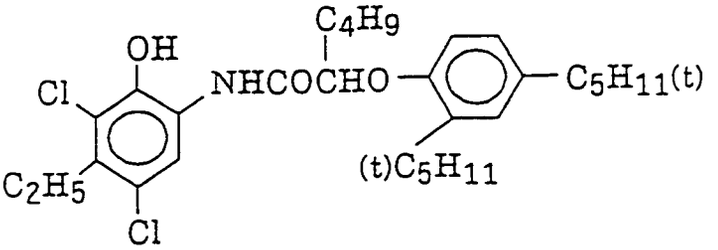

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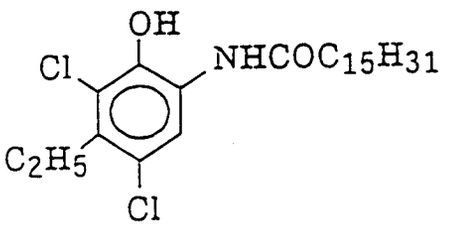

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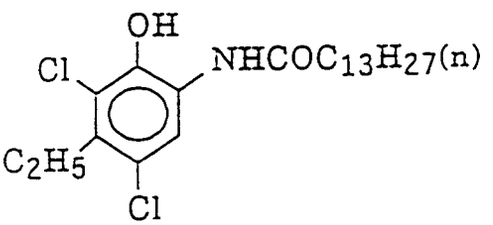

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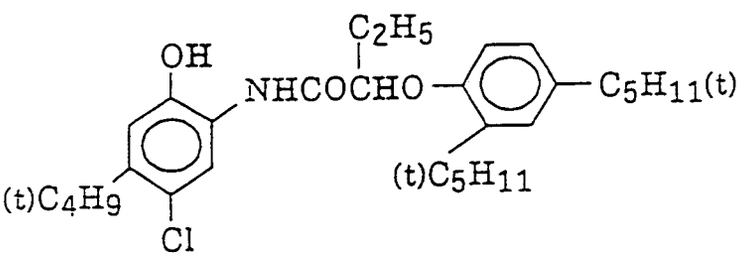

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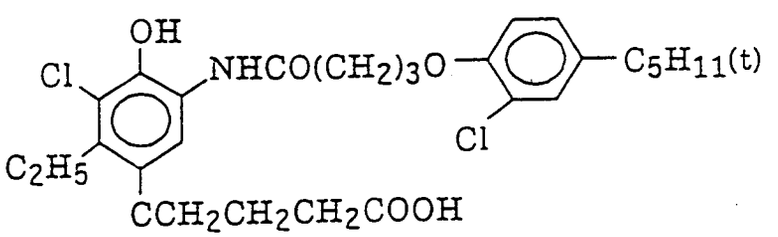

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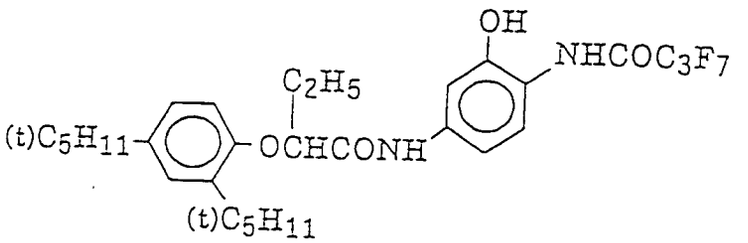

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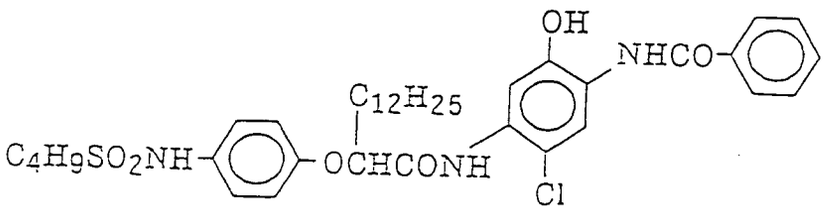

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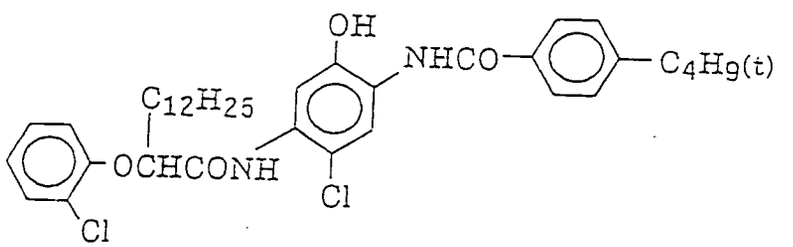

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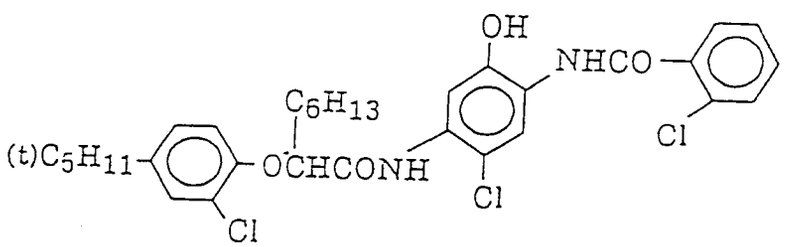

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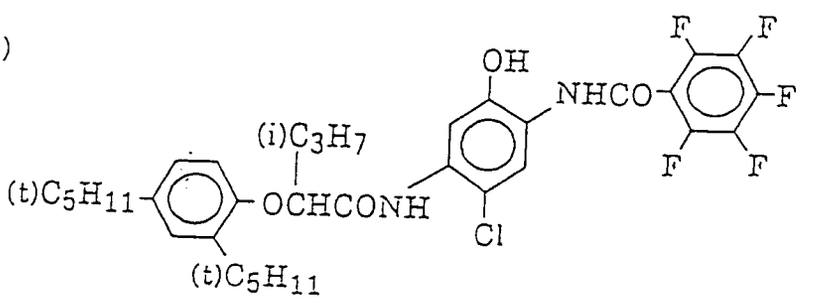

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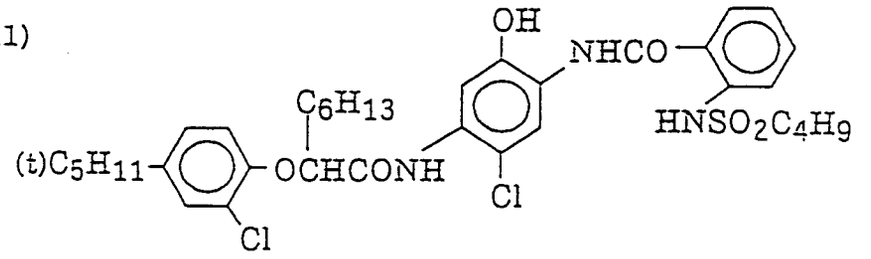

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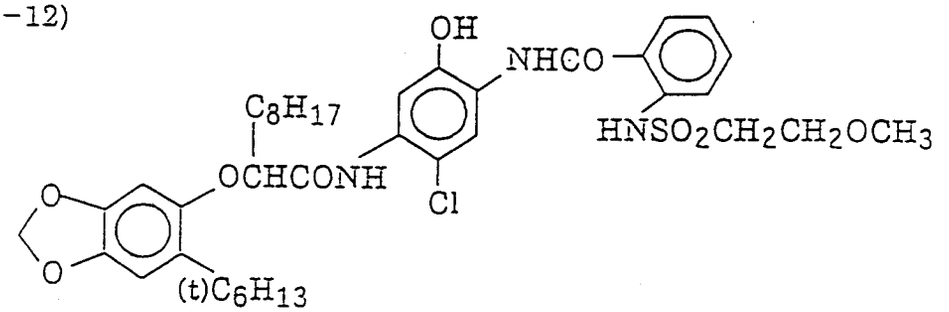

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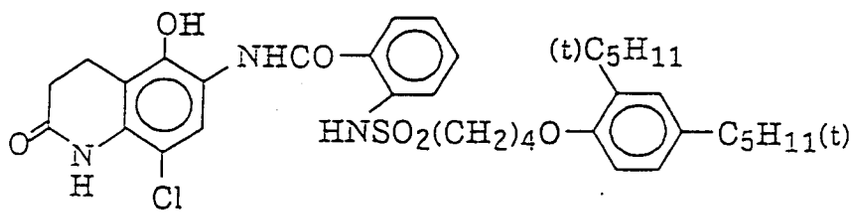

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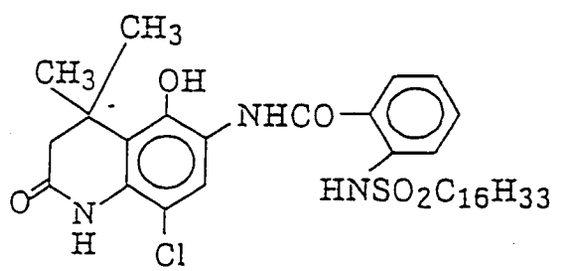

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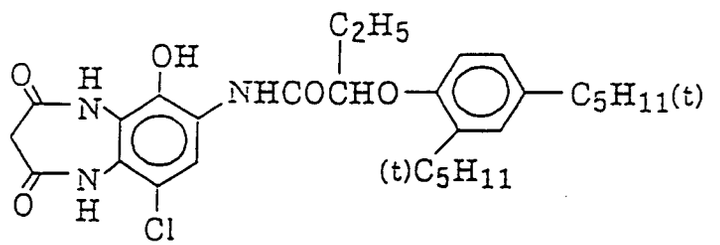

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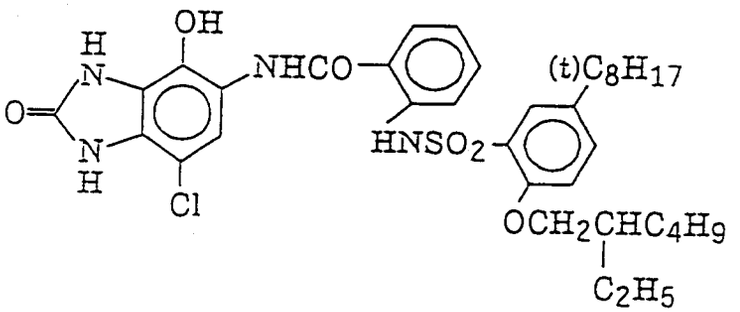

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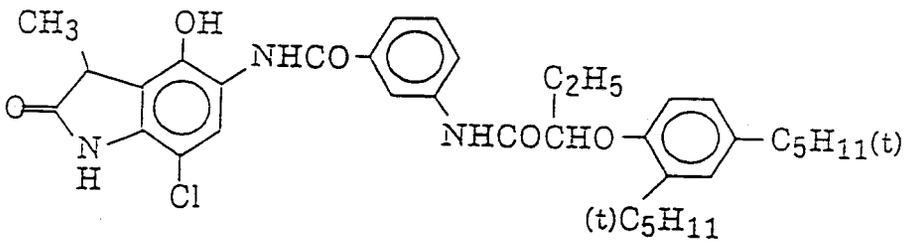

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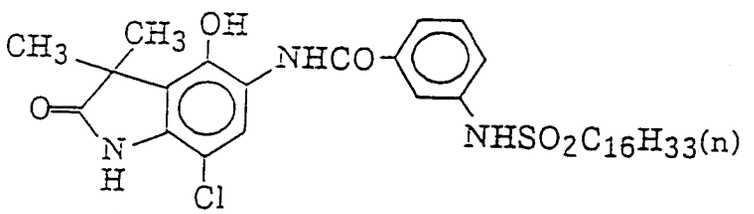

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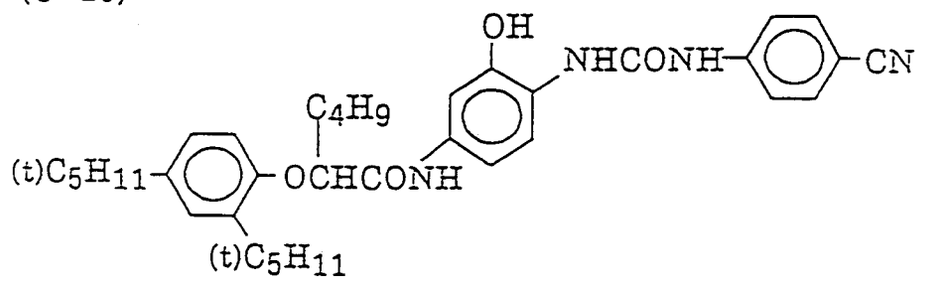


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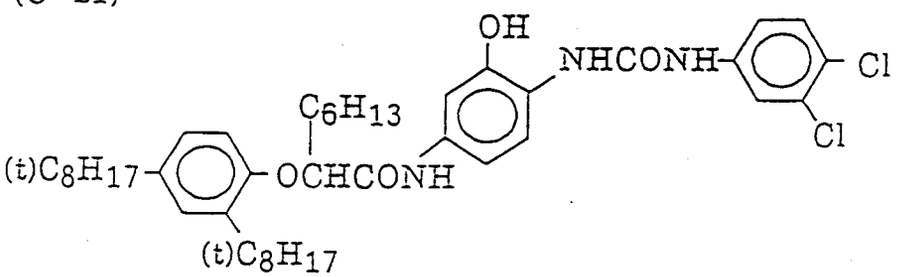


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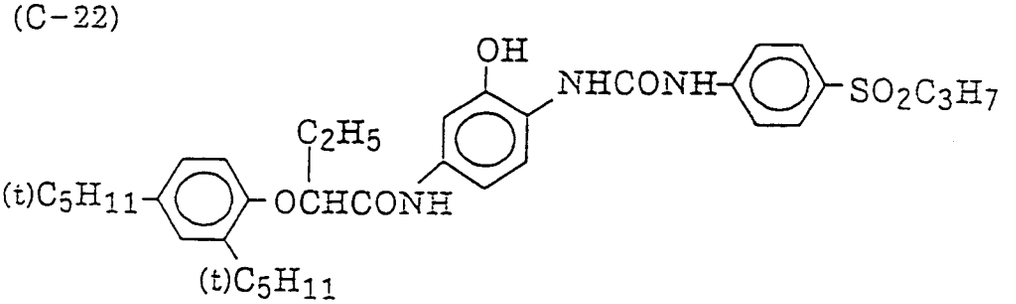


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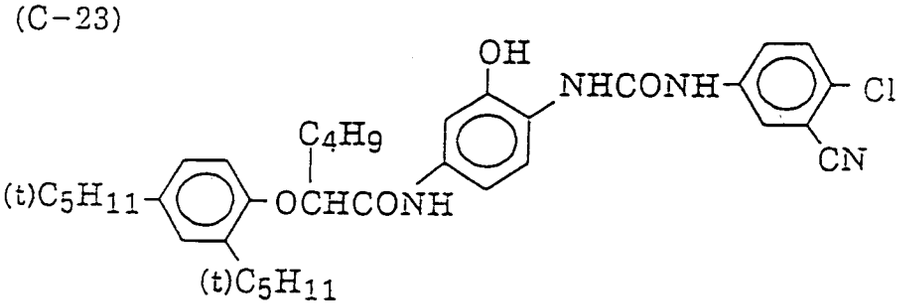

