(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 742 106 A1**

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
10.01.2007 Bulletin 2007/02

(21) Application number: **05736658.5**

(22) Date of filing: **27.04.2005**

(51) Int Cl.:
G03C 7/42 *(2006.01)* ***G03C 7/407*** *(2006.01)*
G03C 7/44 *(2006.01)*

(86) International application number:
PCT/JP2005/008045

(87) International publication number:
WO 2005/106583 (10.11.2005 Gazette 2005/45)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: **30.04.2004 JP 2004135681**
30.04.2004 JP 2004135684

(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
Minamiashigara-shi, Kanagawa-ken 250-0193
(JP)

(72) Inventor: **HAIJIMA, Akimitsu c/o FUJIFILM**
Corporation
Kanagawa (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) # BLEACH CONCENTRATE COMPOSITION FOR SILVER HALIDE COLOR- PHOTOGRAPHIC MATERIALS, ONE-PART TYPE CONCENTRATE COMPOSITION FOR REPLENISHMENT COLOR DEVELOPERS, AND METHOD OF PROCESSING

(57) A concentrated bleach composition for a silver halide color photographic photosensitive material, containing a single liquid including an ethylenediaminetetraacetic acid-iron (III) complex salt of from 0.10 to 0.42 mol/L as a bleaching agent, an uncomplexed ethylenediaminetetraacetic acid of from 0.5 to 10 mol% with respect to the bleaching agent and a dibasic acid having a pKa of from 2.0 to 5.0 in an amoount from 0.10 to 0.40 mol/L, and having a pH value of from 2.0 to 3.5; and a concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material, containing (A) a p-phenylenediamine color developing agent of from 0.08 to 0.12 mol/L, (B) a substituted hydroxyamine derivative of a specified structure of from 0.06 to 0.16 mol/L and (C) an ethylene glycol compound from 0.05 to 1.0 mol/L, and (D) having a pH value of from 12.5 to 12.8 when diluted to 3.84 times with water, and (E) substantially not containing an alkanolamine. Also a processing method for a silver halide color photographic photosensitive material, wherein a bleach-fix tank is replenished with the composition above and a concentrated fixing composition containing a thiosulfate salt from 1.0 to 3.0 mol/L in a ratio of 1:1, and the bleach-fix step is executed in a period of from 10 to 30 seconds.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to liquid photographic processing materials for a silver halide color photographic photosensitive material (hereinafter also simply referred to as photosensitive material), and particularly to a concentrated bleach composition, a bleaching replenisher prepared therefrom and a photographic processing method utilizing the same.

[0002] The present invention also relates to a one-part concentrated processing composition for color development of a silver halide color photographic photosensitive material, a color developer replenisher prepared therefrom, and a processing method utilizing the same.

BACKGROUND TECHNOLOGY

[0003] In recent years, for achieving a prompt service to general users and for rationalizing the delivery logistic operations between photo retailers and processing laboratories, automatic processors or so-called minilabs, installed in the photo retailers for processing photographic photosensitive materials within the photo retailers, are popular. The processing material for such minilab is often supplied in the form of a liquid composition, prepared by dissolving constituent chemicals in advance in a solvent such as water, since the processing solution can be prepared by a simple operation such as a mixing and a dilution with water at the use. However, since such liquid composition is disadvantageous in transportation cost, because of a large amount of water contained in the composition and of a container required for holding the composition, it is commonly supplied in the form of a concentrated processing liquid composition having a volume reduced by a condensing (in this field, a term "concentrated" is used instead of "condensed", and the term "concentrated" does not mean a condensing operation such as evaporation or dehydration).

[0004] Also a concentrated liquid processing material for bleach-fix is commonly of a two-liquid form, which is stabler than a single-liquid form, and is constituted of two parts including a concentrated bleach composition part containing a bleaching agent (hereinafter also called bleaching agent part) and a concentrated fixing composition part containing a fixing agent (hereinafter also called fixing agent part).

[0005] In the processing in mini-labs, there are required, in addition to the aforementioned convenience in transportation, a faster processing for the user service and a lower replenishment rate for reducing the discharged used solutions. For achieving a lower replenishment rate and a faster process in the bleach-fix step, it is conceivable to increase the concentration of the bleaching agent and to reduce pH value for maintaining the bleaching ability of the bleach-fix solution. However, a lower pH value in the fixing agent part is not permissible as it induces a decomposition and a precipitation/deposition of the fixing agent. Also a lower pH value of the bleaching agent part and a higher concentration of the bleaching agent induce precipitation/deposition of different components in a storage or in a use at a low or high temperature, thus causing troubles in the works and the processing chemicals in the lab. Also under a high temperature, the storage stability is deteriorated to result in a problem that the bleaching agent is decomposed to a ferrous compound to deteriorate the bleaching ability. Therefore, the higher concentration and the lower pH value in the bleaching agent part involve problems of deteriorating the storage stability and the handling property of the processing material.

[0006] Properties required for the concentrated bleach composition include a stability that, even in a concentrated composition, constituents such as the bleaching agent do not deposit and an iron (III) complex is not reduced to a ferrous complex, a bleach fog resistance not causing a bleach fog while maintaining a sufficient bleaching activity, absence of an acetic acid odor or the like which is detrimental to the work environment, and an ability for enabling efficient silver recovery. However, as represented by the aforementioned example that the higher concentration and the lower pH value deteriorate the storage stability and the handling property of the processing solution, it has not been possible to obtain a concentrated bleach composition, which sufficiently satisfies all these requirements and is free from subsidiary defects.

[0007] Various technical developments have been made in order to meet all the properties required for the concentrated bleach composition at the same time, but no technology has been proposed capable of satisfying all the properties required for the concentrated bleach composition at the same time, as improvements in some of the properties required for the concentrated bleach composition result in a situation that other properties cannot be satisfied.

[0008] For example, Patent Reference 1 discloses use of 1,3-propanediaminetetraacetic acid-iron (III) complex for achieving a faster processing and an improved desilvering property, but this technology, involving an increase in the bleach fog, is unsuitable for processing a color photographic paper. Also Patent Reference 2 discloses use of diethylenetriaminepentaacetic acid-iron (III) complex for preventing a precipitation/deposition in a bleach-fix tank, but this technology involves a problem of generating a yellow edge stain in processing a color photographic paper. Also Patent Reference 3 discloses use of a polybasic organic acid for improving the odor in the work environment, but this technology suppresses a swelling of the emulsion layer of the photosensitive material, thereby lowering the bleaching speed. Also

Patent Reference 4 discloses use of an organic acid-iron (III) complex having a redox potential of 200 mV or higher and an organic acid of specified pKa for achieving a faster bleaching and an improved desilvering property, but this technology reduces a silver recovery rate from an overflow liquid of the bleach-fix solution.

[0009] In contrast to these related technologies, Patent Reference 5 proposes to use an aminopolycarboxylic acid-iron (III) complex at a high concentration of 0.5 mol/L or more, to set the pH value as low as from 2.0 to 3.5, and to utilize an aminopolycarboxylic acid not forming a complex, thereby providing a concentrated bleach composition, capable of reducing precipitation/deposition in time, also securing a stability that the iron (III) complex is not reduced to a ferrous complex, also capable of removing the acetic acid odor and excellent in the fast processing property and in the low replenishing rate.

[0010] However, even such improved concentrated bleach composition is associated with instability in time, such as an iron deposition in a prolonged storage (particularly under a high storage temperature) and generation of a sulfide precipitation in a state of a bleach-fix solution, prepared by mixing with the fixing agent, and in a low processing rate state (particularly when the bleach-fix solution is diluted in a subsequent rinsing tank). Also it is insufficient in the bleach fog resistance. A decrease in the amount of the bleaching agent, for solving these problems, has not been investigated at all as it is estimated to deteriorate the desilvering property.

[0011] As will be understood from the foregoing related technologies, there has not been found means that can satisfy all the properties required for the concentrated bleach composition.

[0012] As regards the composition for color development process, a composition constituted of plural parts is advantageous in improving the stability of the composition and in achieving an even higher condensed state and a smaller volume, but involves disadvantages of requiring mixing of plural condensed liquids rather than a simple dilution with water, and of requiring a larger number of containers for the composition, thus increasing the burdens on work and on environment for disposing of the used containers. Therefore, a single constitution (hereinafter called one-part form, having the same meaning as one-liquid form) will be much more convenient as long as the storage stability and the condensed state can be attained.

[0013] Based on these standpoints, the concentrated compositions of a one-part form for color developer replenisher have been developed and commercialized, and in fact match the market needs in the simplicity of operation and handling, in reduction of wastes and in economical property, but are unable to meet the requirements of the market in following points and in fact a concentrated processing composition of plural-part form is often selected.

[0014] The problems associated with the concentrated composition of one-part form for the color developer replenisher includes, firstly, that the components of the composition are liable to be precipitated and deposited during storage, secondly that the developer replenisher prepared from the concentrated composition shows a creeping-up phenomenon along an internal wall or a rack of a replenishing tank thereby causing a deposition of the components of the replenisher and a stain on processing tanks, thirdly that the processed photosensitive material is liable to show a loss in the sensitivity, fourthly that so-called edge stain tends to be generated on a cross section of the substrate of the processed photosensitive material, and fifthly that the processing material cannot accomplish a cost level required in the market.

[0015] As to the first problem, it is disclosed that the deposition during storage can be prevented by an addition, in the liquid development composition, of an alkanolamine according to Patent Reference 6, an arylamine according to Patent Reference 7, an anionic surfactant according to Patent Reference 8, or an aromatic sulfonic acid according to Patent Reference 9.

[0016] As to the second problem, for example Patent Reference 10 discloses that presence of dialkylhydroylamine or hydroxyalkylamine suppresses the creep-up phenomenon thereby preventing deposition of the replenisher components and stain of the processing tanks.

[0017] As to the third problem, Patent Reference 11 discloses that presence of p-toluenesulfonic acid enhances the color developing property.

[0018] As to the fourth problem, Patent Reference 12 discloses that presence of an alkylene glycol or an alkylsulfonic acid suppresses the edge stain and the stain in the processing tanks and rack.

[0019] As described above, though a solution has been found for each of the problems in the concentrated liquid processing composition, such solutions, when employed in combination, show certain effects on the aforementioned first to fourth problems but not in sufficient levels, thus not providing complete solutions.

[0020] Under such situation, Patent Reference 13 discloses that the first to fourth problems above can be solved by a developer replenisher composition which has, in combination with benzenesulfonic acid or lactam specified in the foregoing, a specified pH range, a specified specific gravity range and a color developing agent of a high concentration. However, the composition of Patent Reference 13, being intended for a rapid processing, involves a higher cost of the processing material because of a higher concentration of the color developing agent and a higher pH, and is therefore unsuitable as a composition for general purposes.

[0021] The aforementioned related arts relating to the invention of the present application include:

Patent Reference 1: JP-A-2-103040

Patent Reference 2: JP-A-61-118752
Patent Reference 3: JP-A-3-155548
Patent Reference 4: JP-A-5-72694
Patent Reference 5: JP-A-2004-53921
Patent Reference 6: JP-A-6-194797
Patent Reference 7: JP-A-7-114163
Patent Reference 8: JP-A-7-043874
Patent Reference 9: JP-A-7-239541
Patent Reference 10: JP-A-4-443
Patent Reference 11: JP-A-7-311453
Patent Reference 12: JP-A-2001-109115
Patent Reference 13: JP-A-2004-54024

DISCLOSURE OF THE INVENTION

Problems the Invention is to Solve

[0022] The present invention has been made in consideration of the above-described background, and a first object thereof is to provide a concentrated bleach-fix processing composition which can secure a stability in time (precipitation/ deposition resistance) as a concentrated bleach composition, and also can secure, in a prepared bleach-fix solution, a stability in use (sulfurization resistance), a bleach fog resistance, an elimination of acetic acid odor and a silver recovery efficiency.

[0023] A second object is to provide, utilizing a bleach-fix solution prepared by combining the concentrated bleach composition with a concentrated fixing composition, a bleach-fix method capable of providing a satisfactory photographic quality in bleaching even in a rapid processing.

[0024] Also a third object of the present invention is to provide a technology, capable of meeting the requirements relating to the processing quality in the color lab market, and more specifically to provide a concentrated one-part composition for color developer replenisher of a practical cost, capable of meeting the requirements firstly that the components of the composition do not cause a precipitation/deposition during storage, secondly that the developing tank and the rack thereof are not stained by the creep-up phenomenon of the developing solution on the tank wall during the processing, thirdly a sufficient color developing activity, and fourthly that an edge stain is not generated on the cross section of the substrate of the processed photosensitive material.

MEANS FOR SOLVING THE PROBLEMS

[0025] As a result of intensive investigations undertaken by the present inventor on various salt concentrations, pH values and buffer concentrations capable of maintaining, among the components of the bleach part, both non-complexed ethylenediaminetetraacetic acid (hereinafter also called free ethylenediaminetetraacetic acid) and ethylenediaminetetraacetic acid-iron (III) complex salt stably in a dissolved state, it is newly found that, by maintaining ethylenediaminetetraacetic acid-iron (III) complex salt at a specified salt concentration of 0.5 mol/L or less and by adding free ethylenediaminetetraacetic acid at a specified concentration with respect to the ethylenediaminetetraacetic acid-iron (III) complex salt, specified ranges exist for the pH value and for a buffer (dibasic acid of specified pKa) capable of preventing the deposition at the low and high temperatures and preventing deterioration in the stability in time under a high temperature as described above, and the present invention has been reached based on this finding. Also a reduction in the iron salt concentration in the bleach-fix solution improves the sulfurization resistance and the bleach fog resistance and achieves a significant improvement in the silver recovering efficiency.

[0026] Thus, the first and second objects above are accomplished by the present invention of following constitution:

1. A concentrated bleach composition for a silver halide color photographic photosensitive material, which comprises a single liquid satisfying following compositional conditions (A) to (D):

    (A) an ethylenediaminetetraacetic acid-iron (III) complex salt as a bleaching agent is contained in an amount of from 0.10 to 0.42 mol/L;
    (B) an uncomplexed ethylenediaminetetraacetic acid is contained in an amount of from 0.5 to 30 mol% with respect to the bleaching agent;
    (C) a dibasic acid having a pKa of from 2.0 to 5.0 is contained in an amount of from 0.10 to 0.40 mol/L; and
    (D) a pH value is from 2.0 to 3.5.

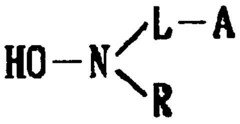
2. The concentrated bleach composition as described in 1 above,
wherein an azole compound is not contained.
3. The concentrated bleach composition as described in 1 or 2 above,
wherein the concentrated bleach composition is used after dilution of from 1.2 to 5.0 times with water.
4. A processing method for a silver halide color photographic photosensitive material, which comprises:

replenishing a bleach-fix tank with a water-diluted solution of a concentrated bleach composition as described in any of 1 to 3 above and a water-diluted solution of a concentrated fixing composition containing a thiosulfate salt in an amount of from 1.0 to 3.0 mol/L in a ratio of 1:1, in which a water-dilution ratio of each of the water-diluted solutions is from 1.2 to 5.0 times,

wherein the silver halide photographic photosensitive material is immersed for a period of from 10 to 30 seconds in a solution in the bleach-fix tank.
Gist of the present invention firstly resides in a fact that a dibasic acid having pKa of from 2.0 to 5.0 is contained in an amount of from 0.10 to 0.40 mol/L, thus removing the acetic acid odor and providing a deposition resistance, namely a stability in time, that cannot be attained by a low pH value with other ordinarily employed acids. Gist of the present invention secondly resides, in the presence of such dibasic acid under the condition of concentration above, in selecting ethylenediaminetetraacetic acid-iron (III) complex salt as the bleaching agent, utilizing ethylenediaminetetraacetic acid-iron (III) complex salt at a specific salt concentration of 0.5 mol/L or less and adding free ethylenediaminetetraacetic acid at a specified concentration with respect to ethylenediaminetetraacetic acid-iron (III) complex salt, thereby achieving improvements against deposition at a low temperature and in the stability in time at a high temperature.
The aforementioned components to be employed in the concentrated bleach composition of the invention are those employed in the already known bleach composition, but the presence of the aforementioned compositional range (dibasic acid of specified pKa, concentration condition thereof, ethylenediaminetetraacetic acid-iron (III) complex salt, free ethylenediaminetetraacetic acid, and pH range from 3.5 to 2.0) in which the concentrated bleach composition is stable and the bleaching ability is maintained satisfactorily, is a new finding and such particular compositional range is not easily conceivable.
The present invention is further characterized in that the bleach composition of the formulation above has a rapid bleach-fix property despite of use of ethylenediaminetetraacetic acid-iron (III) complex salt which is not so high in an oxidation potential as a bleaching agent, and, by setting the formulation of the bleaching agent within such specified range, in maintaining a finished quality and in realizing a rapid/low-replenishment process with a replenishment rate as low as from 20 to 50 ml/m^2 and/or a short bleach-fix process of 30 seconds or less, without causing a deposition or a deterioration in the processing solution.
The third object can be accomplished by the present invention of following constitution:
5. A concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material, which satisfies following compositional conditions:

(A) a p-phenylenediamine color developing agent is contained in an amount of from 0.08 to 0.12 mol/L;
(B) a substituted hydroxyamine derivative represented by formula (I) is contained in an amount of from 0.06 to 0.16 mol/L:

Formula (I)



$$\mathrm{HO-N}\begin{matrix}\diagup \mathrm{L-A}\\ \diagdown \mathrm{R}\end{matrix}$$

wherein L represents an alkylene group that may be substituted;
A represents a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group or an amino group that may be substituted with an alkyl; and
R represents a hydrogen atom or an alkyl group that may be substituted;
(C) an ethylene glycol compound is contained in an amount of from 0.05 to 1.0 mol/L;
(D) a pH value is from 12.5 to 12.8 when the composition is diluted to 3.84 times with water; and

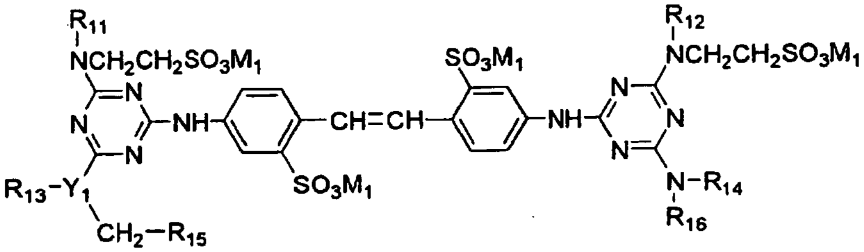
(E) an alkanolamine is not substantially contained.

6. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material as described in 5 above,
wherein the ethylene glycol compound comprises at least a combination of diethylene glycol and polyethylene glycol having a molecular weight of from 200 to 600.
7. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material as described in 5 or 6 above, which comprises a sulfinic acid compound represented by formula (II) in an amount of from 0.01 to 0.2 mol/L:

Formula (II) **RSO_2M**

wherein R represents an alkyl group, a cycloalkyl group, an alkenyl group, an alkinyl group, an aralkyl group or an aryl group; and
M represents a hydrogen atom or an alkali metal atom.
8. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material as described in any of 5 to 7 above, which comprises a diaminostilbene derivative represented by formula (III) and/or formula (IV) in an amount of from 1 to 50 mmol/L:

Formula (III)



wherein R_{11} and R_{12} each independently represents a hydrogen atom or an alkyl group;
R_{13} and R_{14} each independently represents a hydrogen atom, an alkyl group or an aryl group;
R_{15} represents an alkyl group containing at least one asymmetric carbon or a group represented by formula (I-a);
R_{16} represents an alkyl group containing at least one asymmetric carbon or a group represented by formula (I-b); and
M_1 represents a hydrogen atom or an alkali metal atom; provided that R_{13} and R_{15}, or R_{14} and R_{16} may be bonded each other to form a ring:

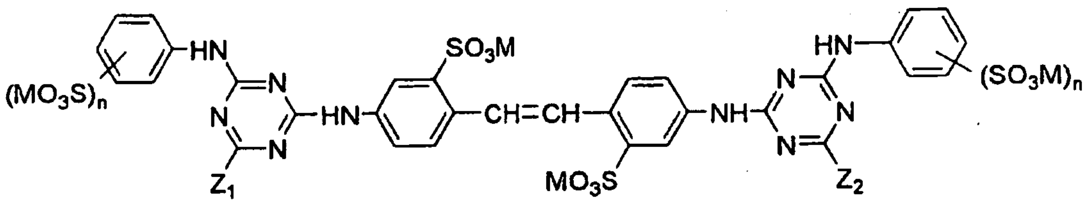
Formula (I-a) **$-CH_2CH_2CH_2O)n_{11}H$**

wherein n_{11} represents an integer of from 1 to 3;

Formula (I-b) **$-(CH_2CH_2O)_{n12}H$**

wherein n_{12} represents an integer of from 2 to 4;

Formula (IV)



wherein Z_1 and Z_2 may be mutually same or different, and each represents an amino group containing from 2 to 3 carbon atoms which is substituted with a hydroxyl group or a sulfonic acid group; and

M represents a hydrogen atom or an alkali metal atom.

9. A processing method for a color photographic photosensitive material, which comprises:

utilizing a concentrated one-part composition for a color developer replenisher as described in any of 5 to 8 above with a dilution of from 3 to 6 times with water as a replenisher.

[0027] As to the first to fourth problems to be solved by the concentrated one-part composition for the color developer replenisher of the invention, solving means are disclosed respectively for such problems as described in the background technology, but the combination of such means is generally unable to solve all the first to fourth problems. However, the particular combination of the invention is capable, within its range, of solving all the problems.

[0028] Gist of the concentrated composition for the color developer replenisher of the invention resides in a finding of specified compositional conditions including selection of specified compounds (an ethylene glycol compound and a compound of the formula (I)), concentration ranges thereof, a pH range and a concentration of the color developing agent, capable of satisfying the aforementioned four requirements relating to the processing quality.

[0029] More specifically, the present invention employs an ethylene glycol compound at a specified concentration, in order to realize a rapid processing property without utilizing the color developing agent at a high concentration, particularly a combination of diethylene glycol and a specified polyethylene glycol, and also employs an optimally selected pH, thereby accomplishing to solve the first to fourth problems without sacrificing the rapid processing property. Also upper limits selected for the concentrations of the color developing agent and other components avoid a loss in the color formation property by an inhibition of diffusion caused by a high salt concentration, and also avoid a cost increase in the processing material.

EFFECT OF THE INVENTION

[0030] The concentrated bleach composition of the present invention for silver halide photographic photosensitive material, formed by specified component compounds of specified density ranges and a specified pH range, is constituted of one part, capable of securing a stability in time (precipitation/deposition resistance), a stability at use (sulfurization resistance) of a bleach-fix solution prepared in combination with a fixing composition, also a bleach fog resistance, an elimination of acetic acid odor, and a silver recovery efficiency, and also maintaining a rapid processing property.

[0031] Also the concentrated composition of the present invention for color developer replenisher for the silver halide photographic photosensitive material, formed by a specified concentration range of the developing agent, specified component compounds of specified density ranges and a specified pH range, is constituted of one part, capable of suppressing precipitation/deposition during storage, stains in the developing tank and the rack by a creeping-up of the developing solution along the tank wall, and an edge stain phenomenon, and of providing a sufficient color development property and a practical cost.

BEST MODE FOR CARRYING OUT THE INVENTION

[0032] In the following, the present invention will be clarified in detail.

[0033] A concentrated processing composition for bleach-fix solution is preferably constituted of a bleaching agent part and a fixing agent part. One aspect of the present invention is an invention on the bleaching agent part, namely a concentrated bleach composition, and an invention on a bleach-fix replenishing method utilizing the same.

[0034] According to the present invention, the bleaching agent part and the fixing agent part may be used by mixing and diluting in advance to prepare a bleach-fix replenisher, or the bleaching agent part and the fixing agent part may be individually replenished into the bleach-fix tank and may be made to substantially function as a bleach-fix replenisher in the tank, but the latter mode is preferable in more eminently exhibiting the effect of the invention and in simplifying the processing operations.

[0035] The concentrated bleach composition of the invention is a constituent of a concentrated bleach-fix solution composition, for the silver halide color photographic photosensitive material, constituted of two-parts, namely a concentrated bleach composition part containing a bleaching agent and a concentrated fixing composition part containing a fixing agent, and is characterized in being formed by a single liquid satisfying the following compositional requirements (A) to (D):

(A) containing, as a bleaching agent, ethylenediamine tetraacetic acid-iron (III) complex salt in an amount of from 0.10 to 0.42 mol/L;
(B) containing uncomplexed ethylenediamine tetraacetic acid in an amount of from 0.5 to 10 mol% with respect to the bleaching agent;
(C) containing a dibasic acid having a pKa of from 2.0 to 5.0 in an amount of from 0.10 to 0.40 mol/L; and
(D) having a pH value of from 2.0 to 3.5.