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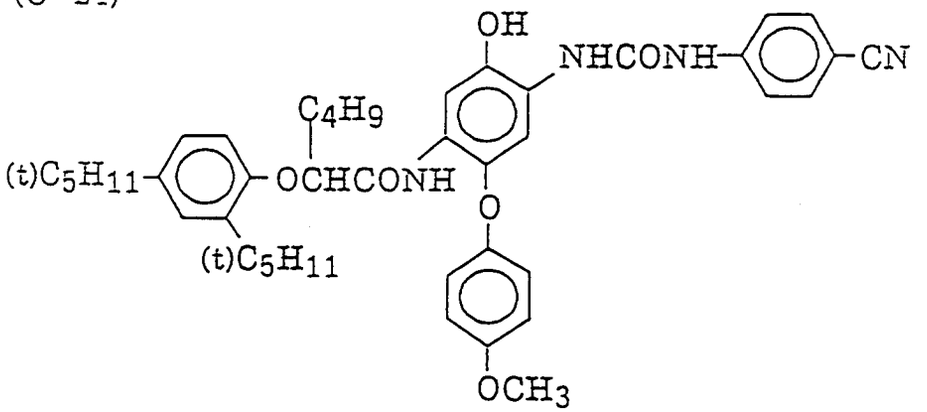

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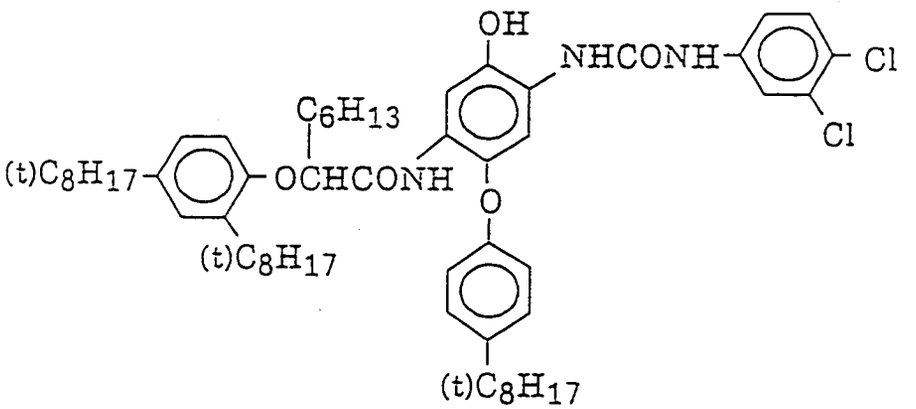

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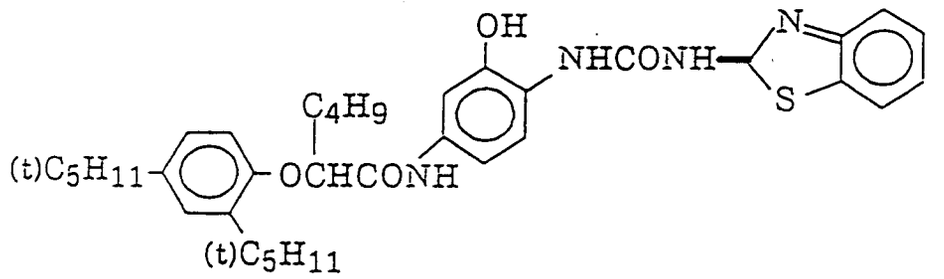


The cyan couplers of formula (I) can be synthesized by the methods described in JP-A-59-166956 and JP-B-49-11572.

Though the amount of the cyan coupler of the present invention to be contained in the photographic material is not particularly limited, it is preferably from $1\times10^{-6}$ to $1\times10^{-2}$ mol, more preferably $1\times10^{-5}$ to $1\times10^{-3}$ mol per $m^2$ of the photographic material.

The compounds of formula (II) which are used in formation of the iron (III) complexes to be contained in the bath having a bleaching ability will be illustrated below.

One feature of the present invention resides in the use of the compounds of formula (II).

The aliphatic group represented by $R_1$, $R_2$, $R_3$, $R_4$, $R_5$ and $R_6$ in formula (II) is preferably a straight chain, branched or cyclic alkyl, alkenyl or alkynyl group having up to 10 carbon atoms. More preferably, the aliphatic group is an alkyl group having 1 to 4 carbon atoms. Particularly preferred are methyl group and ethyl group.

The aromatic group represented by $R_1$, $R_2$, $R_3$, $R_4$, $R_5$ and $R_6$ is preferably a monocyclic or bicyclic aryl group. Examples of the aryl group include phenyl group and naphthyl group. 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 be substituted by one or more substituent groups such as an alkyl group (e.g., methyl, and ethyl), an aralkyl group (e.g., phenylmethyl), an alkenyl group (e.g., allyl), an alkynyl group, an alkoxy group (e.g, methoxy, and ethoxy), an aryl group (e.g., phenyl, and p-methylphenyl), an amino group (e.g., dimethylamino), an acylamino group (e.g., acetylamino), a sulfonylamino group (e.g., methanesulfonylamino), a ureido group, a urethane group, an aryloxy group (e.g., phenyloxy), a sulfamoyl group (e.g., methylsulfamoyl), a carbamoyl group (e.g., carbamoyl, and 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, and fluorine atom), a cyano group, a sulfo group, a carboxy group, a phosphono group, an aryloxycarbonyl group (e.g., phenyloxycarbonyl), an acyl group (e.g., acetyl, and 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 product or a salt, if possible.

When the above-described substituent groups have a carbon atom, the number of carbon atoms contained therein is preferably 1 to 4.

$R_1$, $R_2$, $R_3$, $R_4$, $R_5$ and $R_6$ are each preferably a hydrogen atom or a hydroxy group, more preferably a hydrogen atom.

W is a bonding group represented by formula (W):

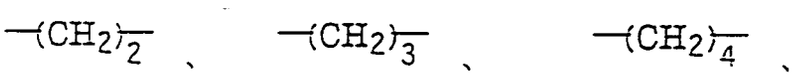
$$-(W_1\text{-}Z)_n\text{-}W_2- \quad (W)$$

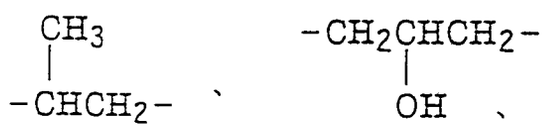
In formula (W), $W_1$ is an alkyl group or a single bond. The alkylene group represented by $W_1$ is preferably a straight chain or branched alkylene group having 1 to 8 carbon atoms (e.g., methylene, ethylene, and propylene) or a cycloalkylene group having 5 to 10 carbon atoms (e.g., 1,2-cyclohexylene). $W_2$ 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 the 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 hydroxy group and a carboxy group. More preferably, $W_1$ and $W_2$ are each an alkylene group having 1 to 3 carbon atoms, particularly preferably methylene group or ethylene group.

Z is a single bond, -O-, -S-, -CO- or -N($R_W$)-wherein $R_W$ 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 carboxy group, a phosphono group, a sulfo group, a hydroxy group and an amino group. Preferably, Z is a single bond.

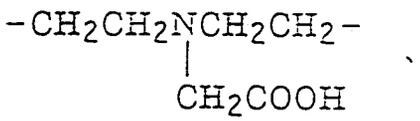
In formula (W), n is preferably 1 or 2, more preferably 1.

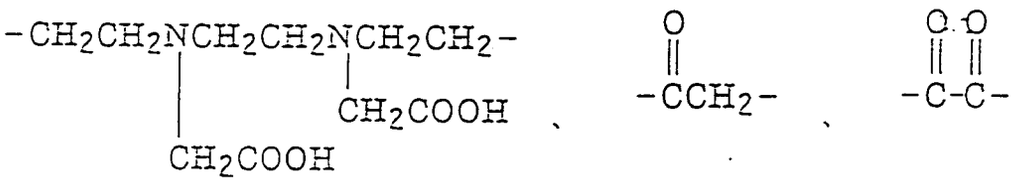
Specific examples of W include the following groups.





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

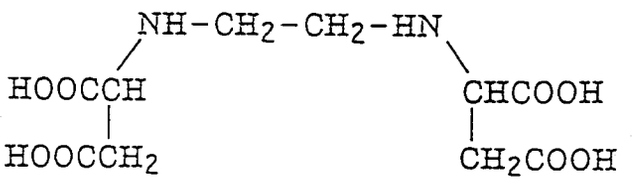




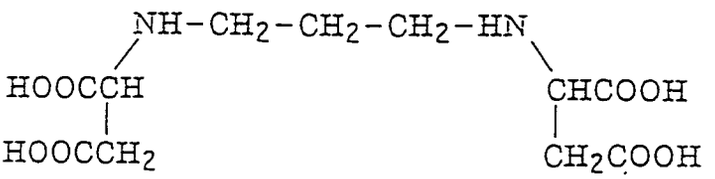
Examples of the cation represented by $M_1$, $M_2$, $M_3$ and $M_4$ include an alkali metal ion (e.g., lithium, sodium, or potassium ion), an ammonium ion (e.g., ammonium or tetraethylammonium ion) and a pyridium ion.

Specific examples of the compounds of formula (II) which can be used in the present invention include the following compounds, but the present invention is not limited thereto.

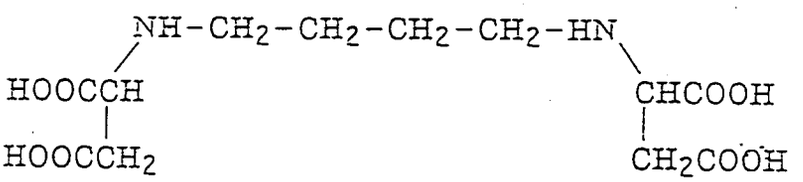
II-1.



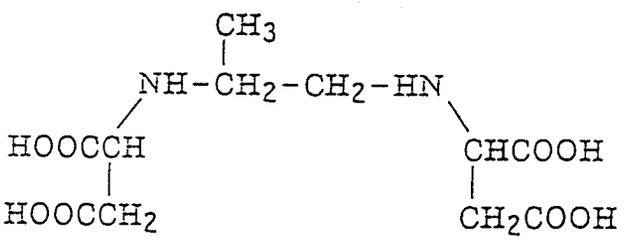
II-2.



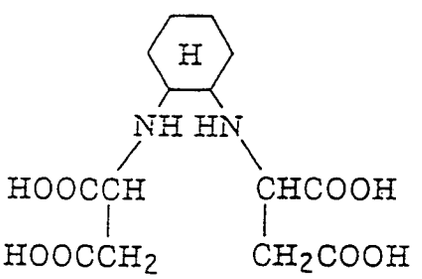
II-3.



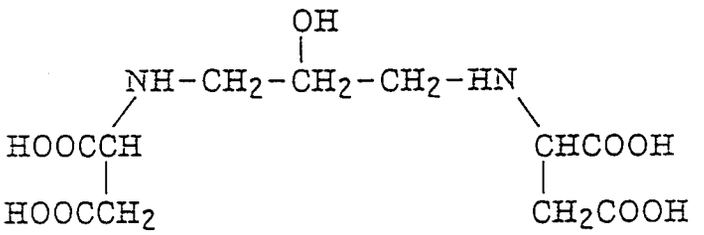
II-4.



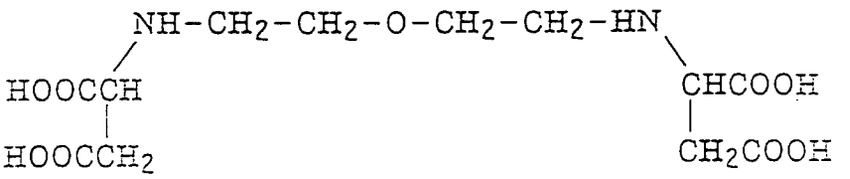
II-5.



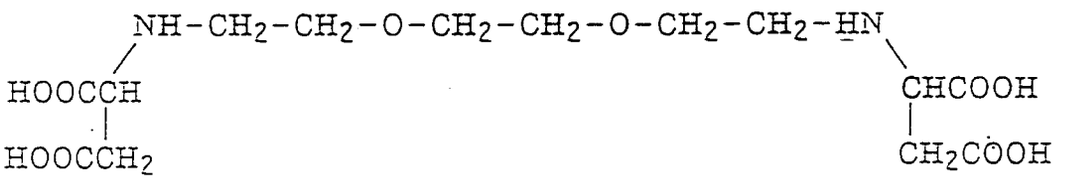
II-6.



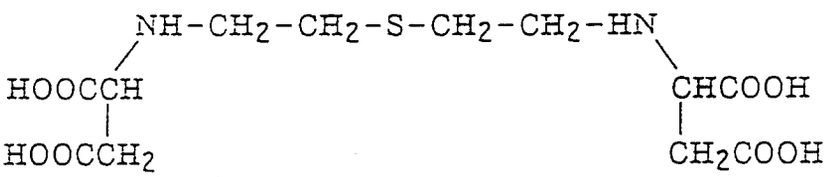
II-7.



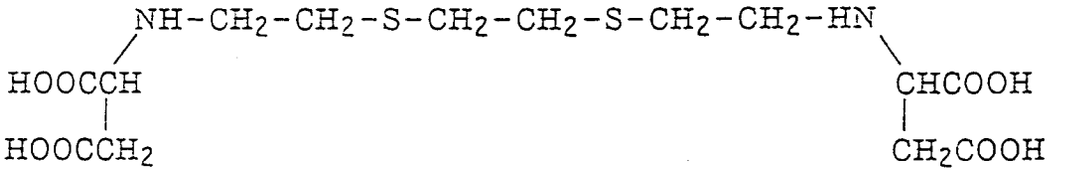
II-8.



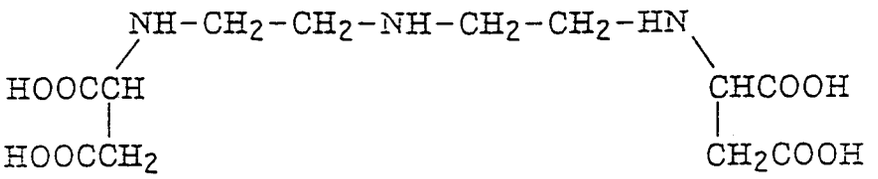
II-9.



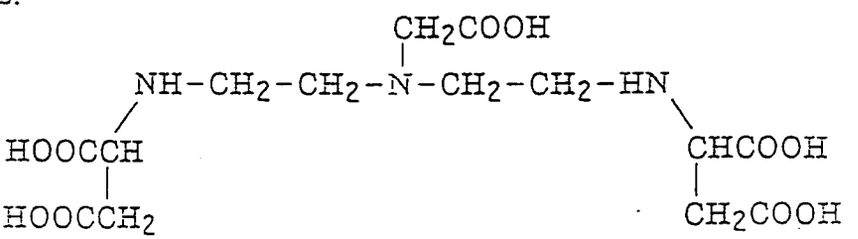
II-10.



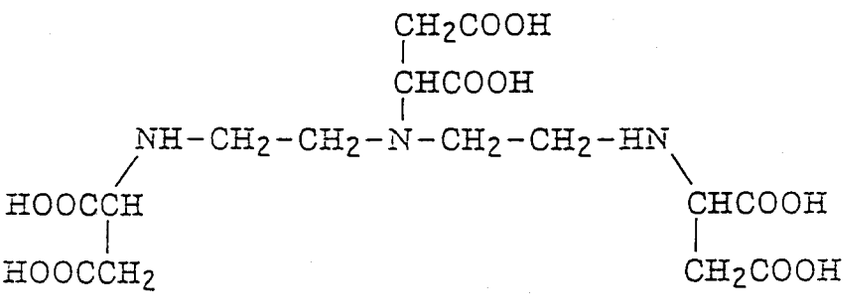
II-11.



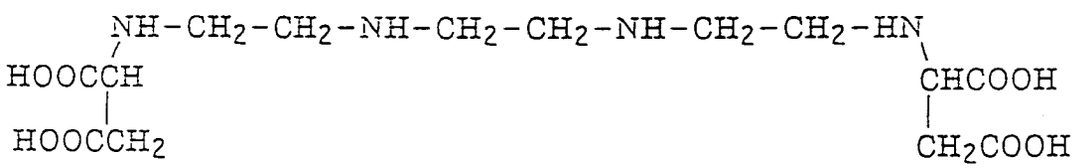
II-12.



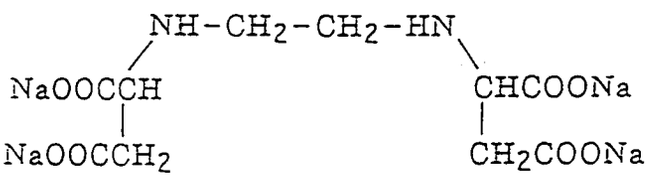
II-13.



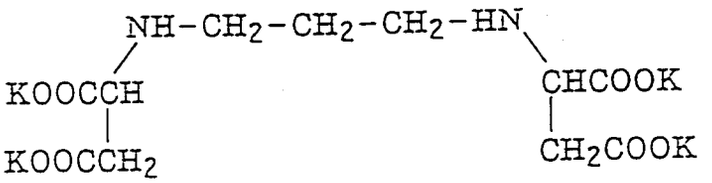
II-14.



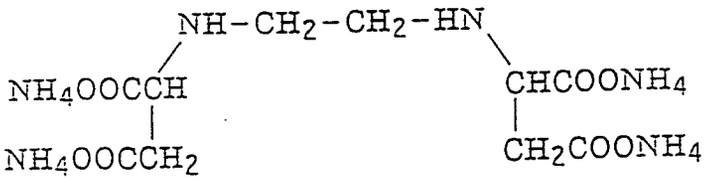
II-15.



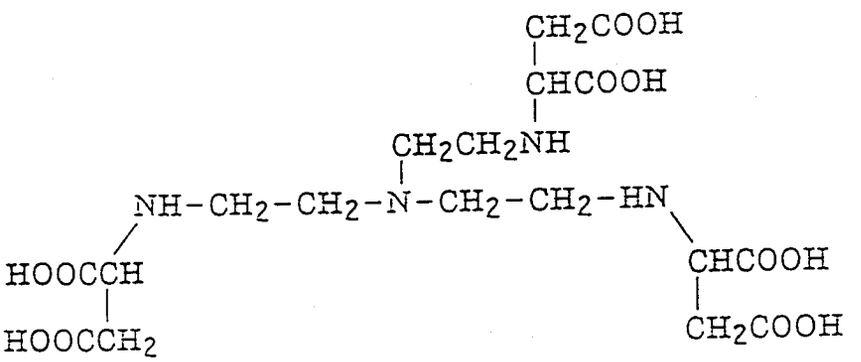
II-16.



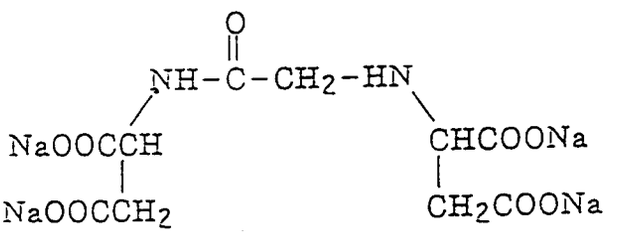
II-17.



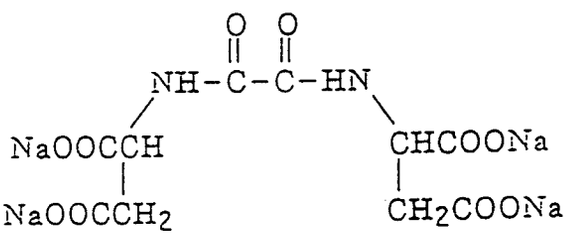
II-18.



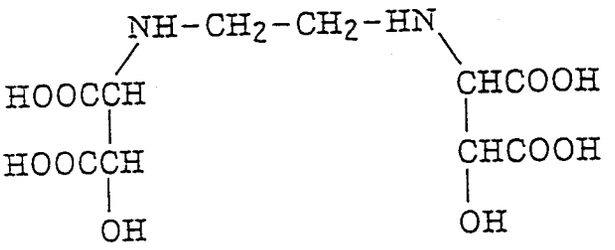
II-19.



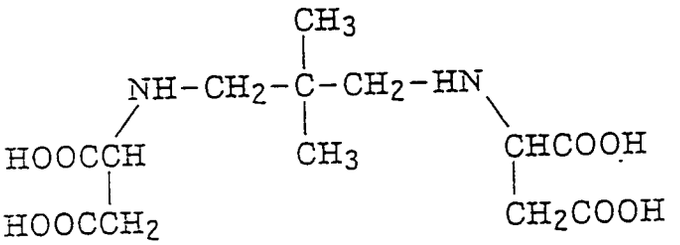
II-20.



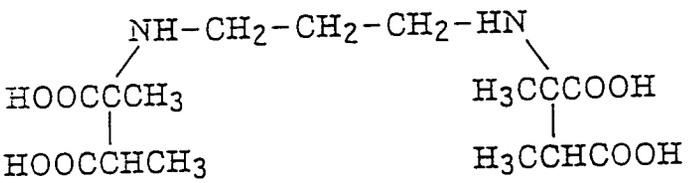
II-21.



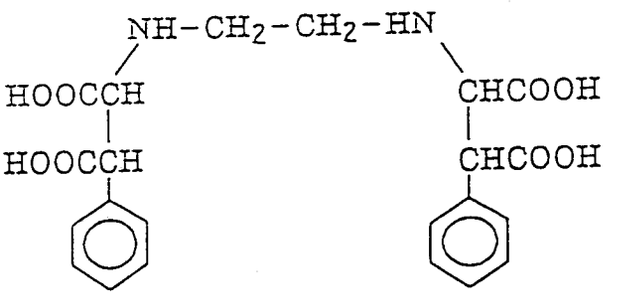
II-22.



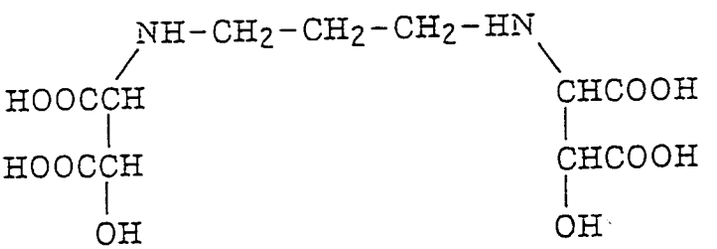
II-23.



II-24.



II-25.



The compounds of formula (II) can be synthesized by referring to the methods described in JP-A-63-199295 and JP-A-3-173857. As described in these patent specifications, the compounds of formula (II) used in the present invention can exist in optically isomeric forms ([R,R], [S,S], [S,R], [R,S]) (while some of the compounds may have the same structure in the [S,R] form and the [R,S] form). For example, compound (II-1) which is exemplified above can exist in three optically isomeric forms ([R,R], [S,S], [S,R] (=[R,S])).

These isomers can be synthesized individually or as a mixture thereof. All such isomeric forms of the compounds are included within the scope of the present invention.

The compound of formula (II) is audinarily synthesized in the form of mixture of the four optical isomers of [R,R], [S,S], [S,R], and [R,S], each being contained in an amount of about 25 %.

Of these optical isomers, the isomer of [S,S] form is preferred for the improvement in color stain, color fading by heat and color restorability. For the reason, it is preferred to use the compound of formula (II) which is predominantly a [S,S] optical isomer, for example, those synthesized from L-amino acids, such as compound (II-1). The [S,S] optical isomer is also advantageous in view of environmetal pollution since it is not likely to decompose spontaneously even when discharged.

The [S,S] optical isomers can be selectively obtained by the above-mentioned method in which L-amino acids are used as a starting material to synthesize the corresponding product of formula (II), or by the method in which the mixture of the optical isomers is subjected to conventional separation using a commercially available column. The former method is preferred and is economical.

The term "predominantly" or "selectively" used herein means that the [S,S] optical isomer is contained in the compound of formula (II) in the largest content among the four optical isomers, generally not less than 50 %, preferably not less than 70 %, more preferably 90% or more. The compound of formula (II) may consist of 100 % of the [S,S] form.

These compounds can also be synthesized by the methods described in Springer and Kopekka, Chem. Zvesti, 20(6): 414-422(1966) and JP-A-3-173857, and the selective synthesis of the [S,S] optical isomer can also be effected by the method described in Umezawa et al. THE JOURNAL OF ANTIBIOTICS, Vol.37, No. 4, P.426 (Apr. 1984).

The iron (III) complexes of the compounds of formula (II) used in the present invention can be prepared by mixing a ferric ion with the compounds of formula (II). When the iron (III) complexes of the compounds of formula (II) are used as bleaching agents, the complexes may be isolated as the iron (III) complexes of the chelating agents and used. In this case, the complexes may be isolated in the form of a salt such as an ammonium salt, a sodium salt or a potassium salt.

The iron (III) complexes are generally used in an amount of 0.02 to 1.0 mol, preferably 0.04 to 0.5 mol per liter of the bath having a bleaching ability. It is preferred that an excess (about 10 to 20% excess) of the compounds of formula (II) in the free form in addition to the iron (III) complexes be present. Of the compounds of formula (II), compounds II-1, II-2, II-3, II-15, II-16 and II-17 are particularly preferred.

The bath having a bleaching ability used in the present invention may be any of bleaching bath and bleaching-fixing bath, to which the iron (III) complexes of the compounds of formula (II) can be added.

The compounds of formula (II) used in the present invention are used as builders in the field of detergents as described in JP-A-63-199295 and JP-A-3-173857. Hence, the compounds are known compounds and belong to polyaminocarboxylic acids. However, the compounds of formula (II) have not been used in photographic processing, and the iron (III) complexes of the compounds of formula (II) have an excellent effect as a bleaching agent in comparison with the iron (III) complexes of EDTA conventionally used.

The processing method of the present invention can be applied to any of silver halide color photographic materials, that is, any of color paper, etc. However, the processing method of the present invention can be particularly preferably applied to color paper.

Silver halide color photographic materials, in which the cyan coupler of formula (I) is incorporated, will be illustrated below.

Silver halide emulsions, other materials (additives, etc.), photographic constituent layers (layer arrangement, etc.), processing methods and processing additives described in the following patent specifications, particularly European Patent EP 0,355,660A2 (JP-A-1-107011) can be preferably applied to the photographic materials used in the present invention.

Places where photographic constituent elements, etc. are described are listed below.

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Silver halide emulsion | The 6th line of right upper column of page 10 to the 5th line of left lower column of page 12; and the 4th line from the bottom of right lower column of page 12 to the 17th line of left upper column of page 13 | The 16th line of right upper column of page 28 to the 11th line of right lower column of page 29; and the 2nd line to the 5th line of page 30 | The 53rd line of page 45 to the 3rd line of page 47; and the 20th line to the 22nd line of page 47 |
| Solvent for silver halide | The 6th line to the 14th line of left lower column of page 12; and the 3rd line from the bottom of left upper column of page 13 to the bottom of left lower column of page 18 | --- | -- |
| Chemical sensitizing agent | The 3rd line from the bottom of left lower column of page 12 to the 5th line from the bottom of right lower column of page 12; and the first line of right lower column of page 18 to the 9th line from the bottom of right upper column of page 22 | The 12th line to the bottom of right lower column of page 29 | The 4th line to the 9th line of page 47 |
| Spectral sensitizing agent (spectral sensitizing method) | The 8th line from the bottom of right upper column of page 22 to the bottom of page 38 | The first line to the 13th line of left upper column of page 30 | The 10th line to the 15th line of page 47 |

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Emulsion stabilizer | The first line of left upper column of page 39 to the bottom of right upper column of page 72 | The 14th line of left upper column of page 30 to the first line of right upper column of page 30 | The 16th line to the 19th line of page 47 |
| Development accelerator | The first line of left lower column of page 72 to the 3rd line of right upper column of page 91 | --- | --- |
| Color coupler (cyan, magenta and yellow couplers) | The 4th line of right upper column of page 91 to the 6th line of left upper column of page 121 | The 14th line of right upper column of page 3 to the bottom of left upper column of page 18; and the 6th line of right upper column of page 30 to the 11th line of right lower column of page 35 | The 15th line to the 27th line of page 4; the 30th line of page 5 to the bottom of page 28; the 29th line to the 31st line of page 45; and the 23rd line of page 47 to the 50th line of page 63 |
| Supersensitizing agent | The 7th line of left upper column of page 121 to the first line of right upper column of page 125 | --- | --- |
| Ultraviolet light absorber | The 2nd line of right upper column of page 125 to the bottom of left lower column of page 127 | The 14th line of right lower column of page 37 to the 11th line of left upper column of page 38 | The 22nd line to the 31st line of page 65 |

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Antifading agent (image stabilizer) | The first line of right lower column of page 127 to the 8th line of left lower column of page 137 | The 12th line of right upper column of page 36 to the 19th line of left upper column of page 37 | The 30th line of page 4 to the 23rd line of page 5; the first line of page 29 to the 25th line of page 45; the 33rd line to the 40th line of page 45; and the 2nd line to the 21st line of page 65 |
| High-boiling and/or low-boiling organic solvent | The 9th line of left lower column of page 137 to the bottom of right lower column of page 144 | The 14th line of right lower column of page 35 to the 4th line from the bottom of left upper column of page 36 | The first line to the 51st line of page 64 |
| Dispersion method of photographic additive | The first line of left lower column of page 144 to the 7th line of right upper column of page 146 | The 10th line of right lower column of page 27 to the bottom of left upper column of page 28; and the 12th line of right lower column of page 35 to the 7th line of right upper column of page 36 | The 51st line of page 63 to the 56th line of page 64 |
| Hardening agent | The 8th line of right upper column of page 146 to the 4th line of left lower column of page 155 | ---- | ---- |
| Developing agent precursor | The 5th line of left lower column of page 155 to the 2nd line of right lower column of page 155 | ---- | ---- |