[0036] In the present invention, ethylenediaminetetraacetic acid-iron (III) complex salt is employed as a bleaching agent, with a concentration range of from 0.10 to 0.42 mol/L, preferably from 0.15 to 0.40 mol/L and more preferably from 0.20 to 0.35 mol/L.

[0037] A high-concentration formulation exceeding the concentration range above is liable to generate a precipitate in time, while a concentration lower than the lower limit of the concentration range above is incapable of providing a rapid bleach-fixing speed, thus often resulting in an insufficient desilvering.

[0038] The concentration bleach composition contains free ethylenediamine tetraacetic acid in an amount of from 0.5 to 30 mol% with respect to ethylenediamine tetraacetic acid-iron (III) complex salt, preferably from 2.0 to 20 mol% and more preferably from 3.0 to 15 mol%.

[0039] A concentration ratio exceeding 30 mol% of uncomplexed (free) ethylenediamine tetraacetic acid with respect to ethylenediamine tetraacetic acid-iron (III) complex salt is liable to induce precipitation of free acid, and reduces a further increase in the stabilizing effect on the iron (III) complex salt. Also a free acid concentration less than 0.5 mol% results in an iron precipitation in time under a high temperature.

[0040] The concentrated bleach composition has a pH value of from 2.0 to 3.5, preferably from 2.2 to 3.3 and more preferably from 2.4 to 3.0.

[0041] It also contains a dibasic acid, having pKa of from 2.0 to 5.0, in an amount of from 0.10 to 0.40 mol/L, preferably from 0.15 to 0.35 mol/L, and more preferably from 0.20 to 0.30 mol/L. In a system in which a dibasic acid having pKa of from 2.0 to 5.0 is present together with free ethylenediaminetetraacetic acid and an iron (III) complex salt thereof, a function of suppressing generation of precipitation and changes to an iron (II) complex salt and a hydroxylated complex is a phenomenon observed in the concentration range and the pH range mentioned above. Also the concentration range above allows to stabilize the pH value of the solution in the bleach-fix tank within a preferable range, and also improves the sulfurization resistance, the bleach fog resisstance and the silver recovery efficiency.

[0042] The concentrated bleach composition of the invention is preferably diluted with water at use. The ratio of dilution is from 1.2 to 5.0 (based on volume ratio), preferably from 1.3 to 3.0. The dilution means a regulation from the concentrated bleach composition of a concentration range suitable for storage stability and transportation, to a concentration suitable for use as a bleach-fix replenisher. Also water to be used for dilution may naturally be an overflow liquid from a rinse tank or an overflow liquid.

[0043] The replenishment in the bleach-fix tank is preferably executed in a mode of diluting the concentrated fixing composition with water to a similar extent and adding it to the bleach-fix tank at a replenishing rate matching the processing rate of the photosensitive material to be processed. However, there can be also utilized a mode of replenishing the concentrated bleach composition and the concentrated fixing composition directly into the bleach-fix tank without dilution with water, and replenishing water or the overflow liquid of the rinse tank at the same time. Further, there can be utilized a mode, as described above, of mixing the concentrated bleach composition, the concentrated fixing composition, and water or an overflow liquid from the rinse tank or the color developing tank to prepare the bleach-fix replenisher and replenishing it directly into the bleach-fix tank.

[0044] Particularly preferable is a processing method of replenishing a water-diluted solution of the concentrated bleach composition of the invention and a water-diluted solution of a concentrated fixing composition containing a thiosulfate salt in an amount of from 1.0 to 3.0 mol/L in a ratio of 1:1, with a water-dilution ratio of from 1.2 to 5.0 times respectively, into the bleach-fix tank, wherein an immersion time of the silver halide photographic photosensitive material in the solution of the bleach-fix tank is from 10 to 30 seconds. Such mode enables a rapid processing even employing, as the bleaching agent, ethylenediamine tetraacetic acid-iron (III) complex which is a compound of a relative low oxidation potential.

[0045] In most cases, the concentrated bleach composition or the bleach-fix replenisher contains, for the purpose of promoting bleaching or reducing bleach fog, an azole compound for example an imidazole compound such as imidazole or dimethylimidazole, a pyrimidine derivative, a triazole, a thiadiazole, an oxadiazole, or 2-picolinic acid. However, in the concentrated bleach composition of the invention, an addition of an azole compound causes precipitation during the storage of the concentrated liquid under a low temperature and also reduces the bleaching speed, whereby the effects of the invention become difficult to obtain. It is therefore preferable that the azole compound is substantially absent.

[0046] The concentrated bleach composition of the invention may contain, as the bleaching agent, other known bleaching agents in addition to ethylenediaminetetraacetic acid-iron (III) complex salt. Examples of the usable bleaching agent include an aminopolyacetic acid-iron (III) complex salt other than ethylenediaminetetraacetic acid-iron (III) complex salt, an iron (III) complex salt of an organic acid such as citric acid, tartaric acid or malic acid, a persulfate salt and hydrogen peroxide. However, in the case that such second bleaching agent is used in combination, a content thereof is 50 mol% or less with respect to ethylenediaminetetraacetic acid-iron (III) complex salt, preferably 30 mol% or less and more preferably the second bleaching agent is absent (namely, ethylenediaminetetraacetic acid-iron (III) complex salt only).

[0047] A concentration of the bleaching agent in the bleach-fix replenisher prepared by mixing the bleaching agent part and the fixing agent part and diluted them with water, in a composition corresponding to the bleach-fix replenisher including the bleaching agent part, the fixing agent part and water contained in the overflow liquid of the color developing tank, or in the solution of the bleach-fix tank, is so selected as from 0.01 to 1.0 mol/L, preferably from 0.03 to 0.80 mol/L, more preferably from 0.05 to 0.70 mol/L, and further preferably from 0.07 to 0.50 mol/L.

[0048] The bleaching agent part contains a dibasic acid having pKa of from 2.0 to 5.0, in an amount of from 0.10 to 0.40 mol/L. A pKa of the dibasic acid less than 2.0 is liable to generate precipitation of free acid, and a pKa exceeding 5.0 tends to generate a precipitate of a hydrolysate of the iron (III) complex bleaching agent. A preferred pKa of the dibasic acid is from 3.5 to 4.5.

[0049] On the other hand, a content of the dibasic acid, even made higher than the range of from 0.10 to 0.40 mol/L, provides little effect for further stabilizing the composition and is liable to cause incomplete dissolution of the composition, and the effects of the invention cannot be obtained at a lower concentration side of the above-mentioned range.

[0050] The bleaching agent part may also contain another monobasic acid or polybasic acid as long as it contains the dibasic acid in an amount of from 0.10 to 0.40 mol/L, but it preferably does not contain such other acids.

[0051] Specific examples of the dibasic acid having pKa of from 2.0 to 5.0 include succinic acid, maleic acid, malonic acid, glutaric acid, phthalic acid, isophthalic acid, and adipic acid, which are particularly excellent in preventing deposition and in being free from delay in bleaching.

[0052] The dibasic acid is preferably succinic acid, maleic acid, malonic acid or glutaric acid, and most preferably succinic acid.

[0053] The fixing agent part, for constituting the bleach-fix processing composition in combination with the bleaching agent part, may contain, as a fixing agent, a known fixing chemical, namely one or a mixture of two or more selected from water-soluble silver halide dissolving agents, for example thiosulfate salts such as sodium thiosulfate or ammonium thiosulfate, thiocyanate salts such as sodium thiocyanate or ammonium thiocyanate, thioether compounds such as ethylenbisthioglycolic acid or 3,6-dithia-1,8-octanediol, and thioureas. Also there may be employed a special bleach-fix solution constituted, as disclosed in JP-A-55-155354, of a combination of a fixing agent and a large amount of halide such as potassium iodide. In the present invention, a thiosulfate salt, particularly ammonium thiosulfate, is preferably employed. In the fixing agent part, a concentration the fixing chemical is preferably designed within a range of from 0.3 to 3 moles, more preferably from 0.5 to 2.0 moles, with respect to 1L of the bleach-fix replenisher prepared from the bleaching agent part and the fixing agent part, or a solution corresponding to the bleach-fix replenisher including the direct replenishing amounts of the bleaching agent part and the fixing agent part, and the overflow from the color developing tank.

[0054] The fixing agent part preferably contains, as a preservative, a sulfite ion-releasing compound for example a sulfite salt (such as sodium sulfite, potassium sulfite or ammonium sulfite), a bisulfite salt (such as ammonium bisulfite, sodium bisulfite, or potassium bisulfite), a metabisulfite salt (such as potassium metabisulfite, sodium metabisulfite, or ammonium metabisulfite), or an arylsulfinic acid such as p-toluenesulfinic acid or m-carboxybenzenesulfinic acid. Such compound is preferably contained, calculated as sulfite ions or sulfinate ions, in an amount of from about 0.02 to 1.0 mol/L (as a concentration of prepared processing solution).

[0055] As the preservative, there may be also utilized, in addition to the foregoing, ascorbic acid, a carbonyl-bisulfuric acid addition product, or a carbonyl compound.

[0056] Now a bleach-fix solution, prepared by mixing the bleach agent part and the fixing agent part and by adding a certain amount of water when necessary, will be explained below, and constituents of the bleach-fix solution, that may be included in either of the bleach agent part and the fixing agent part, will also be discussed.

[0057] The bleach-fix replenisher or a solution corresponding to the bleach-fix replenisher preferably has, at the dissolution, a pH within a range of from 3 to 8, more preferably from 4 to 8. A pH lower than this range improves the desilvering property but promotes a deterioration of the solution and a leuco formation of the cyan dye. On the other hand, a pH higher than this range retards the desilvering and is liable to generate a stain.

[0058] For regulating pH, it is possible to add, if necessary in the fixing agent part, an alkali such as potassium hydroxide, sodium hydroxide, lithium hydroxide, lithium carbonate, sodium carbonate, or potassium carbonate, or an acidic or alkaline buffer.

[0059] Also in either or both of the bleach agent part and the fixing agent part of the bleach-fix processing composition, there may be added a fluorescent whitening agent, a defoamer, a surfactant or polyvinylpyrrolidone.

[0060] The bleach-fix processing composition is generally supplied in a state contained in a container. The container for the composition part containing the bleach agent preferably has a certain oxygen permeating rate for the stability in time of the composition, and is therefore different, in this point, from the containers for other processing materials. The oxygen permeability may be realized not necessarily by selecting an oxygen-permeating material for the container but for example by a structure of a stopper of the container that loosens the hermetic property. A preferred oxygen permeability is an oxygen permeation of 4 mL or more per day, but is preferably 13 mL or less, in consideration of a limitation on the thickness of the container wall for maintaining the shape of the container.

[0061] A preferred example of the container, to be employed in a typical storage form of the bleach agent, is a container formed by high-density polyethylene (hereinafter represented as HDPE) having a density of from 0.941 to 0.969 and a melt index of from 0.3 to 5.0 g/10min as a single constituent resin. The density is more preferably from 0.951 to 0.969, and further preferably from 0.955 to 0.965, and the melt index is more preferably from 0.3 to 5.0 and further preferably from 0.3 to 4.0. The melt index is measured, according to the method defined in ASTM D1238, under conditions of a temperature of 190°C and a load of 2.16 kg. This container is preferably formed with a thickness of from 500 to 1500 μm. However, the container for the processing material to be employed in the present invention is not limited to such HDPE container suitable for mounting on a developing equipment, but other containers prepared from general container materials other than HDPE such as polyethylene terephthalate (PET), polyvinyl chloride (PVC) or low-density polyethylene (LDPE) or from HDPE not falling within the aforementioned ranges of density and melt index.

[0062] Also there is preferred a form contained in so-called Cubitainer, which is inserted in and according to an internal dimension of a reinforcing corrugated cardboard box.

[0063] Also containers to be explained later for other processing materials may also be utilized, but the aforementioned oxygen permeability is preferably secured.

[0064] The concentrated composition for color developer replenisher of one-part form can provide a color developer replenisher by a mere dilution with a predetermined amount of water. Therefore, the composition contains all the components of the color developer replenisher in a concentrated state, and still constitute a system stable for example against a temperature change during storage. Processing chemicals dissolved in the concentrated composition for color developer replenisher generally include (1) a color developing agent as an essential component, (2) an alkali component for activating the color developing agent, (3) an antioxidant (preservative) for preventing an oxidative deterioration of the color developing agent for example by an oxidation with air, (4) a water softening agent (metal chelating agent) for masking a metallic impurity which generates a turbidity in the developing solution or promoting an oxidation thereof, (5) an auxiliary dissolving agent for further elevating the concentration of the processing composition thereby achieving a further compactness, (6) a surfactant for preventing a bubble formation on the surface of the processed photosensitive material or in the developing tank, (7) an antifoggant for preventing a development fog or an air fog, (8) a fluorescent whitening agent for improving a whiteness of the background of a finished photograph (in case of a reflective print) or for improving fastness of a color image, and (9) compounds for executing necessary functions according to the purpose of application of the developer. Among these, groups from (1) to (3) are most common components in the developing material, while groups from (4) to (9) may not be included depending on the object photosensitive material or on the form of processing. Also in each group, it is possible to select one or select plural compounds.

[0065] Within the constitution described above, the concentrated composition for color developer replenisher of the invention particularly satisfy following requirements:

(A) containing p-phenylenediamine color developing agent in an amount of from 0.08 to 0.12 mol/L;
(B) containing a substituted hydroxyamine derivative, represented by the aforementioned formula (1), in an amount of from 0.06 to 0.16 mol/L;
(C) containing an ethylene glycol compound in an amount of from 0.05 to 1.0 mol/L;
(D) having a pH value of from 12.5 to 12.8 when diluted to 3.84 times with water; and
(E) being substantially free from an alkanolamine.

[0066] Preferred ranges for the requirements on the constitution of the composition are as follows:

As to (A), the concentration of p-phenylenediamine color developing agent is preferably from 0.09 to 0.115 mol/L, and more preferably from 0.095 to 0.110 mol/L.

As to (B), the concentration of the substituted hydroxyamine derivative, represented by the formula (1), is preferably from 0.07 to 0.15 mol/L, and more preferably from 0.08 to 0.12 mol/L.
As to (C), the concentration of ethylene glycol compound is preferably from 0.08 to 0.80 mol/L, and more preferably from 0.10 to 0.50 mol/L.
As to (D), the pH is preferably from 12.50 to 12.70, and more preferably from 12.55 to 12.65.
As to (E), the composition of the invention is substantially free from an alkanolamine such as diethanolamine, triethanolamine or triisopropanolamine, but being substantially free from an alkanolamine means that an alkanolamine is not intentially added and that an alkanolamine, even when present in a minute amount, is present at such concentration that an influence thereof is not perceivable. Such concentration level is generally 1 g/L or less, and preferably 0.1 g/L or less.

[0067] Outside the aforementioned constitution, the concentrated composition becomes unable to satisfy at least one of the stability, concentration, rapid processing property and low replenishing rate, intended in the present invention.

[0068] Representative examples of the p-phenylenediamine color developing agent contained in the concentrated composition for color developer replenisher of the invention are shown below, but the present invention is not limited to such examples:

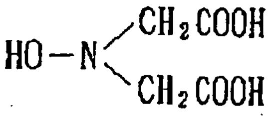
1) N,N-dimethyl-p-phenylenediamine
2) 4-amino-3-methyl-N,N-diethylaniline
3) 4-amino-N-(β-hydroxyethyl)-N-methylaniline
4) 4-amino-N-ethyl-N-((3-hydroxyethyl)aniline
5) 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline
6) 4-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline
7) 4-amino-3-methyl-N-ethyl-N-(4-hydroxybutyl)aniline
8) 4-amino-3-methyl-N-ethyl-N-((3-methanesulfonamidethyl)aniline
9) 4-amino-N,N-diethyl-3-(β-hydroxyethyl)aniline
10) 4-amino-3-methyl-N-ethyl-N-(β-methoxyethyl)aniline
11) 4-amino-3-methyl-N-(β-ethoxyethyl)-N-ethylaniline
12) 4-amino-3-methyl-N-(3-carbamoylpropyl)-N-n-propyl-aniline
13) 4-amino-N-(4-carbamoylbutyl)-N-n-propyl-3-methylaniline
15) N-(4-amino-3-methylphenyl)-3-hydroxypyrrolidine
16) N-(4-amino-3-methylphenyl)-3-(hydroxymethyl)pyrrolidine and
17) N-(4-amino-3-methylphenyl)-3-pyrrolidine carboxamide.

[0069] Among the p-phenylenediamine derivatives, particularly preferable are example compounds 5) and 8), and most preferable is the compound 8). Such p-phenylenediamine derivatives, in a state of a solid material, generally assume a salt state such as a sulfate salt, a hydrochlorate salt, a sulfite salt, a naphthalenedisulfonate salt or a p-toluenesulfonate salt.

[0070] The content of the aromatic primary amine developing agent in the processing composition is as described above, and a concentration of the color developing agent in the developer replenisher, prepared by diluting the composition 3 to 6 times with water, is regulated at from 10 to 40 mmol with respect to 1L of the developer replenisher, preferably from 12 to 35 mmol, and more preferably from 15 to 30 mmol.

[0071] Now the compound of the formula (I) of the invention will be explained in more details. In the formula (I), L represents a linear or branched alkylene group that may be substituted, containing from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms. Specific preferred examples include methylene, ethylene, trimethylene, and propylene. Examples of the substituent include a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group and an amino group that may be substituted, preferably a carboxyl group, a sulfo group and a hydroxyl group. A represents a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group or an amino group that may be substituted with an alkyl, preferably a carboxyl group, a sulfo group or a hydroxyl group. These may be in the form of a salt of sodium, potassium, or lithium. Preferred examples of -L-A include a carboxymethyl group, a caraboxyethyl group, a carboxypropyl group, a sulfoethyl group, a sulfopropyl group and a hydroxyethyl group. R represents a hydrogen atom or a linear or branched alkyl group that may be substituted, containing from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms. Examples of the substituent include a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group and an amino group that may be substituted, preferably a carboxyl group, a sulfo group and hydroxyl group. Such substituent may be in the form of a salt of sodium, potassium or lithium. Now specific examples of the compound of the formula (I) are shown, but the compound of the formula (I) to be employed in the invention is not limited to such examples.

(1)



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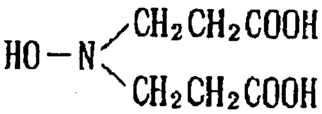

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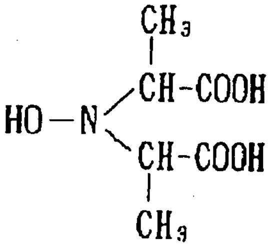

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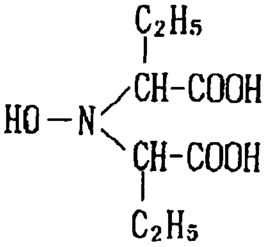

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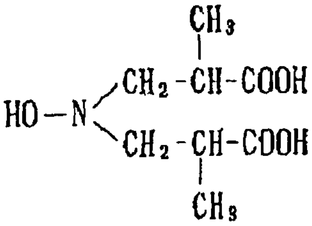

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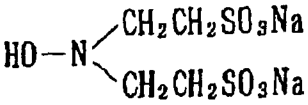

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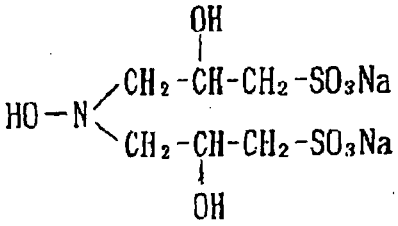

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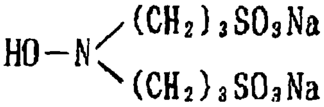

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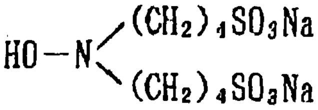

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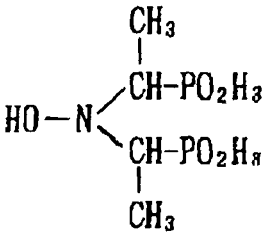

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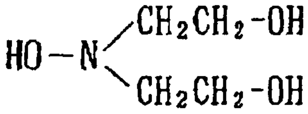
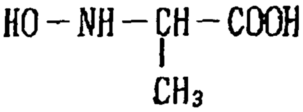


(13) $HO-NH-CH_2CO_2H$

(14) $HO\text{-}NH\text{-}CH_2CH_2COOH$

(15)



$HO-NH-\underset{\displaystyle CH_3}{\underset{|}{C}H}-COOH$

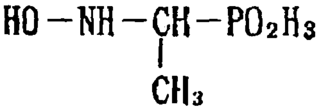
(16) $HO\text{-}NH\text{-}CH_2CH_2\ \text{-}SO_8H$

(17) $HO\text{-}NH\text{-}(CH_2)_3\text{-}SO_3H$

(18) $HO\text{-}NN\text{-}\ (CH_2)_4\text{-}SO_3H$

(19) $HO\text{-}NH\text{-}CH_2\text{-}PO_2HO_3$

(20)



$HO-NH-\underset{\displaystyle CH_3}{\underset{|}{C}H}-PO_2H_3$

(21) $HO\text{-}NH\text{-}CH_2CH_2OH$

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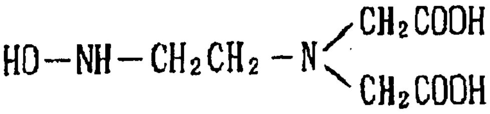

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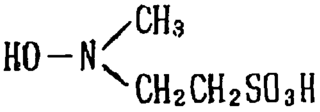

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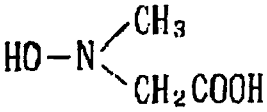

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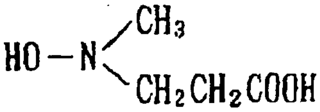

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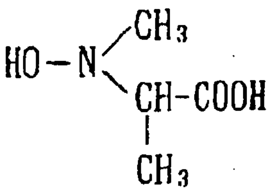

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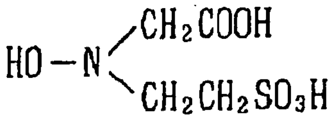

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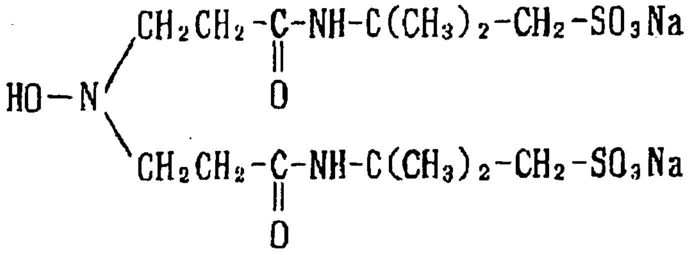


[0072] Among these specific compounds, the example compounds (2), (6) and (16) are preferable, and the example compound (6) is particularly preferable. These compounds may be synthesized by synthesizing methods described in JP-A-3-56456 (corresponding to USP Nos. 5,262,563 and 5,248,811), and JP-A-3-157354.

[0073] In the invention, the liquid replenisher for color developer, obtained by diluting the one-part concentrated composition for color developer replenisher, preferably contains the compound of the formula (I) in an amount of from 0.001 to 0.05 mol/L, more preferably from 0.005 to 0.04 mol/L, and further preferably from 0.01 to 0.03 mol/L. The one-part concentrated composition for color developer replenisher may contain only one of the aforementioned comopounds, or two or more thereof in combination. In case of use in combination, a total concentration of the compounds of the formula (I) in the color developer replenisher preferably is preferably within the range above.

[0074] In the one-part concentrated composition for color developer replenisher of the invention, hydroxylamine may be contained at a concentration of 0.02 mol/L or less, but is preferably not contained at all.

[0075] The ethylene glycol compound to be employed in the one-part concentrated composition for color developer replenisher of the invention will be explained in more details.

[0076] The ethylene glycol compound is preferably diethylene glycol, triethylene glycol, polyethylene glycol having a molecular weight of from 200 to 600, or a polyethylene glycol-propylene glycol block copolymer having a molecular weight of from 200 to 600, and more preferably diethylene glycol or polyethylene glycol having a molecular weight of from 200 to 600.

[0077] In order to realize the effects of the invention, it is preferable to use diethylene glycol and polyethylene glycol having a molecular weight of from 200 to 600 in combination.

[0078] Diethylene glycol and polyethylene glycol having a molecular weight of from 200 to 600 are used preferably with a molar ratio of from 10:1 1 to 1:10, more preferably from 5:1 to 1:1 and particularly preferably from 4:1 to 2:1.

[0079] The sulfinic acid compound, represented by a following formula (II), to be employed in the one-part concentrated composition for color developer replenisher of the invention will be explained below:

Formula (II) $\mathbf{RSO_2M}$

wherein R represents an alkyl group, a cycloalkyl group, an alkenyl group, an alkinyl group, an aralkyl group or an aryl group; and M represents a hydrogen atom or an alkali metal atom.