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Restrainer releasing compound | The 3rd line to the 9th line of page 155 | ---- | ---- |
| Support | The 19th line of right lower column of page 155 to the 14th line of left upper column of page 156 | The 18th line of right upper column of page 38 to the 3rd line of left upper column of page 39 | The 29th line of page 66 to the 13th line of page 67 |
| Layer structure | The 15th line of left upper column of page 156 to the 14th line of right lower column of page 156 | The first line to the 15th line of page 28 | The 41st line to the 52nd line of page 45 |
| Dye | The 15th line of right lower column of page 156 to the bottom of right lower column of page 184 | The 12th line of left upper column of page 38 to the 7th line of right upper column of page 38 | The 18th line to the 22nd line of page 66 |
| Color mixing inhibitor | The first line of left upper column of page 185 to the 3rd line of right lower column of page 188 | The 8th line to the 11th line of right upper column of page 36 | The 57th line of page 64 to the first line of page 65 |
| Gradation controller | The 4th line to the 8th line of right lower column of page 188 | --- | --- |
| Stain inhibitor | The 9th line of right lower column of page 188 to the 10th line of right lower column of page 193 | The bottom of left upper column of page 37 to the 13th line of right lower column of page 37 | The 32nd line of page 65 to the 17th line of page 66 |

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Surfactant | The first line of left lower column of page 201 to the bottom of right upper column of page 210 | The first line of right upper column of page 18 to the bottom of right lower column of page 24; and the 10th line from the bottom of left lower column of page 27 to the 9th line of right lower column of page 27 | --- |
| Fluorine-containing compound (antistatic agent, coating aid, lubricant, antisticking agent, etc.) | The first line of left lower column of page 210 to the 5th line of left lower column of page 222 | The first line of left upper column of page 25 to the 9th line of right lower column of page 27 | --- |
| Binder (hydrophilic colloid) | The 6th line of left lower column of page 222 to the bottom of left upper column of page 225 | The 8th line to the 18th line of right upper column of page 38 | The 23rd line to the 28th line of page 66 |
| Thickener | The first line of right upper column of page 225 to the 2nd line of right upper column of page 227 | ---- | --- |
| Antistatic agent | The 3rd line of right upper column of page 227 to the first line of left upper column of page 230 | --- | --- |

| Photographic constituent element, etc. | JP-A-62-215272 | JP-A-2-33144 | EP0,355,660A2 |
|---|---|---|---|
| Polymer latex | The 2nd line of left upper column of page 230 to the bottom of page 239 | --- | --- |
| Matting agent | The first line of left upper column of page 240 to the bottom of right upper column of page 240 | --- | --- |
| Photographic processing method (processing stage, additive, etc.) | The 7th line of right upper column of page 3 to the 5th line of right upper column of page 10 | The 4th line of left upper column of page 39 to the bottom of left upper column of page 42 | The 14th line of page 67 to the 28th line of page 69 |

Note The cited places of JP-A-62-215272 include an amendment dated March 16, 1987 and attached to the end of the publication.

Among the above-described color couplers, so-called short wave type yellow couplers described in JP-A-63-231451, JP-A-63-123047, JP-A-63-241547, JP-A-1-173499, JP-A-1-213648, and JP-A-1-250944 are preferably used as yellow couplers.

In the photographic element, etc., examples of cyan couplers which can be used together with the cyan couplers of formula (I) include diphenylimidazole cyan couplers described in JP-A-2-33144; 3-hydroxypyridine cyan couplers (particularly two equivalent type coupler obtained by introducing a chlorine eliminable group into a four equivalent type coupler designated as coupler (42); and couplers (6) and (9)) described in EP 0,333,185A2; and cyclic active methylene cyan couplers (particularly coupler Nos. 3, 8 and

34) described in JP-A-64-32260.

Examples of silver halide which can be used in the present invention include silver chloride, silver chlorobromide, and silver iodochlorobromide. For the purpose of the present invention, silver halides having a high silver chloride content are preferred. More specifically, silver chlorobromide containing substantially no silver iodide and having a silver chloride content of preferably at least 90 mol%, more preferably at least 95 mol%, particularly preferably at least 98 mol%, or silver chloride is preferred.

The wordings "containing substantially no silver iodide" used herein imply that the silver iodide content is not more than 1 mol% and preferably 0.5 mol% or less, and it may be 0 mol%.

The silver halide emulsion used in the present invention is preferably a monodisperse emulsion and more preferably that having a coefficient of variation of 0.2 % or less, particularly preferably 0.1 % or less.

From the standpoint of improving sharpness of images, etc. it is preferred that dyes decolorized by processing (particularly oxonol dyes) described in EP 0,337,490A2 (pages 27 to 76) are added to hydrophilic colloid layers of the photographic materials in such an amount as to provide an optical density of at least 0.70 at 680 nm, or that at least 12 wt% (more preferably at least 14 wt%) of titanium oxide having a surface treated with a dihydric to tetrahydric alcohol (e.g., trimethylol ethane) is contained in a water-resistant resin layer of the support.

The photographic materials used in the present invention preferably contain dye image preservability improvers described in EP 0,277,589A2 together with the couplers, particularly pyrazoloazole couplers.

Namely, the photographic materials preferably contain a compound (F) and/or a compound (G), said compound (F) being chemically bonded to the aromatic amine color developing agent left behind after color development to form a compound which is chemically inert and substantially colorless, and said compound (G) being chemically bonded to an oxidation product of the aromatic amine color developing agent left behind after color development to form a compound which is chemically inert and substantially colorless. The use of the compound (F) and/or the compound (G) is preferred from the standpoint of preventing stain from being formed by developed dyes produced by the reaction with the color developing agents or the oxidation product thereof left in the layers during storage after processing and preventing other side effects from being caused.

Further, it is preferred that antifungal agents as described in JP-A-63-271247 are added to the photographic materials to prevent the image from being deteriorated by the growth of mildew or microbe in the hydrophilic layers.

Examples of supports for display which can be used for the photographic materials of the present invention include white polyester supports and supports having a white pigment-containing layer provided on the silver halide emulsion layer side thereof. It is preferred that an antihalation layer is coated on the silver halide emulsion layer-coated side of the support or the back side thereof. It is particularly preferred that the transmission density of the support is set to from 0.35 to 0.8 so as to allow display to be enjoyed by reflected light and transmitted light.

The coated amount of silver in the photographic material used in the present invention is preferably 1 g or less, more preferably from 0.4 to 0.8 g, particularly preferably from 0.5 to 0.7 g, per $m^2$ of the photographic material. The dry thickness of the entire photographic constituent layers (all layers other than the support, composed mainly of photosensitive emulsion layers and interlayers) is preferably from 6 to 11 μm.

The photographic materials of the present invention may be exposed to visible light or infrared light. Exposure may be any of low-illumination exposure and high-illumination short-time exposure. In the latter case, a laser scanning exposure system wherein the exposure time is shorter than $10^{-4}$ sec per one pixel is preferred.

It is preferred that when exposure is conducted, a band stop filter described in U.S. Patent 4,880,726 is used, whereby light color mixing can be eliminated, and color reproducibility can be greatly improved.

The processing method of the present invention will be illustrated below. The color developing solutions used in the development of the photographic materials in the present invention are preferably aqueous alkaline solutions containing aromatic primary amine color developing agents as principal ingredients. Aminophenol compounds are useful as the color developing agents. However, p-phenylenediamine compounds can be preferably used as the color developing agents. Typical examples of the p-phenylenediamine compounds include 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, 3-methyl-4-amino-N-ethyl-N-δ-hydroxybutylaniline and their sulfates, hydrochlorides and p-toluenesufonates. These compounds may be used in combination of two or more thereof according to purpose.

Generally, the color developing solutions contain pH buffering such as alkali metal carbonates, borates and phosphates and restrainers or anti-fogging agents such as bromides, iodides, benzimidazoles, benzthiazoles and mercapto compounds. If desired, the color developing solutions may optionally contain preservatives such as hydroxylamine, N,N-di(sulfoethyl)-hydroxylamine, diethylhydroxylamine, sulfites, hydrazines, phenylsemicarbazides, triethanolamine and catecholdisulfonic acids; organic solvents such as ethylene glycol and diethylene glycol; development accelerators such as benzyl alcohol, polyethylene glycol and quaternary ammonium salts; dye forming couplers; competitive couplers; fogging agents such as sodium boron hydride; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; tackifiers; and various chelating agents such as typically aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof. The color developing solutions have generally a pH of 9 to 12.

The replenishment rate of the color developing solution varies depending on the color photographic materials to be processed, but is generally one liter or less per $m^2$ of the photographic material. The replenishment rate can be reduced to 300 ml or less when the concentration of bromide ions in the replenisher is reduced. The replenishment rate is preferably 30 to 150 ml/$m^2$. It is preferred that when the replenishment rate is to be reduced, the contact area of the developing solution with air in the processing bath is decreased to thereby prevent the developing solution from evaporating or being oxidized by air. Further, the replenishment rate can be reduced by using a means for preventing bromide ions in the developing solution from being accumulated.

After color development, the photographic emulsion layers are bleached with a bath having a bleaching ability. Bleaching and fixing may be simultaneously conducted (bleaching-fixing) or may be separately conducted. After bleaching, bleaching-fixing may be carried out to expedite processing. Processing may be conducted by using a bleaching-fixing bath composed of two consecutive baths. Fixing may be conducted before bleaching-fixing, or after bleaching-fixing. The iron (III) complexes of the compounds of formula (II) must be used as the bleaching agents as described above. If desired, other bleaching agents may be used together with the iron (III) complexes of the compounds of formula (II). Typical examples of bleaching agents which can be used together with the iron (III) complexes of the compounds of formula (II) include ferricyanides; dichromates; organic complex salts of iron (III) or cobalt (III), for example, iron (III) or cobalt (III) complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid and glycol ether diaminetetraacetic acid or organic acids such as citric acid, tartaric acid and malic acid; persulfates; bromates; permanganates; and nitrobenzenes.

The bleaching bath, the bleaching-fixing bath and the prebath thereof may optionally contain bleaching accelerators. Specific examples of useful bleaching accelerators include compounds having a mercapto group or a disulfide bond described in U.S. Patent 3,893,858, West German Patent 1,290,812, JP-A-53-95630 and Research Disclosure No. 17,129 (July 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in U.S Patent 3,706,561; iodides described in JP-A-58-16235; polyoxyethylene compounds described in West German Patent 2,748,430; polyamine compounds described in JP-B-45-8836; and bromide ions. Of these compounds, the compounds having a mercapto group or a disulfide bond are preferred from the standpoint of providing a high accelerating effect. The compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are particularly preferred. Further, compounds described in U.S. Patent 4,552,834 are preferred. These bleaching accelerators may be added to the photographic materials. The bleaching accelerators are particularly effective in conducting the bleaching-fixing of the color photographic materials for photographing. The processing time with the bath having a bleaching ability is preferably 15 to 60 seconds, more preferably 20 to 50 seconds from the standpoint of rapid processing. When the processing time is too short, a failure in desilverization occurs and the effect of the present invention can be hardly obtained.

The replenishment rate of the bleaching or bleaching-fixing solution is generally one liter or less, preferably 300 ml or less, more preferably from 30 to 150 ml, per $m^2$ of the photographic material. Bleaching components and fixing components may be separately replenished so as to avoid problems with respect to stability and crystallization of the components in the replenisher.

Examples of fixing agents include thiosulfates, thiocyanates, thioether compounds, thioureas and many iodides. Thiosulfates are generally used. Particularly, ammonium thiosulfate is most widely used. Examples of preservatives which can be preferably used in the bleaching-fixing solution and the fixing solution include sulfites, bisulfites, benzenesulfonic acids and carbonyl bisulfite adducts.

After desilverization, the silver halide color photographic materials are generally subjected to the rinsing stage and/or the stabilizing stage. The amount of rinsing water in the rinsing stage widely varies depending on the characteristics (e.g., materials used such as couplers used) and use of the photographic materials, the temperature of rinsing water, the number of rinsing tanks (the number of stages), replenishment system (countercurrent or direct flow), other conditions. The relationship between the number of rinsing tanks and the amount of rinsing water in a multi-stage countercurrent system can be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, No. 64, pages 248 to 253 (May 1955).

According to the multi-stage countercurrent system described in the above literature, the amount of rinsing water can be greatly reduced. However, since the residence time of water in the tank is prolonged, there is caused a problem that bacteria are grown and suspended matters formed are deposited on the photographic materials. The method for reducing calcium ion and magnesium ion described in JP-A-62-288838 can be very effectively used as a means for solving the problem in the processing of the color photographic materials. Further, antibacterial agents and antifungal agents described hereinafter can be added.

The pH of rinsing water in the processing of the photographic materials of the present invention is 4 to 9, preferably 5 to 8. The temperature of rinsing water and the rinsing time can be widely varied depending on the characteristics and use of the photographic materials. The temperature of rinsing water and the rinsing time in the present invention are 15 to 45 °C for 10 sec to 2 min, preferably 25 to 40 °C for 20 to 90 sec. Further, the photographic materials may be processed directly with a stabilizing solution in place of rinsing water in the present invention. All of conventional methods described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be used in the stabilization stage.

It is preferred that rinsing water and the stabilizing solution contain various surfactants to prevent water spots from being formed during the drying of the photographic materials after processing. Examples of the surfactants include polyethylene glycol type nonionic surfactants, polyhydric alcohol type nonionic surfactants, alkylbenzenesulfonate type anionic surfactants, higher alcohol sulfuric ester salt type anionic surfactants, alkylnaphthalenesulfonate type anionic surfactants, quaternary ammonium salt type cationic surfactants, amine salt type cationic surfactants, amine salt type ampholytic surfactants and betaine type ampholytic surfactants. Of these surfactants, nonionic surfactants are preferred. Particularly preferred are the ethylene oxide adducts of alkylphenols. Octyl-, nonyl-, dodecyl- and dinonylphenols are particularly preferred as the alkylphenols. The number of moles of the addition of ethylene oxide is preferably 8 to 14. It is also preferred that silicone surfactants having a high anti-foaming effect are used.

It is preferred that rinsing water and the stabilizing solution contain various antibacterial agents and antifungal agents to prevent fur from forming and to prevent mold from growing on the photographic materials. Examples of the antibacterial agents and the antifungal agents include thiazolylbenzimidazole compounds described in JP-A-57-157244 and JP-A-58-105145, isothiazolone compounds described in JP-A-57-8542, chlorophenol compounds such as typically trichlorophenol, bromophenol compounds, organotin compounds, organozinc compounds, acid amide compounds, diazine and triazine compounds, benztriazole compounds, alkylguanidine compounds, quaternary ammonium salts such as typically benzaluminium chloride, antibiotics such as typically penicillin and general-purpose antifungal agents described in J. Antibacterial and Anti-fungus Agents, Vol. 1, No. 5, pp. 207-223 (1983). These agents may be used in combination of two or more of them. Further, various microbicides described in JP-A-48-83820 can be used.