[0080] In the formula (II), R represents an alkyl group, a cycloalkyl group, an alkenyl group, an alkinyl group, an aralkyl group or an aryl group, and, in the case that R is an alkyl group, it contains from 1 to 10 carbon atoms and preferably from 1 to 3 carbon atoms. Also in case of a cycloalkyl group, it contains from 6 to 10 carbon atoms, and most preferably 6 carbon atoms. In case of an alkenyl group or an alkinyl group, it contains from 3 to 10 carbon atoms, and preferably from 3 to 6 carbon atoms. In case of an aralkyl group, it contains from 7 to 10 carbon atom. In case of an aryl group, it contains from 6 to 10 carbon atoms, and most preferably 6 carbon atoms. These groups may be further substituted with a substituent, and preferred examples of the substituent include a hydroxyl group, an amino group, a sulfonic acid group, a carboxylic acid group, a nitro group, a phosphoric acid group, a halogen atom, an alkoxy group, a mercapto group, a cyano group, an alkylthio group, a sulfonyl group, a carbamoyl group, a carbonamide group, a sulfonamide group, an acyloxy group, a sulfonyloxy group, an ureido group and a thioureido group. Also when such substituent is an acid group, it includes a case of a salt involving M above.

[0081] Among these, R is preferably an alkyl group containing from 1 to 3 carbon atoms, or a phenyl group, and the substituent is preferably an amino group, a carboxylic acid group or a hydroxyl group. In the formula (II), M represents a hydrogen atom, an alkali metal atom, ammonium or quaternary ammonium, and is preferably a hydrogen atom, a sodium atom or a potassium atom.

[0082] Specific examples of the compound of the formula (II) are shown below, but the compound of the formula (II) is not limited to such examples. Also in the example compounds below, the sulfinic acid group or the carboxylic acid group is mainly represented in an acid form, or a Na or K metal salt, but other alkali metal salts may also be usable.

I-1. CH_3SO_2H

I-2. CH_3SO_2Na

I-3. CH_3SO_2K

I-4. $C_2H_5SO_2H$

I-5. $C_2H_5SO_2Na$

I-6. $H_2MCH_2CH_2SO_2H$

I-7. $H_2NCH_2CH_2SO_2Na$

I-8. $H_3N^+CH_2CH_2SO_2-$

I-9. $HOCH_2CH_2SO_2Na$

I-10. $HOCH_2CH_2SO_2H$

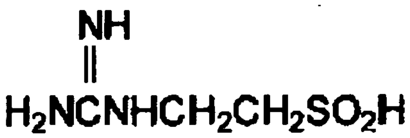
I-11. $HOOCCH_2CH_2SO_2Na$

I-12, $H_4NOOCCH_2CH_2SO_2H$

I-13. F_3CSO_2H

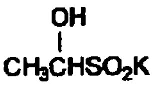
I-14. $NaSO_2CH_2CH_2SO_2Na$

I-15.



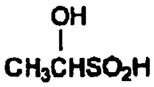
$H_2N\overset{\overset{\displaystyle NH}{\|}}{C}NHCH_2CH_2SO_2H$

I-16.



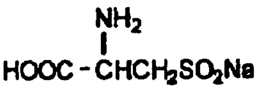
$CH_3\overset{\overset{\displaystyle OH}{|}}{C}HSO_2K$

I-17.



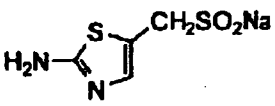
$CH_3\overset{\overset{\displaystyle OH}{|}}{C}HSO_2H$

I-18.



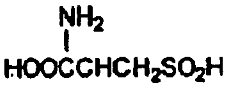
$HOOC-\overset{NH_2}{\overset{|}{C}}HCH_2SO_2Na$

I-19.



I-20. CH_3SO_2Li

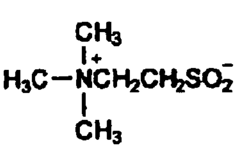
I-21.



$HOOC\overset{NH_2}{\overset{|}{C}}HCH_2SO_2H$

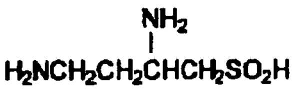
I- 22. CH3SO2- N+ (CH3)4

I-23.



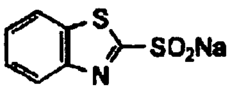
$H_3C-\overset{CH_3}{\underset{CH_3}{N^+}}CH_2CH_2SO_2^-$

I-24.

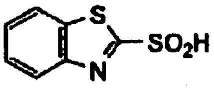


$H_2NCH_2CH_2\overset{NH_2}{\overset{|}{C}}HCH_2SO_2H$

I-25.



I-26.



I-27. $C_3H_7SO_2H$

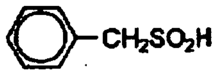
I-28. $C_3H_7SO_2Na$

I- 29. C4H9SO2H

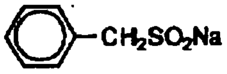
I- 30. C6H13SO2Na

I-31. $CH_3CONHCH_2SO_2H$

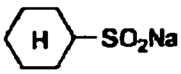
I-32.



I-33.

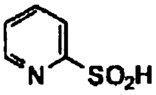


I-34.

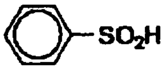


I-35.

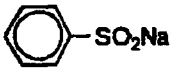
I-36.



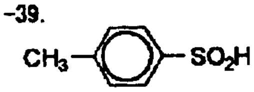
I-37.



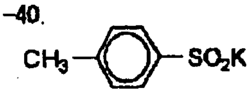
I-38.



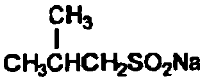
I-39.



I-40.

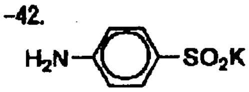


I-41.



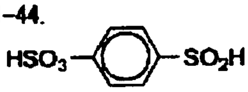
$CH_3CH(CH_3)CH_2SO_2Na$

I-42.



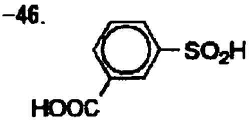
I-43.

I-44.

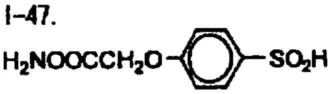


I-45. CH2=CHCH2SO2Na

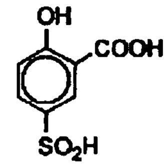
I-46.



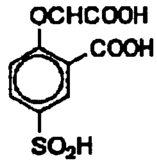
I-47.



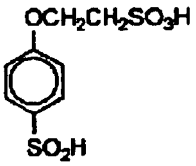
1-48.



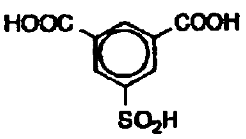
1-49.



1-50.



1-51.



[0083] Among the compounds represented by the formula (II), a benzenesulfinic acid compound, made present in the concentration composition, improves a stability against air oxidation and suppresses the creep-up phenomenon of the developer. The preferred benzenesulfinic acid compound is m-carboxybenzenesulfinic acid, p-carboxybenzenesulfinic acid, 2,4-dicarboxybenzenesulfinic acid or 4-acetylcarboxybenzenesulfinic acid, particularly m-carboxybenzenesulfinic acid. These compounds may be utilized in a free acid form, or in an alkali metal salt form such as potassium salt, sodium salt or lithium salt.

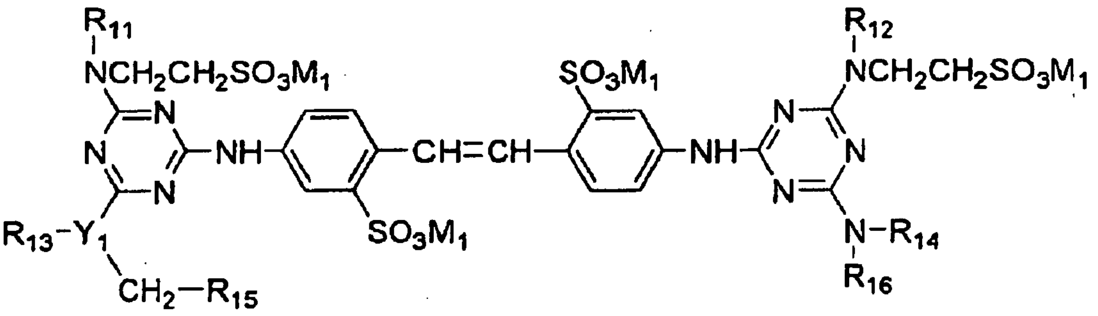
[0084] A preferred amount of addition of the benzenesulfinic acid compound is from 0.01 to 0.2 moles, more preferably from 0.03 to 0.1 moles per 1L of the concentrated composition.

[0085] The compound represented by the formula (II) is generally synthesized by a method of reducing a sulfonyl chloride compound, utilizing zinc powder, sulfite ion or an alkali metal sulfide as a reducing agent. Also other methods are known. Including these, the general synthesizing methods for the compounds of the formula (II) are described for example in Chem. Rev., vol. 4508, 69(1951), Organic Synthesis, Collective Vol. 1, 492(1941), J. Am. Chem. Soc., vol. 72, 1215(1950) and ibid., vol. 50, 792, 274 (1928).

[0086] The concentrated composition for color developer replenisher of the invention preferably contains a fluorescent whitening agent. A preferred fluorescent whitening agent is a bis(triazinylamino)stilbenesulfonic acid compound, for which a known or commercially available diaminostilbene whitening agent may be utilized. Among the known bis(triazinylamino)stilbenesulfonic acid compounds, those described in JP-A-6-329936, JP-A-7-140625 and JP-A-10-140849 are preferable. The commercially available compounds are described for example in "Senshoku Note" 9th ed., p.165-168 (Shikisen-sha Co.), and, among those described therein, preferred are Blankophor BSU, Hakkol BRK and a fluorescent whitening agent shown below.

[0087] Among the fluorescent whitening agents of bis(triazinylamino)stilbenesulfonic acid type, a compound represented by the formula (III) or (IV) is particularly preferable as it is effective for the stability of the composition.

Formula (III)



[0088] In the formula (III), R_{11} and R_{12} each independently represents a hydrogen atom or an alkyl group; R_{13} and R_{14} each independently represents a hydrogen atom, an alkyl group or an aryl group; R_{15} represents an alkyl group containing at least an asymmetric carbon atom or a group represented by a following formula (I-a); R_{16} represents an alkyl group containing at least an asymmetric carbon atom or a group represented by a following formula (I-b); and M_1 represents a hydrogen atom or an alkali metal atom; provided that R_{13} and R_{15}, or R_{14} and R_{16} may be bonded each other to form a ring.

Formula (I-a) **-CH2O (CH2CH2O) n11H**

[0089] In the formula (I-a), n_{11} represents an integer of from 1 to 3.

Formula (I-b) **-(CH2CH2O) n12H**

[0090] In the formula (I-b), n_{12} represents an integer of from 2 to 4.

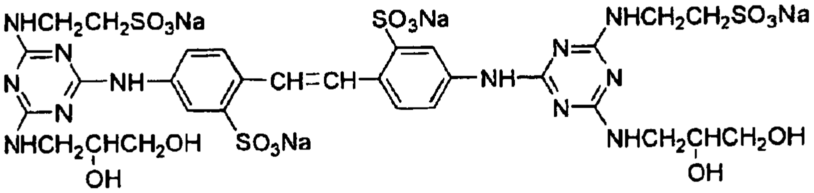
[0091] Now the formula (III) will be explained in detail. The alkyl group represented by R_{11} and R_{12} is a substituted or non-substituted alkyl group preferably containing from 1 to 20 carbon atoms, more preferably from 1 to 8 carbon atoms and particularly preferably from 1 to 4 carbon atoms. Examples of the substituent include a hydroxyl group, an alkoxy group (such as methoxy or ethoxy), a sulfonic acid group and an ethyleneoxy group, which may be further substituted with the substituent described above. Specific examples of the alkyl group represented by R_{11} and R_{12} include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-octyl group, a 2-hydroxyethyl group, a 3-hydroxypropyl group, a 2-hydroxylpropyl group, a 2-sulfoethyl group, a 2-methoxyethyl group, a 2-(2-hydroxyethoxy) ethyl group, a 2-[2-(2-hydroxyethoxy)ethoxy]ethyl group, and a 2-(2-[2-(2-hydroxyethoxy)ethoxy]ethoxy)ethyl group. R_{11} and R_{12} each is preferably a hydrogen atom, a methyl group, an ethyl group, an n-propyl group, an n-butyl group, or a 2-sulfoethyl group, more preferably a hydrogen atom, a methyl group, an ethyl group, or a 2-sulfoethyl group, and particularly preferably a hydrogen atom or a methyl group.