It is preferred that rinsing water and the stabilizing solution contain chelating agents. Examples of the chelating agents which can be preferably used include aminopolycarboxylic acids such as ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetraacetic acid, and diethylenetriamine-N,N,N',N'-tetramethylenephosphonic acid, and the hydrolyzates of maleic anhydride polymers described in European Patent 345,172A1.

The stabilizing solution contains compounds capable of stabilizing the dye image such as formalin, hexamethylenetetramine and derivatives thereof, hexahydrotriazine and derivatives, dimethylol urea and N-methylol compounds such as N-methylol pyrazole, organic acids and pH buffering agents. These compounds are used in an amount of preferably 0.001 to 0.02 mol per liter of the stabilizing solution. It is preferred that the concentration of free formaldehyde is as low as possible because the evolution of formaldehyde gas is reduced. From this point of view, hexamethylenetetramine, N-methylol azoles such as N-methylol pyrazole described in Japanese Patent Application No. Hei 3-318644 and azolylmethylamines such as N,N'-bis(1,2,4-triazole-1-yl)-piperazine described in JP-A-4-313753 are preferred as dye image stabilizers. Further, it is preferred that the stabilizing solution optionally contains ammonium compounds

such as ammonium chloride and ammonium sulfite, metallic (e.g., Bi, Al) compounds, fluorescent brighteners, hardening agents, alkanolamines (described in U.S. Patent 4,786,583) and preservatives which can be contained in the bleaching solution and the bleaching-fixing solution. Of these compounds, sulfinic acid compounds (e.g., benzenesulfinic acid, toluenesulfinic acid or sodium or potassium salt thereof) are preferred. These compounds are used in an amount of preferably $1\times10^{-5}$ to $1\times10^{-3}$ mol, particularly preferably $3\times10^{-5}$ to $5\times10^{-4}$ mol per liter of the stabilizing solution.

The replenishment rate of the rinsing water and the stabilizing solution is preferably low and it is desirably within the range of 0.1 to 50 times, more preferably 3 to 30 times, the amount thereof carried out with the unit area of the photographic material into the pre-bath.

In the present invention, various processing solutions are used at a temperature of 10 to 50 °C. Usually, a temperature of 33 to 42 °C is used. However, it is possible that a higher temperature is used to accelerate processing and to shorten the processing time, while a lower temperature is used to improve image quality and the stability of the processing solutions. If desired, treatments using cobalt intensification or hydrogen peroxide intensification described in West German Patent 2,226,770 and U.S. Patent 3,674,499 may be carried out to save silver of the photographic materials.

The present invention is now 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

Both sides of a paper support were laminated with polyethylene. The surface of the support was subjected to a corona discharge treatment. A gelatin subbing layer containing sodium dodecylbenzenesulfonate was provided thereon. Further, the following photographic constituent layers were coated thereon to prepare a multi-layer color photographic paper having the following layer structure. Coating solutions were prepared in the following manner.

### Preparation of Coating Solution for the Fifth Layer

32.0 g of cyan coupler (ExC), 3.0 g of dye image stabilizer (Cpd-2), 2.0 g of dye image stabilizer (Cpd-4), 18.0 g of dye image stabilizer (Cpd-6), 40.0 g of dye image stabilizer (Cpd-7) and 5.0 g of dye image stabilizer (Cpd-8) were dissolved in a mixture of 50.0 cc of ethyl acetate and 14.0 g of solvent (Solv-6). The resulting solution was emulsified and dispersed in 500 cc of a 20% aqueous gelatin solution containing 8 cc of sodium dodecylbenzenesulfonate by using an ultrasonic homogenizer to prepare an emulsified dispersion.

Separately, a silver chlorobromide emulsion (cubic; a 1:4 (by Ag mol) mixture of a larger-size emulsion having a mean grain size of 0.58 μm and a smaller-size emulsion having a mean grain size of 0.45 μm; a coefficient of variation in a grain size distribution being 0.09 and 0.11, respectively; 0.6 mol% of AgBr being localized on a part of the surface of the grain in each size emulsion) was prepared. To the emulsion, there was added the following red-sensitive sensitizing dye E ($0.9\times10^{-4}$ mol was added to the larger-size emulsion, and $1.1\times10^{-4}$ mol was added to the smaller-size emulsion, each amount being per mol of silver). The chemical ripening of the emulsion was carried out by adding a sulfur sensitizing agent and a gold sensitizing agent. The above emulsified dispersion and the red-sensitive silver chlorobromide emulsion were mixed and dissolved, and a coating solution for the fifth layer was prepared so as to give the composition as described later.

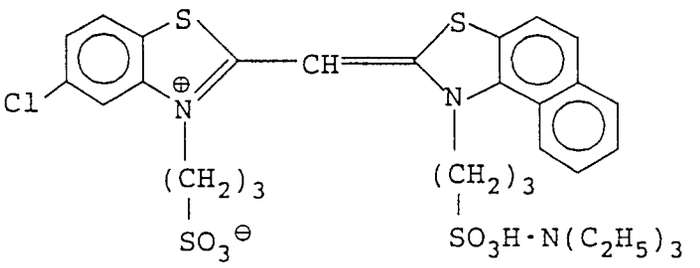
Coating solutions for the first through fourth layers, the sixth layer and the seventh layer were prepared in the same manner as in the preparation of the coating solution for the fifth layer as described above.

Sodium salt of 1-oxy-3,5-dichloro-s-triazine was used as a hardening agent for gelatin in each layer. Further, Cpd-10 and Cpd-11 were added to each layer in such an amount as to give 25.0 mg/m$^2$ and 50.0 mg/m$^2$ in total, respectively.

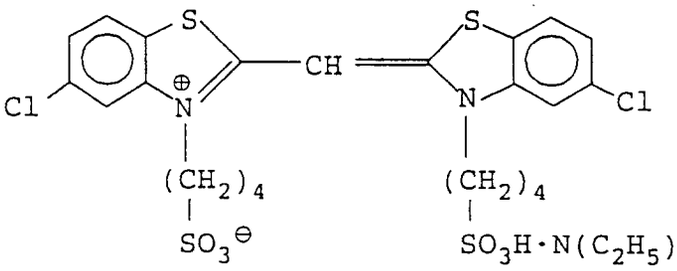
The following spectral sensitizing dyes were used in the silver chlorobromide emulsion of each light-sensitive emulsion layer.

Blue-Sensitive Emulsion Layer

Sensitizing Dye A



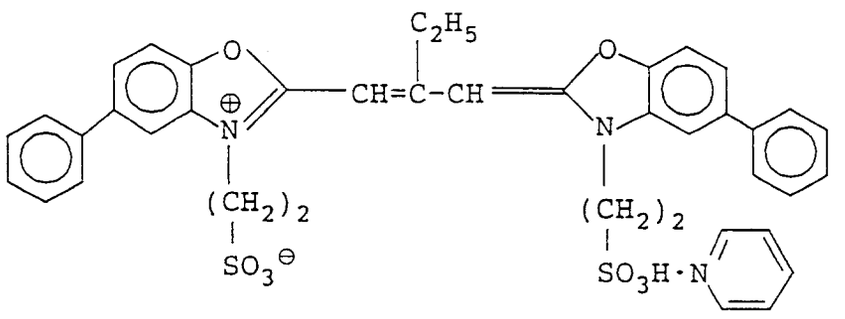
Sensitizing Dye B



($2.0\times10^{-4}$ mol of each of the sensitizing dyes A and B was added to the larger-size emulsion, and $2.5\times10^{-4}$ mol of each of the dyes was added to the smaller-size emulsion, each amount being per mol of silver halide)

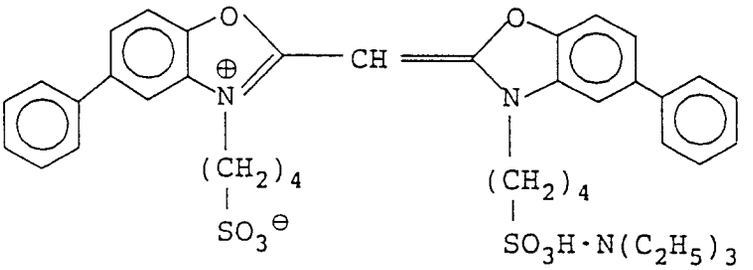
Green-Sensitive Emulsion Layer

Sensitizing Dye C



($4.0\times10^{-4}$ mol was added to the larger-size emulsion, and $5.6\times10^{-4}$ mol was added to the smaller-size emulsion, each amount being per mol of silver halide)

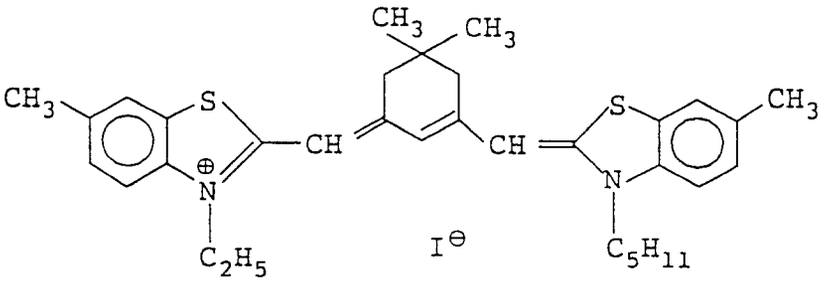
Sensitizing Dye D



($7.0\times10^{-5}$ mol was added to the larger-size emulsion, and $1.0\times10^{-5}$ mol was added to the smaller-size emulsion, each amount being per mol of silver halide)

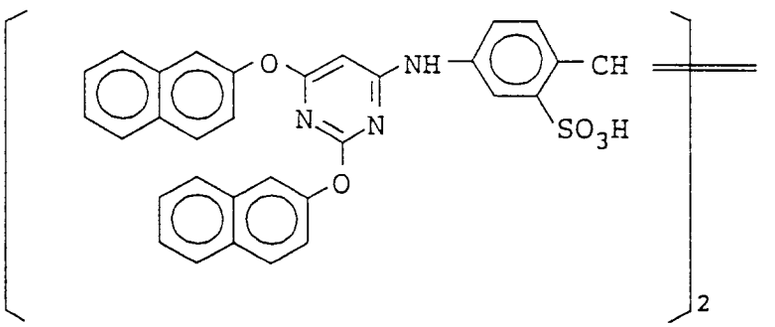
Red-Sensitive Emulsion Layer

Sensitizing Dye E



($0.9\times10^{-4}$ mol was added to the larger-size emulsion, and $1.1\times10^{-4}$ mol was added to the smaller-size emulsion, each amount being per mol of silver halide)

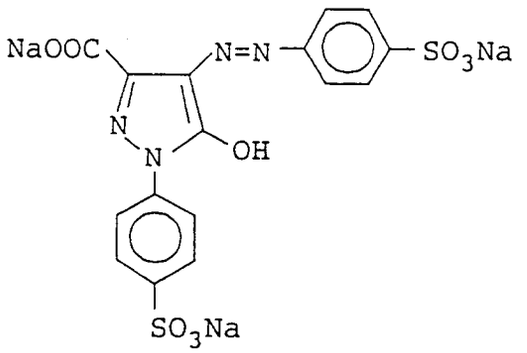
Further, $2.6\times10^{-3}$ mol of the following compound per mol of silver halide was added in the red-sensitive emulsion layer.



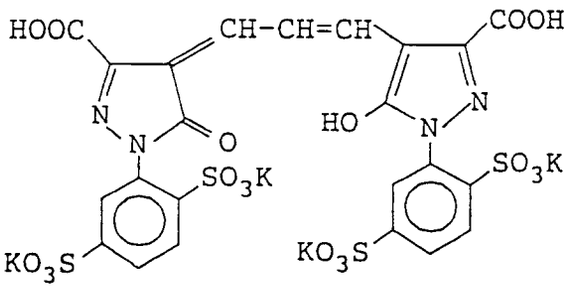
Further, $8.5\times10^{-5}$ mol, $7.7\times10^{-4}$ mol and $2.5\times10^{-4}$ mol of 1-(5-methylureidophenyl)-5-mercaptotetrazole were added to the blue-sensitive emulsion layer, the green-sensitive emulsion layer and the red-sensitive emulsion layer, respectively, each amount being per mol of silver halide.

Furthermore, $1\times10^{-4}$ mol and $2\times10^{-4}$ mol of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were added to the blue-sensitive emulsion layer and the green-sensitive emulsion layer, respectively, each amount being per mol of silver halide.

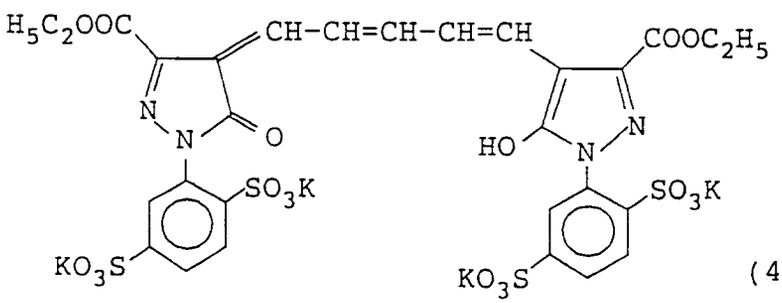
The following dyes (parenthesized numerals being coating weights) were added to the emulsion layers.



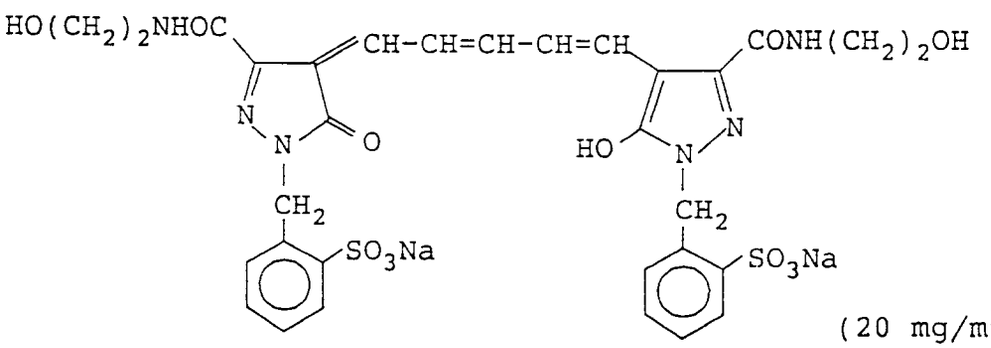
(10 mg/m$^2$)



(10 mg/m$^2$)



(40 mg/m$^2$)



(20 mg/m$^2$)

Layer Structure

Each layer had the following composition. Numerals represent coating weights (g/m$^2$). The amount of silver halide emulsion is represented by the coating weight in terms of silver.