[0092] In the alkyl group represented by R_{13} and R_{14}, a preferable number of carbon atoms, a preferable substituent and specific examples are similar to those shown for R_{11} and R_{12} above. The aryl group represented by R_{13} and R_{14} is preferably a substituted or non-substituted aryl group containing from 6 to 20 carbon atoms, more preferably from 6 to 10 carbon atoms and particularly preferably from 6 to 8 carbon atoms. Examples of the substituent include a hydroxyl group, an alkoxy group (such as methoxy or ethoxy), a carboxyl group, an alkyl group (such as methyl, ethyl or propyl), a sulfonic acid group, an amino group, and a carbamoyl group, which may be further substituted with the substituent described above. Examples of the aryl group represented by R_{13} and R_{14} include a phenyl group, a naphthyl group, a 3,5-dicarboxyphenyl group, a 4-methoxyphenyl group, and a 3-isopropylphenyl group. R_{13} and R_{14} each is preferably a hydrogen atom, a methyl group, an ethyl group, an n-propyl group, a 2-hydroxyethyl group, a 3-hydroxypropyl group, a 2-hydroxypropyl group, a 2-sulfoethyl group, a 2-(2-hydroxyethoxy)ethyl group or a 2-[2-(2-hydroxyethoxy)ethoxy] ethyl group, more preferably a hydrogen atom, a methyl group, an ethyl group, a 2-hydroxyethyl group, a 2-hydroxypropyl group, or a 2-(2-hydroxyethoxy)ethyl group, and particularly preferably a hydrogen atom or a methyl group.

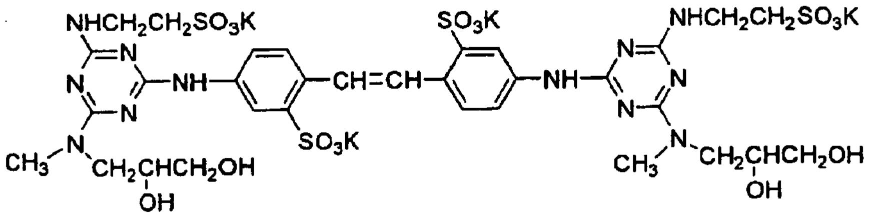
[0093] The alkyl group containing at least an asymmetric carbon atom, represented by R_{15} preferably contains from 1 to 20 carbon atoms, more preferably from 1 to 8 carbon atoms and particularly preferably from 1 to 4 carbon atoms, and may have a linear, branched or cyclic structure. Examples of the substituent include a hydroxyl group, an amino group and a carboxyl group, and a hydroxyl group is preferable. Specific examples of the alkyl group including at least an asymmetric carbon atom, represented by R_{15}, include hydroxyalkylalkyl groups such as a 1,2-dihydroxyethyl group, a 2-ethyl-1-hydroxyethyl group, a 1,2-dihydroxypropyl group, and a 1,2-dihydroxy-3-hydroxyethylpropyl group.

[0094] Specific examples of the compound represented by the formula (III), but such examples are not restrictive.

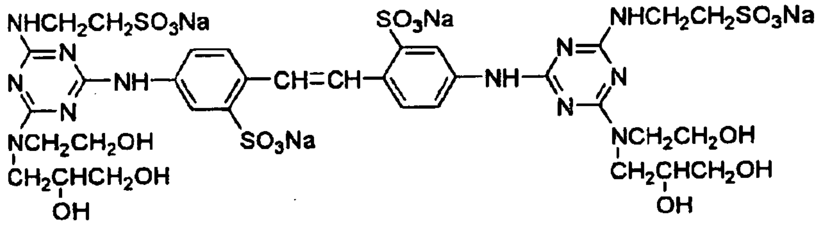
III-1)



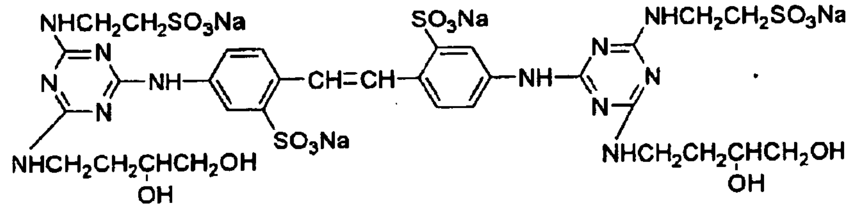
III-2)



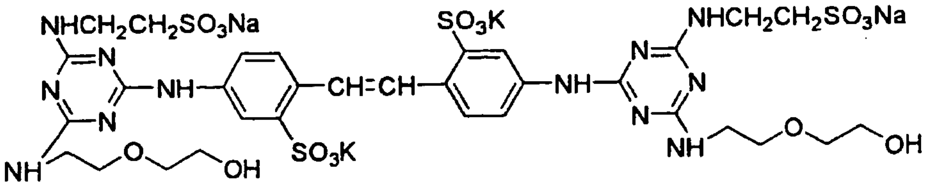
III-3)



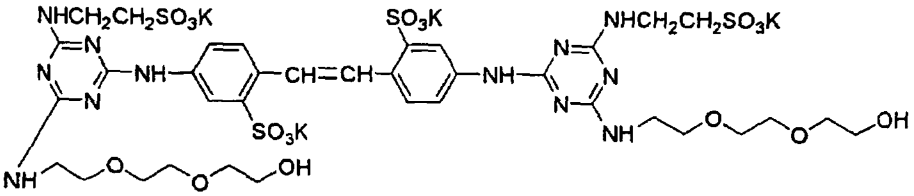
III-4)



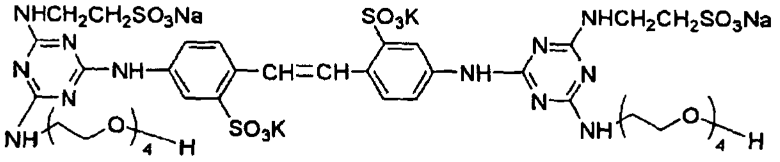
III- 5)



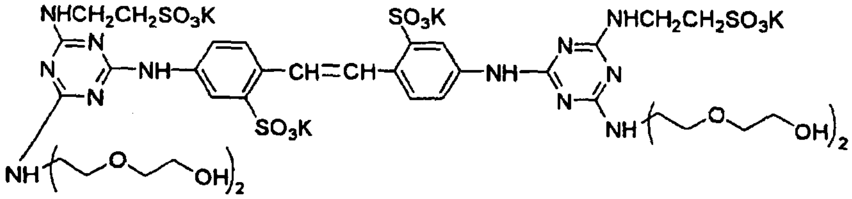
III- 6)



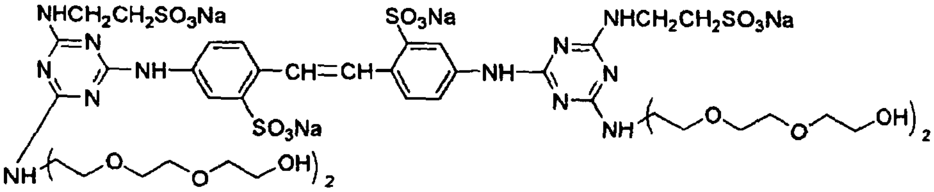
III- 7)



III- 8)



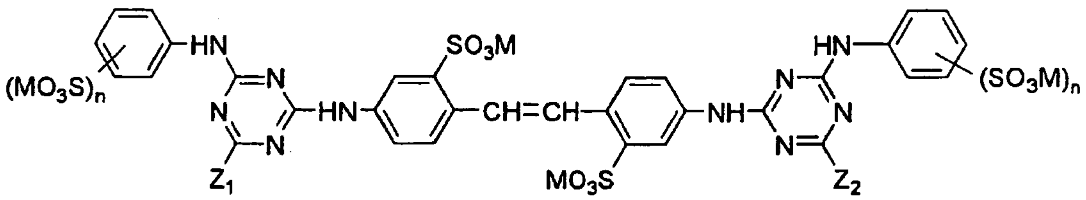
III- 9)



[0095] Among the compounds represented by the formula (III), the example compound III-5 is particularly preferable.

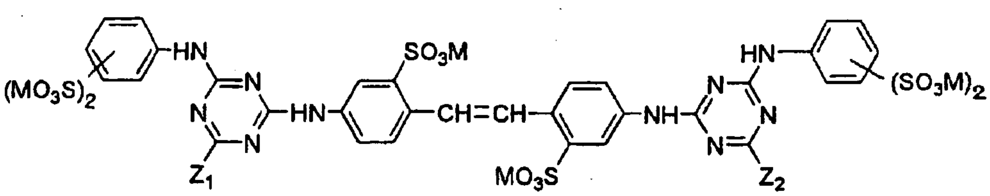
[0096] Now there will be given an explanation on, among the bis(triazinylamino)stilbenesulfonic acid type fluorescent whitening agents, a compound represented by a formula (IV), which is effective and preferable for the stability of the composition of the invention, together with the compound represented by the formula (III).

Formula (IV)



[0097] In the compound represented by the formula (IV), Z_1 and Z_2 may be same or different each other and each represents an amino group containing from 2 to 3 carbon atoms and substituted with a hydroxyl group or a sulfonic acid group; and M represents an alkali metal atom such as sodium, potassium or lithium. Specific examples of the compound represented by the formula (IV) are shown below, but these examples are not restrictive.

Table 1



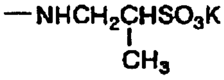
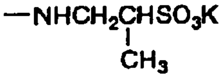
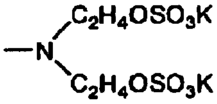
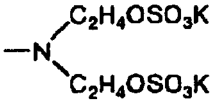
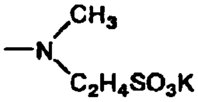
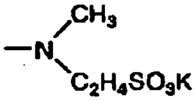
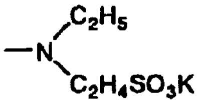
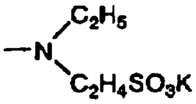
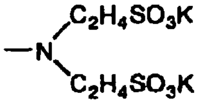
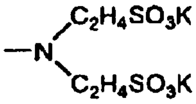
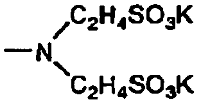
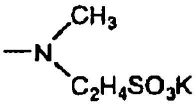
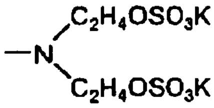
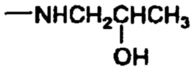
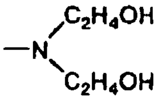
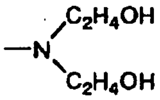
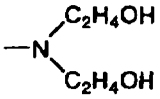
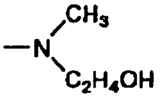
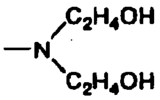
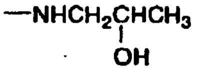
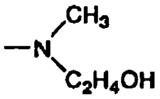
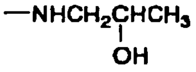
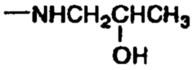
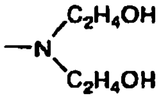
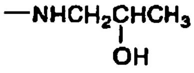
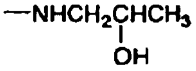
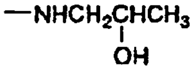
Compound No.	Z_1	Z_2
IV- 1	 $-NHCH_2CH(CH_3)SO_3K$	 $-NHCH_2CH(CH_3)SO_3K$
IV-2	 $-N(C_2H_4OSO_3K)_2$	 $-N(C_2H_4OSO_3K)_2$
IV-3	$-NHC_2H_4SO_3Na$	$-NHC_2H_4SO_3Na$
IV-4	$-NHC_2H_4SO_3H$	$-NHC_2H_4SO_3H$
IV-5	$-NHC_2H_4SO_3K$	$-NHC_2H_4SO_3K$
IV-6	 $-N(CH_3)C_2H_4SO_3K$	 $-N(CH_3)C_2H_4SO_3K$
IV-7	 $-N(C_2H_5)C_2H_4SO_3K$	 $-N(C_2H_5)C_2H_4SO_3K$
IV-8	 $-N(C_2H_4SO_3K)_2$	 $-N(C_2H_4SO_3K)_2$
IV-9	 $-N(C_2H_4SO_3K)_2$	$-NHC_2H_4OH$
IV-10	$-NHC_2H_4SO_3Na$	 $-N(CH_3)C_2H_4SO_3K$
IV-11	$-NHC_2H_4SO_3Na$	 $-N(C_2H_4OSO_3K)_2$

Table 2

Compound No.	**Z_1**	Z_2
IV-12	**$-NHC_2H_4SO_3Na$**	 $-NHCH_2\underset{OH}{CH}CH_3$
IV-13	 $-N\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$	 $-N\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$
IV-14	 $-N\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$	**$-NHC_2H_4OH$**
IV-15	$-NHC_2H_4OH$	 $-N\begin{matrix}CH_3\\C_2H_4OH\end{matrix}$
IV-16	$-NHC_2H_4OH$	 $-N\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$
IV-17	$-NHC_2H_4OH$	**$-NHC_2H_4OH$**
IV-18	 $-NHCH_2\underset{OH}{CH}CH_3$	 $-N\begin{matrix}CH_3\\C_2H_4OH\end{matrix}$
IV-19	 $-NHCH_2\underset{OH}{CH}CH_3$	$-NHCH(CH_3)CH_2OH$
IV-20	 $-NHCH_2\underset{OH}{CH}CH_3$	 $-N\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$
IV-21	 $-NHCH_2\underset{OH}{CH}CH_3$	$-NHC_2H_4OH$
IV-22	 $-NHCH_2\underset{OH}{CH}CH_3$	 $-NHCH_2\underset{OH}{CH}CH_3$

formula (II) may be synthesized by known methods, and are also commercially available.

[0098] The compound represented by the formula (III) and the compound represented by the formula (IV) are preferably used in combination, with a molar ratio thereof preferably of from 5:1 to 1:5, more preferably from 3:1 to 1:3 and particularly preferably from 2:1 to 1:2.

[0099] A total concentration of these compounds in 1 L of the concentrated composition is preferably from 1 to 50 mmol, and more preferably from 3 to 30 mmol.

[0100] In the concentrated composition of the present invention, the effects thereof may be further enhanced by adding a compound selected from benzenesulfonic acids that may be substituted with an alkyl group, and lactams.

[0101] The preferable alkyl group as the substituent on benzenesulfonic acid is an alkyl group containing 3 or less carbon atoms, more preferably a methyl group or an ethyl group. The substituting positions include mono-substitution and di-substitution, and a 4-position substitution is preferable for the former and a 2,4-di-substitution is preferable for the latter.

[0102] Preferable examples of benzenesulfonic acid, that may be alkyl-substituted, include benzenesulfonic acid, p-toluenesulfonic acid, xylenesulfonic acid, and 4-ethylsulfonic acid, among which preferred are benzenesulfonic acid and p-toluenesulfonic acid, and most preferred is p-toluenesulfonic acid. These compounds may be used in a free acid form or in an alkali metal salt such as potassium salt, sodium salt or lithium salt.

[0103] Examples of lactam that may be contained in the concentrated composition of the invention include β-propiolactam, γ-butyrolactam, δ-valerolactam, ε-caprolactam, N-methyl-β-propiolactam, N-methyl-γ-butyrolactam, N-methyl-δ-valerolactam, and N-methyl-ε-caprolactam, among which δ-valerolactam and ε-caprolacam are preferable and ε-caprolactam is most preferable.

[0104] The concentrated developing composition of the invention may contain either of benzenesulfonic acids and lactams, and a preferable concentration range, showing particular effects, is from 3 to 6 times of the concentration of the solution for use, namely the developer replenisher or the base solution (solution in tank). Therefore the concentration in the concentrated composition is so designed, when diluted with a ratio above, to provide a concentration of from 0.01 to 200 g, preferably from 1 to 100 g and more preferably from 5 to 50 g per 1L of the replenisher or the base solution.

[0105] The concentrated composition for color developer replenisher of the invention is applicable to the color photographic photosensitive materials of image capturing purpose and printing purpose, but the effects of the invention are exhibited particularly in an application to a color photographic paper.

[0106] In the following, there will be explained a color developing process utilizing the concentrated bleach composition and the concentrated composition for color developer replenisher of the invention.

[0107] The color developing process, in which the concentrated bleach composition and the concentrated composition for color developer replenisher of the invention are applicable, is constituted of a color development step, a desilvering step, a washing or stabilizing step and a drying step, and auxiliary steps such as a rinsing step, an intermediate washing step, and a neutralizing step may be inserted between these steps. The desilvering step is executed by a single step with a bleach-fix solution, and the concentrated bleach composition is used in this step. Also, in addition to a washing-replacing stabilizing bath, an image stabilizing bath for the purpose of image stabilization may be provided between the washing or stabilizing step and the drying step.

[0108] The developing process of the invention is so designed as to be applicable to a general-purpose process for color photosensitive materials, and a replenishing amount of the color developer replenisher is preferably from 20 to 50 ml, per 1 m^2 of the photosensitive material, more preferably from 25 to 45 ml and most preferably from 25 to 40 ml. The concentrated composition is so designed as to provide the aforementioned concentration after dilution with water. A replenishing amount of the bleach-fix solution is preferably from 20 to 60 ml, per 1 m^2 of the photosensitive material, more preferably from 25 to 50 ml and most preferably from 25 to 45 ml. The replenishing amount of the bleach-fix solution is preferably divided into a bleach agent part and a fixing agent part, and, in such case, the replenishing amount of the bleach-fix solution is a total of the replenishing amounts of the bleach agent part and the fixing agent part. Also a replenishing amount of a rinse solution (washing water and/or a stabilizing solution) is preferably from 50 to 200 ml in the entire rinsing solution.

[0109] A color developing time (time for color developing step) is preferably 45 seconds or less, more preferably 40 seconds or less, further preferably 30 seconds or less, and particularly preferably from 25 to 6 seconds. Similarly a bleach-fix time (time for bleach-fix step) is preferably 45 seconds or less, more preferably 30 seconds or less, and further preferably from 25 to 6 seconds. Also a rinsing (washing or stabilizing) time (time for rinsing step) is preferably 90 seconds or less and more preferably from 30 to 6 seconds.

[0110] The color developing time means a period from a time at which the photosensitive material is introduced into the color developing solution to a time at which the photosensitive material is introduced into the bleach-fix solution in a next process step. In case of a process for example in an automatic processor, the color developing time means a sum of a period (so-called in-liquid time) during which the photosensitive material is immersed in the color developing solution, and a period (so-called in-air time) during which the photosensitive material is conveyed, after exiting from the color developing solution, toward the bleach-fix solution in the next step. Similarly, the bleach-fix time means a period from a time at which the photosensitive material is introduced into the bleach-fix solution to a time at which the photosensitive material is introduced into a next washing or stabilizing bath. Also a rinsing (washing or stabilizing) time means a period (so-called in-liquid time) in which the photosensitive material, after being introduced into the rinsing solution (washing water or stabilizing solution), remains in the solution toward the drying step.

[0111] In the color developing step, the bleach-fix step and the rinsing step, the processing solutions generally have a temperature of from 30 to 40˚C, but a high-temperature rapid process at from 38 to 60˚C, preferably from 40 to 50˚C, is also included in the embodiments of the invention.

[0112] Also the amount of rinsing solution may be selected within a wide range, depending on characteristics (for example according to used materials such as a coupler) and application of the photosensitive material, a temperature of the rinsing solution (washing water), a number (number of steps) of the rinsing solution (washing water), and other various conditions. Among these conditions, a relationship between a number of rinsing tanks (washing tanks) and an amount of water in a multi-step countercurrent system can be determined according to a method described in Journal of the Society of Motion Picture and Television Engineers, vol. 64, p.248 - 253(May 1955). In the multi-step countercurrent system, a number of steps is preferably from 3 to 10 steps, and more preferably from 3 to 5 steps.

[0113] The multi-step countercurrent system can significantly reduce the amount of rinsing solution, but, because of a longer stay time of water in the tanks, results in drawbacks of bacteria growth and a deposition of resulting floating substances onto the photosensitive material, and there is preferred, as a countermeasure, a rinsing solution containing an antibacterial or antifungal agent to be explained later.

[0114] The silver halide color photographic photosensitive material, after the developing process, is subjected to a post-process such as a drying step. In the drying step, the drying may be executed faster by absorbing water with a squeeze roller or a cloth immediately after the developing process (rinsing step), for the purpose of reducing water intake into the image forming film of the silver halide color photographic photosensitive material. It is naturally possible also to quicken the drying by elevating the temperature or by modifying a shape of a nozzle thereby increasing the power of drying air. The drying may also be made faster, as disclosed in JP-A-3-157650, by regulating an angle of a drying air to the photosensitive material or by a discharge method of an exhaust air.

[0115] In the following, constituent chemicals other than the aforementioned characteristic constitution, in the bleach-fix processing composition and the concentrated color developer replenisher of the invention, will be explained. The description will be made, rather than on each of the processing composition and the replenisher prepared by mixing the same with water in a predetermined ratio, on both in combination, and the concentration of the component will be explained principally on the concentration in the solution for use.

[0116] The color developing process composition contains a color developing agent.

[0117] A preferred example of the color developing agent is a known aromatic primary amine color developing agent, particularly a p-phenylenediamine derivative, and representative examples are shown below but are not restrictive.

1) N,N-dimethyl-p-phenylenediamine
2) 4-amino-3-methyl-N,N-diethylaniline
3) 4-amino-N-(β-hydroxyethyl)-N-methylaniline
4) 4-amino-N-ethyl-N-(β-hydroxyethyl)amtine
5) 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline
6) 4-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline
7) 4-amino-3-methyl-N-ethyl-N-(4-hydroxybutyl)aniline
8) 4-amino-3-methyl-N-ethyl-N-(β-methanesulfonamidethyl)aniline
9) 4-amino-N,N-diethyl-3-(β-hydroxyethyl)aniline
10) 4-amino-3-methyl-N-ethyl-N-(β-methoxyethyl)aniline
11) 4-amino-3-methyl-N-(β-ethoxyethyl)-N-ethylaniline
12) 4-amino-3-methyl-N-(3-carbamoylpropyl)-N-n-propyl-aniline
13) 4-amino-N-(4-carbamoylbutyl)-N-n-propyl-3-methylaniline
15) N-(4-amino-3-methylphenyl)-3-hydroxypyrrolidine
16) N-(4-amino-3-methylphenyl)-3-(hydroxymethyl)pyrrolidine and
17) N-(4-amino-3-methylphenyl)-3-pyrrolidine carboxamide.

[0118] Among the p-phenylenediamine derivatives, particularly preferable are example compounds 5), 6), 7), 8) and 12), particularly preferable are the compounds 5) and 8). Such p-phenylenediamine derivatives, in a state of a solid material, generally assume a salt state such as a sulfate salt, a hydrochlorate salt, a sulfite salt, a naphthalenedisulfonate salt or a p-toluenesulfonate salt.

[0119] As to the content of the aromatic primary amine developing agent in the processing material, such developing agent is so added that a concentration thereof in the solution for use becomes from 2 to 200 mmol per 1 L of the developer, preferably from 6 to 100 mmol and more preferably from 10 to 40 mmol.

[0120] In the color developing material, an organic preservative may be added as the preservative. The organic preservative means all the organic compounds, of which presence in the processing solution for the photosensitive material retards the deterioration rate of the aromatic primary amine developing agent. The are organic compounds having a function of preventing oxidation for example by air of the color developing agent, and particularly effective organic preservatives include, not only hydroxylamine derivatives, but also hydroxamic acids, hydrazides, phenols, α-hydroxyketones, α-aminoketones, sugars, monoamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and condensed-ring amines. These are disclosed in JP-A Nos. 63-4235, 63-30845, 63-21647, 63-44655, 63-53551, 63-43140, 63-56654, 63-58346, 63-43138, 63-146041, 63-44657 and 63-44656, USP Nos. 3,615,503 and 2,494,903, JP-A-52-143020 and JP-B-48-30496.

[0121] Also other preservatives may be included when necessary, such as metals described in JP-A-57-44148 and JP-A-57-53749, salicylic acids described in JP-A-59-180588, alkanolamines described in JP-A-54-3532, polyethylenimines described in JP-A-56-94349, and aromatic polyhydroxy compounds described in USP 3,746,544. In particular, an alkanolamine such as triethanolamine or triisopropanolamine, a substituted or non-substituted dialkylhydroxylamine such as disulfoethylhydroxylamine or diethylhydroxylamine, or an aromatic polyhydroxy compound may be added. Among the organic preservatives above, the hydroxylamine derivative is described in detail in JP-A-1-97953, JP-A-1-186939, JP-A-1-186940 and JP-A-1-187557. In particular, a hydroxylamine derivative and an amine in combination may be effective in improving the stability of the color developer and the stability in continuous processing. Also the amines mentioned above include cyclic amines as described in JP-A-63-239447, amines as described in JP-A-63-128340 and amines as described in JP-A-1-186939 and JP-A-1-187557. An amount of the preservative in the processing material is variable depending on the type of the preservative, but it is generally so added to obtain a concentration, in the solution for use, of from 1 to 200 mmol per 1L of the developer, and preferably from 10 to 100 mmol.