Support

Polyethylene-laminated paper [Polyethylene on the first layer side contained a white pigment ($TiO_2$) and bluish dye (Ultramarine)]

First Layer (blue-sensitive emulsion layer)

| | |
|---|---|
| Silver Chlorobromide Emulsion (cubic; a 3:7 (by Ag mol) mixture of a larger-size emulsion having a mean grain size of 0.88 μm and a smaller-size emulsion having a mean grain size of 0.70 μm; a coefficient of variation in grain size distribution being 0.08 and 0.10, respectively; 0.3 mol% of silver bromide being localized on a part of the surface of the grain in each size emulsion) | 0.30 |
| Gelatin | 1.86 |
| Yellow Coupler (ExY) | 0.82 |
| Dye Image Stabilizer (Cpd-1) | 0.19 |
| Solvent (Solv-3) | 0.18 |
| Solvent (Solv-7) | 0.18 |
| Dye Image Stabilizer (Cpd-7) | 0.06 |

Second Layer (color mixing inhibiting layer)

| | |
|---|---|
| Gelatin | 0.99 |
| Color Mixing Inhibitor (Cpd-5) | 0.08 |
| Solvent (Solv-1) | 0.16 |
| Solvent (Solv-4) | 0.08 |

Third Layer (green-sensitive emulsion layer)

| | |
|---|---|
| Silver Chlorobromide Emulsion (cubic; a 1:3 (by Ag mol) mixture of a larger-size emulsion having a mean grain size of 0.55 μm and a smaller-size emulsion having a mean grain size of 0.39 μm; a coefficient of variation in a grain size distribution being 0.10 and 0.08, respectively; 0.8 mol% of silver bromide being localized on a part of the surface of the grain in each size emulsion) | 0.12 |
| Gelatin | 1.24 |
| Magenta Coupler (ExM) | 0.23 |
| Dye Image Stabilizer (Cpd-2) | 0.03 |
| Dye Image Stabilizer (Cpd-3) | 0.16 |
| Dye Image Stabilizer (Cpd-4) | 0.02 |
| Dye Image Stabilizer (Cpd-9) | 0.02 |
| Solvent (Solv-2) | 0.40 |

Fourth Layer (ultraviolet light absorbing layer)

| | |
|---|---|
| Gelatin | 1.58 |
| Ultraviolet Light Absorber (UV-1) | 0.47 |
| Color Mixing Inhibitor (Cpd-5) | 0.05 |
| Solvent (Solv-5) | 0.24 |

Fifth Layer (red-sensitive emulsion layer)

| | |
|---|---|
| Silver Chlorobromide Emulsion (cubic; a 1:4 (by Ag mol) mixture of a larger-size emulsion having a mean grain size of 0.58 μm and a smaller-size emulsion having a mean grain size of 0.45 μm; a coefficient of variation in a grain size distribution being 0.09 and 0.11, respectively; 0.6 mol% of silver bromide being localized on a part of the surface of the grain in each size emulsion) | 0.23 |
| Gelatin | 1.34 |
| Cyan Coupler (ExC) | 0.32 |
| Dye Image Stabilizer (Cpd-2) | 0.03 |
| Dye Image Stabilizer (Cpd-4) | 0.02 |
| Dye Image Stabilizer (Cpd-6) | 0.18 |
| Dye Image Stabilizer (Cpd-7) | 0.40 |
| Dye Image Stabilizer (Cpd-8) | 0.05 |
| Solvent (Solv-6) | 0.14 |

Sixth Layer (ultraviolet light absorber)

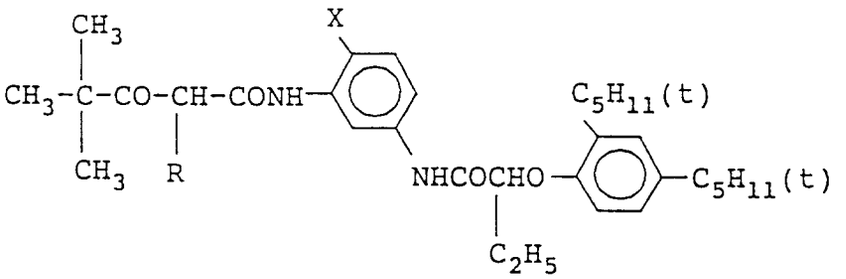
| | |
|---|---|
| Gelatin | 0.53 |
| Ultraviolet Light Absorber (UV-1) | 0.16 |
| Color Mixing Inhibitor (Cpd-5) | 0.02 |
| Solvent (Solv-5) | 0.08 |

Seventh Layer (protective layer)

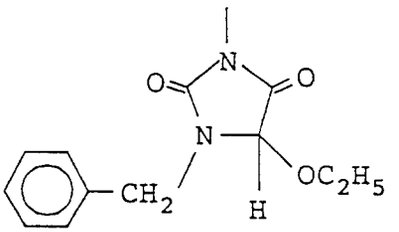
| | |
|---|---|
| Gelatin | 1.33 |
| Acrylic-modified copolymer of Polyvinyl Alcohol (a degree of modification: 17%) | 0.17 |
| Liquid paraffin | 0.33 |

The compounds used in the layers described above have the following chemical formulas.

Yellow Coupler (ExY)



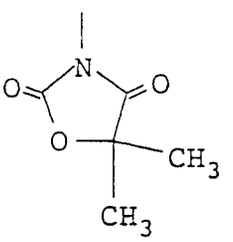
R =



, X=Cl

and

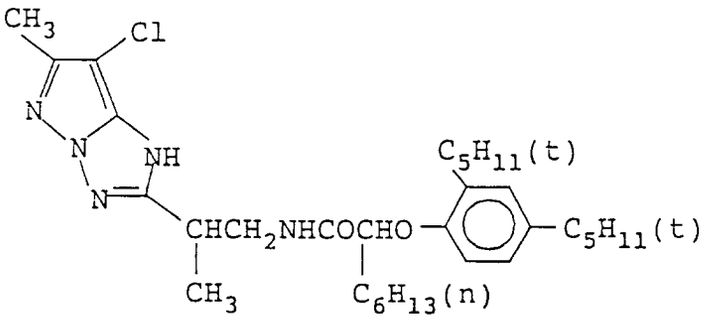
R =



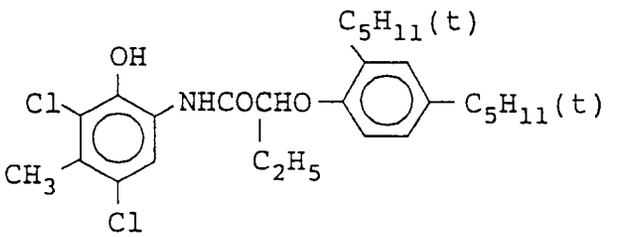
, $X=OCH_3$

1:1 Mixture (by mol)

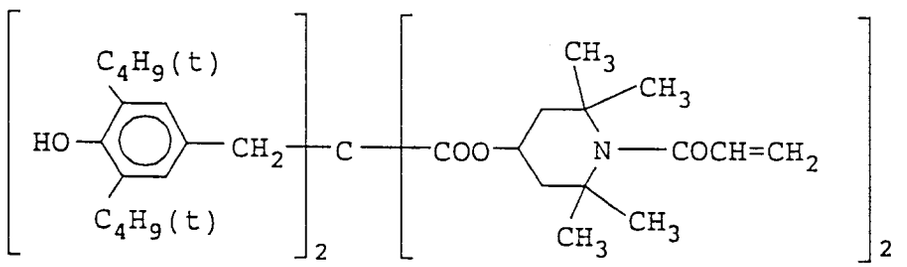
Magenta Coupler (ExM)



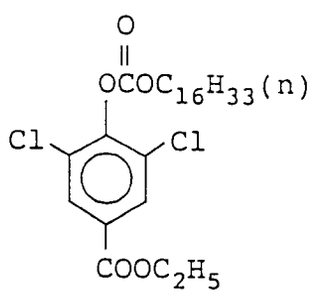
Cyan coupler (ExC)



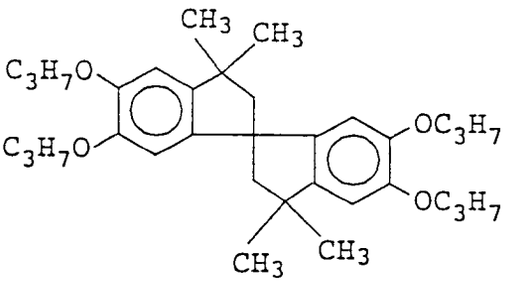
Dye Image Stabilizer (Cpd-1)



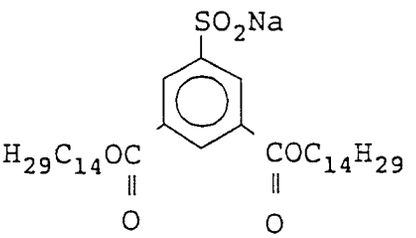
Dye Image Stabilizer (Cpd-2)



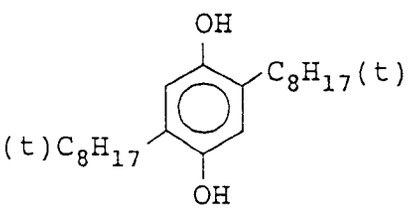
Dye Image Stabilizer (Cpd-3)



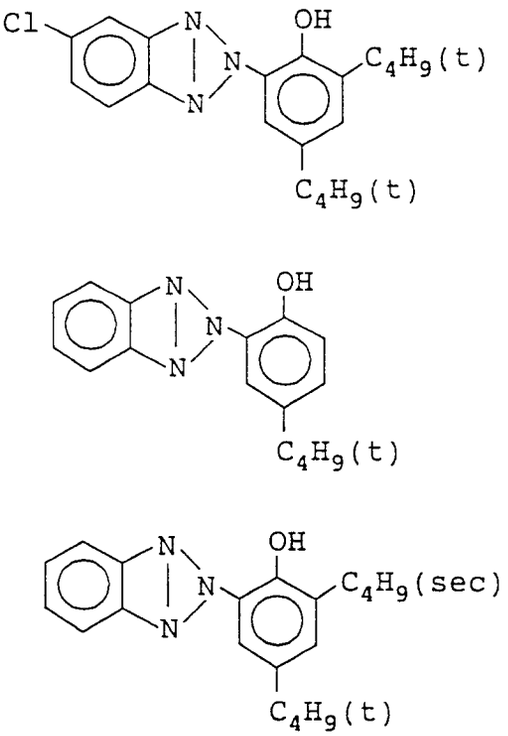
Dye Image Stabilizer (Cpd-4)



Dye Image Stabilizer (Cpd-5)

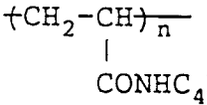


Dye Image Stabilizer (Cpd-6)



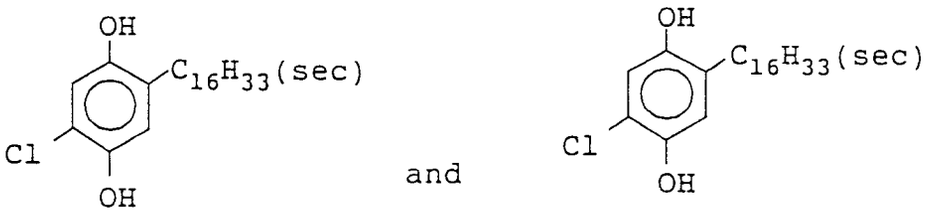
2:4:4 Mixture (by weight)

Dye Image Stabilizer (Cpd-7)



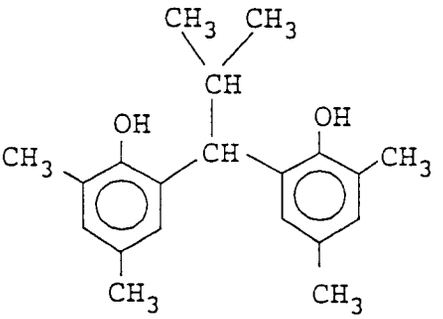
(mean molecular weight 60,000)

Dye Image Stabilizer (Cpd-8)

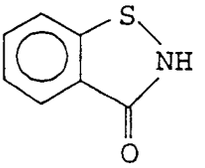


1:1 Mixture (by weight)

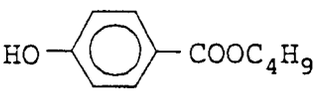
Dye Image Stabilizer (Cpd-9)



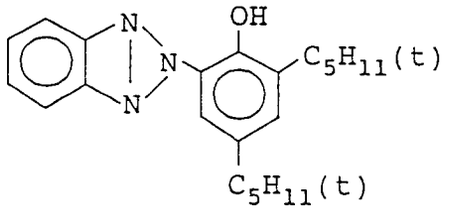
Antiseptic (Cpd-10)

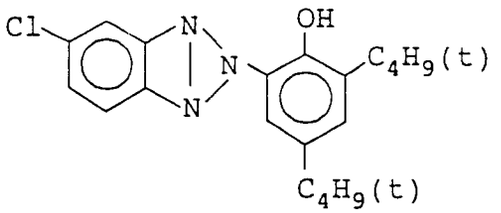


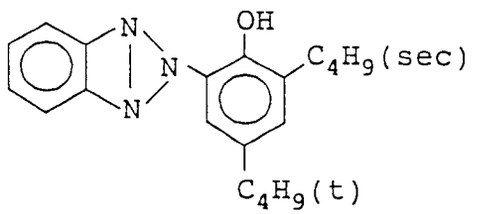
Antiseptic (Cpd-11)



Ultraviolet Light Absorber (UV-1)

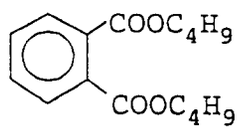




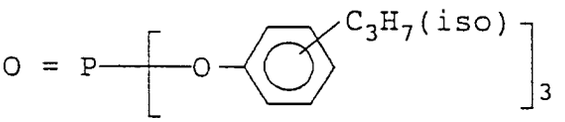


4:2:4 Mixture (by weight)

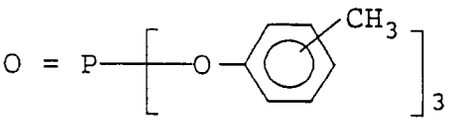
Solvent (Solv-1)



Solvent (Solv-2)

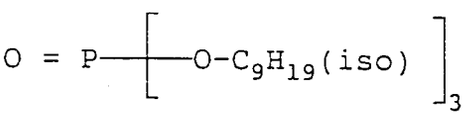


and

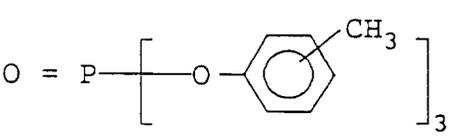


1:1 Mixture (by volume)

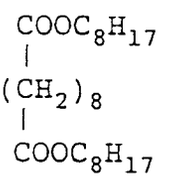
Solvent (Solv-3)



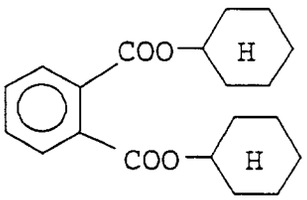
Solvent (Solv-4)



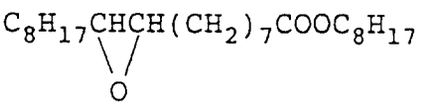
Solvent (Solv-5)



Solvent (Solv-6)

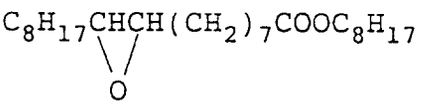


and



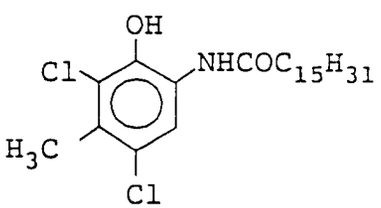
80:20 Mixture (by volume)

Solvent (Solv-7)



The photographic material prepared above is referred to as sample 1-A. Each of the following cyan couplers was used in place of the cyan coupler (ExC) to prepare each of samples 1-B, 1-C, 1-D and 1-E.

Sample 1-B The following cyan coupler



Sample 1-C: cyan coupler (C-1)

Sample 1-D: cyan coupler (C-2)

Sample 1-E: cyan coupler (C-9)

Each of the above samples was subjected to a running test. In the running test, the photographic materials were imagewise exposed to light by using an automatic printer FAP3500 (a product of Fuji Photo Film Co., Ltd.), and continuously processed (continuous test) in the following stages with the following processing solutions until the amount of the replenisher of the bleaching-fixing solution reached twice the amount of the tank solution. In the running test, the compound capable of forming the iron (III) complex (bleaching agent) in the composition of the bleaching-fixing solution was changed as shown in Table 1 below.

| Processing Stage | Temperature (°C) | Time (sec.) | Replenishment Rate (ml/m$^2$) | Tank Capacity (liter) |
|---|---|---|---|---|
| Color Development | 38.5 | 45 | 60 | 17 |
| Bleach-Fixing | 30-35 | 30 | 40 | 17 |
| Rinse (1) | 30-35 | 20 | - | 8 |
| Rinse (2) | 30-35 | 20 | - | 8 |
| Rinse (3) | 30-35 | 20 | - | 8 |
| Rinse (4) | 30-35 | 30 | 160 | 8 |
| Rinse was carried out by a four tank counter-current system of (4) → (3) → (2) → (1). | | | | |

Each processing solution had the following composition.

Color Developing Solution

| | Tank Solution | Replenisher |
|---|---|---|
| Water | 800 ml | 800 ml |
| EDTA•2Na | 3 g | 3 g |
| Sodium Catechol-3,5-disulfonate | 0.3 g | 0.3 g |
| Triethanolamine | 8.0 g | 8.0 g |
| Potassium Bromide | 0.03 g | - |
| Sodium Chloride | 6.0 g | - |
| N,N-Di(sulfoethyl)hydroxylamine | 5.0 g | 8.0 g |
| Fluorescent Brightener (WHITEX 4, a product of Sumitomo Chemical Co., Ltd.) | 1.0 g | 2.0 g |
| Sodium Sulfite | 0.2 g | 0.2 g |
| N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate | 5.0 g | 12.0 g |
| Water to make | 1000 ml | 1000 ml |
| pH (25 °C) | 10.05 | 11.15 |

Bleaching-Fixing Solution (tank solution)

| | |
|---|---|
| Water | 800 ml |
| Ammonium Thiosulfate (50 wt%) | 120 ml |
| Ammonium Sulfite | 17 g |
| Iron (III) Complex | 0.15 ml |
| Complex-Forming Compound | 0.01 mol |
| Glacial Acetic Acid | 8 g |
| Water to make | 1000 ml |
| pH (25 °C) | 5.00 |

Bleaching-Fixing Solution (replenisher)

| | |
|---|---|
| Water | 500 ml |
| Ammonium Thiosulfate (50 wt%) | 250 ml |
| Ammonium Sulfite | 35 g |
| Iron (III) Complex (Ammonium Salt) | 0.35 ml |
| Complex-Forming Compound | 0.01 mol |
| Glacial Acetic Acid | 25 g |
| Water to make | 1000 ml |
| pH (25 °C) | 4.50 |

Rinsing Water

Tank solution and replenisher being the same.

Ion-exchanged water (the concentration of each of calcium ion and magnesium ion was reduced to 3 ppm or lower).

In each running test, each sample was subjected to gradation exposure through a filter for sensitometry at the time of the start of running and at the time of the end thereof by using a sensitometer (FWH type, the color temperature of light source: 3200 °K, a product of Fuji Photo Film Co., Ltd.) (the exposure to light was made such that the exposure time was 0.1 sec and an exposure amount of 250 CMS was given). The exposed samples were processed. The density of each of the processed samples was measured with an autographic densitometer, and a difference ($\Delta D_{Bmin}$) in the change of the minimum density of yellow density in the unexposed area between the start of the running and the end thereof was determined.

Subsequently, the maximum density area was immersed in a bleaching solution for color negative films (CN-16X $N_2$ bleach, a product of Fuji Phofo Film Co., Ltd.) for 4 minutes, rinsed and dried, and the cyan density was re-measured. The ratio of an increase in the maximum cyan density (a degree of a failure in color restoration) was referred to as color development ratio P(%). P(%) was determined from the following formula:

$$P(\%) = (\text{cyan density after processing}/\text{cyan density after re-bleach}) \times 100\ (\%)$$

Further, the processed samples were stored at 80 °C and 70% RH for 20 days, and a rate of a lowering in the maximum cyan density was determined (fading, $\Delta D_{Rmax}$).

The results obtained are shown in Table 1 below.

According to the present invention, an increase in yellow stain on the white ground is small, and at the same time, the fading of cyan color and a failure in color restoration are reduced. Accordingly, it can be found that good results can be obtained by the processing method of the present invention. In particular, the fading of cyan color and the failure in color restoration can be further reduced when compounds II-1 and II-2 each predominantly composed of a [S,S] optical isomer are used as in Run No. 1-8 and 1-9, respectively.

TABLE 1

| Run No. | Compound | Sample 1-A $\Delta D_{Bmin}$ | 1-A $\Delta D_{Rmax}$ | 1-A P (%) | 1-B $\Delta D_{Bmin}$ | 1-B $\Delta D_{Rmax}$ | 1-B P (%) |
|---|---|---|---|---|---|---|---|
| I-1 | Ethylenediaminetetraacetic acid | +0.05 | -0.28 | 75 | +0.04 | -0.29 | 72 |
| I-2 | Diethylenetriaminepenta-acetic acid | +0.06 | -0.28 | 74 | +0.06 | -0.30 | 70 |
| I-3 | Nitrilotriacetic acid | +0.05 | -0.29 | 73 | +0.05 | -0.30 | 70 |
| I-4 | II-1 * | +0.03 | -0.26 | 79 | +0.03 | -0.26 | 80 |
| I-5 | II-2 * | +0.04 | -0.25 | 80 | +0.03 | -0.26 | 81 |
| I-6 | II-3 * | +0.03 | -0.25 | 80 | +0.03 | -0.26 | 81 |
| I-7 | II-6 * | +0.04 | -0.25 | 78 | +0.04 | -0.25 | 80 |
| I-8 | II-1 ** | +0.03 | -0.24 | 81 | +0.03 | -0.24 | 82 |
| I-9 | II-2 ** | +0.03 | -0.24 | 82 | +0.03 | -0.24 | 82 |

(Cont'd)

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TABLE 1 (continued)

| Run No. | Compound | Sample 1-C $\Delta D_{Bmin}$ | 1-C $\Delta D_{Rmax}$ | 1-C P (%) | 1-D $\Delta D_{Bmin}$ | 1-D $\Delta D_{Rmax}$ | 1-D P (%) | 1-E $\Delta D_{Bmin}$ | 1-E $\Delta D_{Rmax}$ | 1-E P (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| I-1 | Ethylenediaminetetraacetic acid | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 78 | +0.04 | -0.23 | 80 |
| I-2 | Diethylenetriaminepenta-acetic acid | +0.06 | -0.25 | 76 | +0.06 | -0.23 | 76 | +0.06 | -0.22 | 77 |
| I-3 | Nitrilotriacetic acid | +0.05 | -0.26 | 75 | +0.05 | -0.25 | 75 | +0.05 | -0.25 | 75 |
| I-4 | II-1 * | +0.01 | -0.12 | 95 | +0.01 | -0.10 | 95 | +0.01 | -0.11 | 96 |
| I-5 | II-2 * | +0.01 | -0.13 | 97 | +0.01 | -0.12 | 98 | +0.01 | -0.11 | 98 |
| I-6 | II-3 * | +0.01 | -0.12 | 98 | +0.01 | -0.11 | 98 | +0.01 | -0.10 | 96 |
| I-7 | II-6 * | +0.01 | -0.12 | 96 | +0.01 | -0.12 | 97 | +0.01 | -0.12 | 98 |
| I-8 | II-1 ** | 0 | -0.09 | 99 | 0 | -0.06 | 100 | 0 | -0.06 | 99 |
| I-9 | II-2 ** | 0 | -0.09 | 100 | 0 | -0.07 | 100 | 0 | -0.06 | 100 |

(Note) * a mixture of [R,R], [S,R], [R,S] and [S,S] optional isomers (Compounds II-1 and II-2 used in Run Nos. I-4 and I-5 were mixtures of [S,S], [R,S] (=[S,R]) and [R,R] optical isomers in the ratio of about 1:2:1)

** a mixture predominantly (98 to 100%) composed of [S,S] optical isomer.

shows the results obtained by the present invention.

EXAMPLE 2

The procedure of each of the Run Nos. I-1, I-4 and I-8 of Example 1 was repeated except that the bleaching-fixing time was changed to 10 sec, 15 sec, 30 sec, 45 sec, 60 sec and 90 sec. The results

obtained are shown in Table 2 below.

According to the present invention, color stain and the fading of cyan color can be reduced and good results can be obtained particularly when the bleaching-fixing time is 15 to 60 sec.

TABLE 2

| Run No. | Processing Condition Bleaching-Fixing Time (sec) | 1-A | | | 1-B | | |
|---|---|---|---|---|---|---|---|
| | No. | $\Delta D_{Bmin}$ | $\Delta D_{Rmax}$ | P (%) | $\Delta D_{Bmin}$ | $\Delta D_{Rmax}$ | P (%) |
| 2-1 | I-1 10 | +0.05 | -0.30 | 72 | +0.04 | -0.31 | 70 |
| 2-2 | " 15 | +0.05 | -0.29 | 74 | +0.04 | -0.30 | 71 |
| 2-3 | " 30 | +0.05 | -0.28 | 75 | +0.04 | -0.29 | 72 |
| 2-4 | " 45 | +0.05 | -0.28 | 76 | +0.05 | -0.29 | 72 |
| 2-5 | " 60 | +0.05 | -0.28 | 76 | +0.05 | -0.29 | 72 |
| 2-6 | " 90 | +0.05 | -0.28 | 76 | +0.05 | -0.28 | 72 |
| 2-7 | I-4 10 | +0.04 | -0.28 | 79 | +0.04 | -0.28 | 78 |
| 2-8 | " 15 | +0.04 | -0.27 | 79 | +0.04 | -0.27 | 79 |
| 2-9 | " 30 | +0.03 | -0.26 | 79 | +0.03 | -0.26 | 80 |
| 2-10 | " 45 | +0.03 | -0.26 | 78 | +0.03 | -0.26 | 80 |
| 2-11 | " 60 | +0.03 | -0.26 | 78 | +0.03 | -0.26 | 80 |
| 2-12 | " 90 | +0.03 | -0.26 | 78 | +0.03 | -0.26 | 80 |

(Cont'd)

TABLE 2 (continued)

| Run No. | Processing Condition No. | Bleaching-Fixing Time (sec) | 1-A $\Delta D_{Bmin}$ | 1-A $\Delta D_{Rmax}$ | 1-A P (%) | 1-B $\Delta D_{Bmin}$ | 1-B $\Delta D_{Rmax}$ | 1-B P (%) |
|---|---|---|---|---|---|---|---|---|
| 2-13 | I-8 | 10 | +0.03 | -0.26 | 81 | +0.03 | -0.26 | 80 |
| 2-14 | " | 15 | +0.03 | -0.25 | 81 | +0.03 | -0.26 | 80 |
| 2-15 | " | 30 | +0.03 | -0.24 | 81 | +0.03 | -0.24 | 81 |
| 2-16 | " | 45 | +0.03 | -0.24 | 80 | +0.03 | -0.24 | 81 |
| 2-17 | " | 60 | +0.03 | -0.24 | 80 | +0.03 | -0.24 | 81 |
| 2-18 | " | 90 | +0.03 | -0.24 | 80 | +0.03 | -0.24 | 81 |

(Cont'd)

TABLE 2 (continued)

| Run No. | Processing Condition No. | Bleaching-Fixing Time (sec) | 1-C | | | 1-D | | | 1-E | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\Delta D_{Bmin}$ | $\Delta D_{Rmax}$ | P (%) | $\Delta D_{Bmin}$ | $\Delta D_{Rmax}$ | P (%) | $\Delta D_{Bmin}$ | $\Delta D_{Rmax}$ | P (%) |
| 2-1 | I-1 | 10 | +0.04 | -0.26 | 76 | +0.04 | -0.25 | 77 | +0.04 | -0.25 | 79 |
| 2-2 | " | 15 | +0.04 | -0.25 | 77 | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 80 |
| 2-3 | " | 30 | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 78 | +0.04 | -0.23 | 80 |
| 2-4 | " | 45 | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 78 | +0.04 | -0.23 | 80 |
| 2-5 | " | 60 | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 78 | +0.04 | -0.23 | 80 |
| 2-6 | " | 90 | +0.04 | -0.25 | 78 | +0.04 | -0.24 | 78 | +0.04 | -0.23 | 80 |
| 2-7 | I-4 | 10 | +0.03 | -0.15 | 90 | +0.03 | -0.16 | 90 | +0.03 | -0.17 | 90 |
| 2-8 | " | 15 | +0.01 | -0.12 | 94 | +0.01 | -0.10 | 94 | +0.01 | -0.11 | 94 |
| 2-9 | " | 30 | +0.01 | -0.12 | 95 | +0.01 | -0.10 | 95 | +0.01 | -0.11 | 96 |
| 2-10 | " | 45 | +0.01 | -0.12 | 95 | +0.01 | -0.10 | 95 | +0.01 | -0.11 | 96 |
| 2-11 | " | 60 | +0.01 | -0.13 | 95 | +0.01 | -0.11 | 95 | +0.01 | -0.11 | 96 |
| 2-12 | " | 90 | +0.02 | -0.16 | 95 | +0.02 | -0.15 | 95 | +0.02 | -0.16 | 95 |

(Cont'd)

TABLE 2 (continued)

| Run No. | Processing Condition No. | Bleaching-Fixing Time (sec) | 1-C $\Delta D_{Rmin}$ | 1-C $\Delta D_{Rmax}$ | 1-C P (%) | 1-D $\Delta D_{Rmin}$ | 1-D $\Delta D_{Rmax}$ | 1-D P (%) | 1-E $\Delta D_{Rmin}$ | 1-E $\Delta D_{Rmax}$ | 1-E P (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-13 | I-8 | 10 | +0.02 | -0.12 | 93 | +0.02 | -0.12 | 93 | +0.02 | -0.12 | 93 |
| 2-14 | " | 15 | +0.01 | -0.08 | 97 | +0.01 | -0.05 | 97 | +0.01 | -0.06 | 96 |
| 2-15 | " | 30 | +0.01 | -0.08 | 98 | +0.01 | -0.05 | 98 | +0.01 | -0.06 | 98 |
| 2-16 | " | 45 | +0.01 | -0.08 | 98 | +0.01 | -0.05 | 99 | +0.01 | -0.06 | 98 |
| 2-17 | " | 60 | +0.01 | -0.08 | 98 | +0.01 | -0.06 | 99 | +0.01 | -0.06 | 98 |
| 2-18 | " | 90 | +0.01 | -0.12 | 98 | +0.01 | -0.10 | 99 | +0.01 | -0.10 | 98 |

shows the results obtained by the present invention.

EXAMPLE 3

Color reversal processings were conducted according to Example 1 of JP-A-4-298742 using sample 101 of said Example 1, except that ethyenediaminetetracetic acid Fe(III) ammonium monohydrate as added in the bleaching-fixing solution was replaced with an equimolar amount of an iron (III) complex of compound

II-1 of the present invention that was predominantly a [S,S] optical isomer.

The properties ($\Delta D_{Bmin}$, $\Delta D_{Rmax}$ and P) of the processed sample were measured in the same manner as in Example 1 and it was found that they were markedly improved as compared to those of the sample processed according to JP-A-4-298742.

EXAMPLE 4

Sample 1-C prepared in Example 1 was subjected to a running test. In the running test, the photographic materials were imagewise exposed to light by using an automatic printer FAP3500 (a product of Fuji Photo Film Co., Ltd.), and continuously processed (continuous test) in the following stages with the following processing solutions until the amount of the replenisher of the bleaching solution reached three times the amount of the tank solution. In the running test, the compound capable of forming the iron (III) complex (bleaching agent) in the composition of the bleaching solution was changed as shown in Table 3 below.

| Processing Stage | Temperature (°C) | Time (sec.) | Replenishment Rate (ml/m$^2$) | Tank Capacity (liter) |
|---|---|---|---|---|
| Color Development | 38 | 45 | 80 | 10 |
| Bleaching | 38 | 45 | 200 | 10 |
| Rinse | 30 | 45 | 100 | 10 |
| Fixing | 38 | 60 | 200 | 15 |
| Rinse | 30 | 90 | 10,000 | 20 |
| Drying | 70-90 | 60 | | |

Each processing solution had the following composition.

Color Developing Solution

| | Tank Solution | Replenisher |
|---|---|---|
| Water | 600 ml | 600 ml |
| 1-Hydroxyethylidene-1,1-diphosphonic acid (60%) | 2.0 g | 2.0 g |
| Triethanolamine | 14.0 g | 14.0 g |
| Lithium Sulfate | 1.0 g | 1.0 g |
| Diethylhydroxyamine | 3.0 g | 4.0 g |
| Sodium Chloride | 3.0 g | - |
| N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate | 4.0 g | 8.5 g |
| Fluorescent Brightener (UNITEX-CK, a product of Cibu-Geigy AG) | 1.5 g | 3.0 g |
| Potassium Carbonate | 27 g | 27 g |
| Water to make | 1000 ml | 1000 ml |
| pH (adjusted with KOH) | 10.0 | 10.0 |

Bleaching Solution

| | Tank Solution | Replenisher |
|---|---|---|
| Water | 600 ml | 600 ml |
| Iron (III) Complex | 0.08 ml | 0.08 ml |
| Complex-Forming Compound | 0.01 mol | 0.01 mol |
| Ammonium Bromide | 50 g | 65 g |
| Nitric acid | 5 g | 8 g |
| Water to make | 1000 ml | 1000 ml |
| pH | 5.0 | 4.5 |

Fixing Solution (replenisher)

| | Tank Solution | Replenisher |
|---|---|---|
| Water | 600 ml | 600 ml |
| Ammonium Thiosulfate | 100 g | 110 g |
| Ammonium Sulfite | 15 g | 20 g |
| EDTA 2Na | 2 g | 2 g |
| Water to make | 1000 ml | 1000 ml |
| pH | 7.0 | 7.3 |

In each running test, each sample was subjected to gradation exposure through a filter for sensitometry at the time of the start of running and at the time of the end thereof by using a sensitometer in the same manner as in Example 1. The exposed samples were processed. The properties ($\Delta D_{Bmin}$, $\Delta D_{Rmax}$ and P) of each of the pocessed samples were measured, and the results are shown in Table 3.

The samples as processed according to the present invention exhibited minimized yellow stain and fading of cyan color and a reduced failure in color restoration.

TABLE 3

| Run No. | Compound | 1-C $\Delta D_{Bmin}$ | 1-C $\Delta D_{Rmax}$ | 1-C P (%) |
|---|---|---|---|---|
| 4-1 | Ethylenediaminetetraacetic acid | +0.04 | -0.25 | 78 |
| 4-2 | Ethylenetriaminepentaacetic acid | +0.06 | -0.25 | 76 |
| 4-3 | 1,3-Diaminopropanetetraacetic acid | +0.07 | -0.26 | 81 |
| 4-4 | Methyliminodiacetic acid | +0.06 | -0.26 | 80 |
| 4-5 | β-Alaninediacetic acid | +0.06 | -0.25 | 80 |
| 4-6 | II-1 * | +0.02 | -0.13 | 93 |
| 4-7 | II-2 * | +0.02 | -0.13 | 94 |
| 4-8 | II-1 ** | +0.01 | -0.08 | 98 |
| 4-8 | II-2 ** | +0.01 | -0.08 | 99 |

(Note)

* a mixture of [R,R], [S,R], [R,S] and [S,S] optical isomers

** a mixture predominantly (99%) composed of a [S,S] optical isomer

shows the results obtained by the present invention.

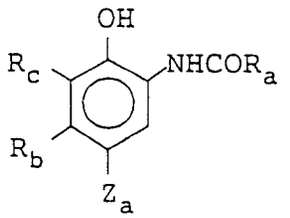
As is apparent from the above description, the processing method of the silver halide color photographic material of the present invention provides excellent effect that color restoration can be improved with a high color restoration ratio, the dyes can be remarkably prevented from being faded by heat, and color staining can be prevented from occurring, even though rapid processing is conducted. These effects can be further enhanced by the use of the compound of formula (II) which is predominantly a [S,S] optical isomer.

According to the present invention, a remarkably excellent effect with regard to color restorability, etc. can be obtained in comparison with processing using an iron (III) complex of ethylenediaminetetraacetic

acid, etc. which is a typical bleaching agent conventionally used.

## Claims

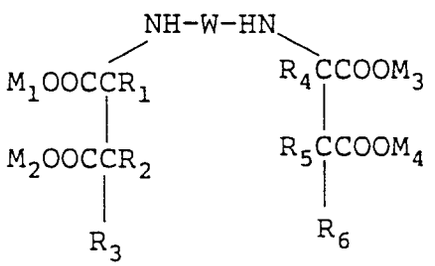
1. A method for processing a silver halide color photographic material, which comprises processing a silver halide color photographic material containing at least one cyan coupler represented by formula (I) with a bath having a bleaching ability and containing at least one iron (III) complex of a compound represented by formula (II) after color development:



(I)

wherein $R_a$ represents an alkyl group, a cycloalkyl group, an aryl group, an amino group or a heterocyclic group; $R_b$ represents an acylamino group or an alkyl group having at least 2 carbon atoms; $R_c$ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; or $R_c$ and $R_b$ may be combined together to form a ring; and $z_a$ represents a hydrogen atom, a halogen atom or a group which is eliminated by the reaction with an oxidation product of an aromatic primary amine color developing agent,

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



(II)

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:

$$-(W_1\text{-}Z)_n\text{-}W_2- \quad (W)$$

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 $-N(R_W)-$ (wherein $R_W$ is a hydrogen atom or an alkyl group which may be substituted), provided that Z and $W_1$ are not simultaneously a single bond; and n represents an integer of 1 to 3.

2. The method as in claim 1, wherein said iron (III) complex of a compound of formula (II) is predominantly a [S,S] optical isomer.

3. The method as in claim 1 or 2, wherein the processing time of the silver halide color photographic material with said bath is from 15 to 60 seconds.

4. The method as in claim 1 or 2, wherein the silver halide color photographic material is subjected to rinsing and/or stabilization for 10 seconds to 2 minutes after the processing of the silver halide color photographic material with said bath.

5. The method as in claim 3, wherein the silver halide color photographic material is subjected to rinsing and/or stabilization for 10 seconds to 2 minutes after the processing of the silver halide color photographic material with said bath.

6. The method as in claim 1, wherein said silver halide color photographic material comprises an emulsion layer of silver halide which is silver chloride or silver chlorobromide containing at least 90 mol% of silver chloride.

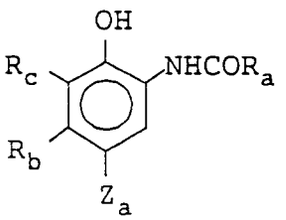
7. The method as in claim 1, wherein said silver halide color photographic material contains silver halide in a coated amount as silver of 1 g or less per $m^2$ of the photographic material.

8. The method as in claim 1, wherein said silver halide color photographic material contains silver halide in a coated amount as silver of from 0.4 to 0.8 g per $m^2$ of the photographic material.

9. The method as in claim 1, wherein the dry thickness of entire layers, other than a support, constituting said silver halide color photographic material is from 6 to 11 $\mu$m.

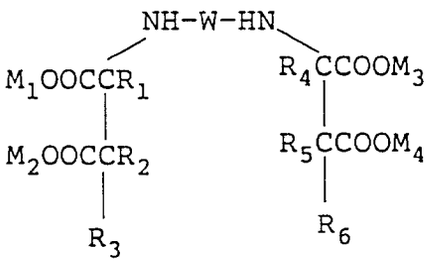
10. The method as in claim 2, wherein said iron (III) complex of a compound of formula (II) is composed of at least 50 % of a [S,S] optical isomer.

11. Use of an iron (III) complex of a compound represented by formula (II) for preventing color stain of a silver halide color photographic material containing at least one cyan coupler represented by formula (I), said iron (II) complex being introduced in a bath having a bleaching ability, with which the photographic material is processed after color development:



(I)

wherein $R_a$ represents an alkyl group, a cycloalkyl group, an aryl group, an amino group or a heterocyclic group; $R_b$ represents an acylamino group or an alkyl group having at least 2 carbon atoms; $R_c$ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; or $R_c$ and $R_b$ may be combined together to form a ring; and $z_a$ represents a hydrogen atom, a halogen atom or a group which is eliminated by the reaction with an oxidation product of an aromatic primary amine color developing agent,



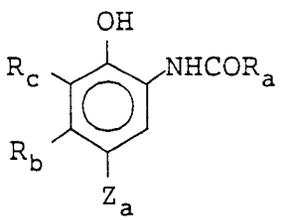
(II)

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:

$$-(W_1\text{-}Z)_n\text{-}W_2- \quad (W)$$

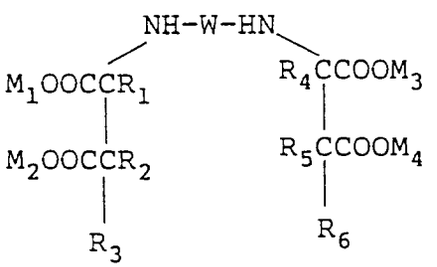
wherein $W_1$ represents an alkylene group or a single bond; $W_2$ represents an alkylene group or -CO-; Z represents a single bond, -O-, -S-, -CO- or -N($R_W$)- (wherein $R_W$ is a hydrogen atom or an alkyl group which may be substituted), provided that Z and $W_1$ are not simultaneously a single bond;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

**12.** Use of an iron (III) complex of a compound represented by formula (II) for improving color fading by heat and color restorability of a silver halide color photographic material containing at least one cyan coupler represented by formula (I), said iron (II) complex being introduced in a bath having a bleaching ability, with which the photographic material is processed after color development:



(I)

wherein $R_a$ represents an alkyl group, a cycloalkyl group, an aryl group, an amino group or a heterocyclic group; $R_b$ represents an acylamino group or an alkyl group having at least 2 carbon atoms; $R_c$ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; or $R_c$ and $R_b$ may be combined together to form a ring; and $z_a$ represents a hydrogen atom, a halogen atom or a group which is eliminated by the reaction with an oxidation product of an aromatic primary amine color developing agent,



(II)

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:

$$-(W_1\text{-}Z)_n\text{-}W_2- \qquad (W)$$

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($R_W$)- (wherein $R_W$ is a hydrogen atom or an alkyl group which may be substituted), provided that Z and $W_1$ are not simultaneously a single bond; and n represents an integer of 1 to 3.

**13.** The use as in claim 11, wherein said iron (III) complex of a compound of formula (II) is predominantly a [S,S] optical isomer.

**14.** The use as in claim 11, wherein said silver halide color photographic material comprises an emulsion layer of silver halide which is silver chloride or silver chlorobromide containing at least 90 mol% of silver chloride.

**15.** The use as in claim 11, wherein said silver halide color photographic material contains silver halide in a coated amount as silver of 1 g or less per $m^2$ of the photographic material.

**16.** The use as in claim 11, wherein the dry thickness of entire layers, other than a support, constituting said silver halide color photographic material is from 6 to 11 μm.

**17.** The use as in claim 12, wherein said iron (III) complex of a compound of formula (II) is predominantly a [S,S] optical isomer.

**18.** The use as in claim 12, wherein said silver halide color photographic material comprises an emulsion layer of silver halide which is silver chloride or silver chlorobromide containing at least 90 mol% of silver chloride.

**19.** The use as in claim 12, wherein said silver halide color photographic material contains silver halide in a coated amount as silver of 1 g or less per $m^2$ of the photographic material.

**20.** The use as in claim 12, wherein the dry thickness of entire layers, other than a support, constituting said silver halide color photographic material is from 6 to 11 μm.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 11 6451

## 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-0 567 126 (FUJI PHOTO FILM CO.)<br>27 October 1993<br>* Example 4 (table 5) * | 1-20 | G03C7/42<br>G03C7/30<br>G03C7/34 |
| P,X | EP-A-0 556 782 (KONICA CORPORATION)<br>25 August 1993<br>* Example 1 (table 3) * | 1-20 | |
| P,X | EP-A-0 553 569 (KONICA CORPORATION)<br>4 August 1993<br>* Example 1 (table 3) * | 1-20 | |
| P,X | EP-A-0 532 003 (KONICA CORPORATION)<br>17 March 1993<br>* Example 1 (table 4) * | 1-20 | |
| A | EP-A-0 430 000 (AGFA-GEVAERT AG)<br>5 June 1991<br>* See claim 1 * | 1-20 | |
| A | EP-A-0 121 365 (FUJI PHOTO FILM CO.)<br>10 October 1984<br>* See claim 1 *<br>& JP-A-59 166 956 (D,A) | 1-20 | TECHNICAL FIELDS SEARCHED (Int. Cl.5)<br>G03C |
| A | US-A-4 983 315 (PROCTER AND GAMBLE CO.)<br>8 January 1991<br>* whole document *<br>& JP-A-3 173 857 (D,A) | 1-20 | |

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
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