[0122] Chlorine ions may be added, when necessary, to the color developing material, for example that for a color photographic paper. The color developing solution (particularly that for a color print material) often contains chlorine ions in an amount of from 3.5×10^{-2} to 1.5×10^{-1} mol/L, but the chlorine ions, being generally released into the developer as a by-product of development, often need not be added to the developer replenisher. Also the developer for a photosensitive material for image capturing need not contain chlorine ions.

[0123] As to bromine ions, the color developing solution preferably contains in an amount of from about $1 - 5 \times 10^{-3}$ mol/L for an image capturing photosensitive material, and an amount of 1.0×10^{-3} mol/L or less for a photosensitive print material. In the color developing solution, bromine ions are often unnecessary as in the case of chlorine ions, but bromine ions may be added, when necessary, into the processing material in such a manner that the bromine ion concentration is within the aforementioned range.

[0124] In the case that the object photosensitive material is prepared with a silver iodobromide emulsion such as a color negative film or a color reversal film, the situation is same also for iodine ions, but iodine ions are usually not contained in the replenisher since the iodine ions are normally released from the photosensitive material to an iodine ion concentration of about from 0.5 to 10 mg per 1L of the developer solution.

[0125] In case of employing a halide as an additive in the developer or the developer replenisher, there may be utilized, as a chlorine ion supplying substance, sodium chloride, potassium chloride, ammonium chloride, lithium chloride, nickel chloride, magnesium chloride, manganese chloride or calcium chloride, among which sodium chloride or potassium chloride is employed preferably.

[0126] As a bromine ion supplying substance, there may be employed sodium bromide, potassium bromide, ammonium bromide, lithium bromide, calcium bromide, magnesium bromide, manganese bromide, cerium bromide, or thallium bromide, among which potassium bromide or sodium bromide is employed preferably.

[0127] As an iodine ion supply substance, there may be employed sodium iodide or potassium iodide.

[0128] In the invention, the developer in the developing tank has a pH of from 9.0 to 12.5, preferably from 9.5 to 11.5, and more preferably from 9.8 to 10.8. Therefore the replenisher is preferably so set as to have pH of from 11.0 to 13.5, more preferably from 11.5 to 13.2, particularly preferably from 12.0 to 13.0 and most preferably from 12.5 to 12.8. On the other hand, in the present invention, an alkali agent, a buffer and if necessary an acid agent may be included so as to have and maintain a pH value of from 12.5 to 12.8 when measured after the concentrated composition for developer replenisher is diluted 3.84 times with water. The pH measurement is executed after dilution of 3.84 times with water because, as the concentrated composition of the invention for developer replenisher has an extremely high pH, a pH obtained by a direct measurement without dilution with water is close to a response limit of the pH measuring electrode and cannot provide a practical precision of measurement.

[0129] As an alkali, various hydroxides may be added, such as potassium hydroxide, sodium hydroxide, lithium hydroxide, tripotassium hydrogenphosphate, or hydrates of these, or triethanolamine or diethanolamine. Also as an acid agent to be added when necessary, an inorganic or organic water-soluble solid acid may be employed, such as succinic acid, tartaric acid, propionic acid or ascorbic acid.

[0130] When a processing solution is prepared by diluting the concentrated composition with water, various buffers are preferably employed for maintaining the pH above. Examples of the buffer include a carbonate salt, a phosphate salt, a borate salt, a tetraborate salt, a hydroxybenzoate salt, a glycine salt, an N,N-dimethylglycine salt, a leucine salt, a norleucine salt, a guanine salt, 3,4-dihydroxyphenylalanine salt, an aminobutyrate salt, a 2-amino-2-methyl-1,3-propanediol salt, a valine salt, a proline salt, a trishydroxyaminomethane salt, and a lysine salt. In particular, a carbonate salt, a phosphate salt, a tetraborate salt or a hydroxybenzoate salt has advantages of showing an excellent buffering property in a high pH range of pH 9.0 or higher, being free from detrimental effects (such as fog) on photographic characteristics when added to a color developing solution, and being inexpensive, and such buffers are employed particularly preferably.

[0131] Specific examples of such buffers include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetrraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate) and potassium

5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, the invention is not limited to these compounds.

[0132] As the buffer is not a reacting or consumed component, an amount thereof in the composition is so determined that the concentration thereof becomes from 0.01 to 2 moles, preferably from 0.1 to 0.5 moles, per 1L of the developer replenisher prepared from the composition.

[0133] The color developing material may further contain other color developer components, for example various chelating agents, which serve as a precipitation inhibitor for calcium or magnesium and also as a stability improving agent for the color developer. Examples thereof include nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenesulfonic acid, transcyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, glycol etherdiaminetetraacetic acid, ethylenediamine-o-hydroxyphenylacetic acid, ethylenediaminedisuccinic acid (SS compound), N-(2-carboxylateethyl)-L-aspartic acid, β-alaninediacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, and 1,2-dihydroxybenzene-4,6-disulfonic acid.

[0134] Such chelating agents may be employed, when necessary, in a mixture of two or more kinds.

[0135] Such chelating agent may be present in an amount enough for masking the metal ions in the prepared color developer, and is added, for example, in an amount of about from 0.1 to 10 g per 1L.

[0136] In the color developing composition of the invention, an arbitrary development promoter may be added when necessary. As the development promoter, there may be added, according to the necessity, thioether compounds described in JP-B Nos. 37-16088, 37-5987, 38-7826, 44-12380 and 45-9019 and USP 3,813,247, p-phenylenediamine compounds described in JP-A-52-49829 and JP-A-50-15554, quaternary ammonium salts described in JP-A-50-137726, JP-B-44-30074, JP-A-56-156826 and JP-A-52-43429, amine compounds described in USP Nos. 2,494,903, 3,128,182, 4,230,796 and 3,253,919, JP-B-41-11431, USP Nos. 2,482,546, 2,596,926 and 3,582,346, polyalkylene oxides described in JP-B Nos. 37-16088 and 42-25201, USP 3,128,183, JP-B Nos. 41-11431 and 42-23883, and USP 3,532,501, also 1-phenyl-3-pyrazolidones or imidazoles. An amount of addition of such compound is so determined that the concentration thereof becomes 0.001 to 0.2 moles, preferably 0.01 to 0.05 moles, per 1L of the developer or the replenisher, prepared from the processing material.

[0137] In the color developing material of the invention, an arbitrary antifoggant may be added, when necessary, in addition to the halogen ions mentioned above. Representative examples of an organic antifoggant include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolidine, and adenine.

[0138] Also in the color developing material, various surfactants may be added when necessary, such as an alkylsulfonic acid, an arylsulfonic acid, an aliphatic carboxylic acid, or an aromatic carboxylic acid. An amount of addition of such compound is so determined that the concentration thereof becomes 0.0001 to 0.2 moles, preferably 0.001 to 0.05 moles, per 1L of the developer or the replenisher, prepared from the processing material.

[0139] In the present invention, a fluorescent whitening agent may be employed, when necessary. A bis(triazinylamino) stilbenesulfonic acid type compound is preferable as the fluorescent whitening agent. Known or commercially available diaminostilbene whitening agents may be utilized as the bis(triazinylamino)stilbenesulfonic acid type compound. As the known bis(triazinylamino)stilbenesulfonic acid compounds, those described in JP-A-6-329936, JP-A-7-140625 and JP-A-10-140849 are preferable. The commercially available compounds are described for example in "Senshoku Note" 9th ed., p.165-168 (Shikisen-sha Co.), and, among those described therein, preferred are Blankophor BSU, and Hakkol BRK.

[0140] After the fixing or bleach-fixing, a washing-replacing stabilizer bath or an image-stabilizing stabilizer bath is often used, and, though such baths are of a low concentration and a processing material is not so effective, a processing material may be prepared if necessary. In the processing material for the stabilizer bath, a method of reducing calcium and magnesium, as described in JP-A-62-288838, may be utilized extremely effectively. Also antibacterial agents may be employed, for example an isothiazolone compound or a thiabendazole described in JP-A-57-8542, chlorine type antibacterial agents such as chlorinated sodium isocyanurate described in JP-A-61-120145, benzotriazole described in JP-A-61-267761, copper ions, and those described in Hiroshi Horiguchi, "Antibacterial and antifungal chemistry" (Sankyo Shuppan, 1986), Eisei Gijutsu-Kai, "Bacterial reduction, sterilization and antifungal technology" (Kogyo Gijutsu-kai, 1982) and Society for Antibacterial and Antifungal Agents, Japan, "Antibacterial and Antifungal Agents Dictionary" (1986).

[0141] The developing process of the present invention is executed by an automatic processor. An automatic processor advantageously employable in the invention will be described below.

[0142] In the invention, the automatic processor has a linear conveying speed preferably of 100 mm/sec or less, more preferably from 27.8 to 80 mm/sec, and particularly preferably from 27.8 to 50 mm/sec.

[0143] The conveying system in the automatic processor for a color photographic paper is divided into a method of executing the developing process after the color photographic paper is cut into a final size (sheet-type conveying system), and a method of executing the developing process in a continuous web and cutting it into a final size after the process (cine-type conveying system). The sheet-type conveying system is preferable, since the cine-type conveying system causes a waste of the photosensitive material of about 2 mm between the images.

[0144] The processing solution of the invention, in the processing tank and in the replenisher tank, preferably has a contact area with air (aperture area) as small as possible. By defining an aperture rate by dividing the aperture area (cm^2) with the liquid volume (cm^3) in the tank, the aperture rate is preferably 0.01 (cm^{-1}) or less, more preferably 0.005 or less and most preferably 0.001 or less.

[0145] The automatic processor includes various materials for the parts, and preferred materials are shown below.

[0146] A tank material for the processing tanks and the temperature regulating tank is preferably denatured PPO (denatured polyphenylene oxide) resin or denatured PPE (denatured polyphenylene ether) resin. Examples of the denatured PPO include Noryl manufactured by Nippon GE Plastic Co., and examples of the denatured PPE include Xylon manufactured by Asahi Kasei Corporation, and Upiace manufactured by Mitsubishi Gas Chemical Co. These materials are suitable for parts that may contact the processing solutions, such as a processing rack or a cross-over.

[0147] For the rollers of processing part, a resinous material, such as PVC (polyvinyl chloride), PP (polypropylene), PE (polyethylene) or TPX (polymethylpentene) is suitable. These materials may also be used in other parts contacting the processing solutions. The PE resin is also preferable as a material for blow molding a replenishing tank.

[0148] For the processing part, gears, sprockets and bearings, a resinous material, such as PA (polyamide), PBT (polybutylene terephthalate), UHMPE (ultra-high molecular polyethylene), PPS (polyphenylene sulfide) or LCP (all-aromatic polyester resin or liquid crystal polymer) is suitable.

[0149] The PA or polyamide resin, such as nylon-66, nylon-12 or nylon-6, when containing glass fibers or carbon fibers, is resistant to swelling by the processing solution and is usable.

[0150] Also a high molecular material such as MC nylon or a compression molded material is usable even without reinforcing fibers. The UHMPE resin is suitable unreinforced state, such as Lubma or Hizex Million manufactured by Mitsui Pterochemical Co., New-Lite manufactured by Sakushin Kogyo Co., or Sunfine manufactured by Asahi Kasei Corp. The molecular weight is preferably 1,000,000 or higher, and more preferably from 1,000,000 to 5,000,000.

[0151] The PPS resin is preferably reinforced with glass fibers of carbon fibers. Examples of the LCP resin include Victorex of ICI Japan Inc., Econol of Sumitomo Chemical Co., Xydar of Nippon Oil Corp., and Vectra of Polypolastic Co.

[0152] As the material for a conveyor belt, an ultra-high strength polyethylene fiber described in Japanese Patent Application No. 2-276886 or a polyvinylidene fluoride resin is preferable.

[0153] As a soft material for squeeze rollers and the like, a foamed vinyl chloride resin, a foamed silicone resin or a foamed urethane resin is suitable. Examples of the foamed urethane resin include Lubicel manufactured by Toyo Polymer Co.

[0154] For a joint of pipings, a joint for an agitation jet pipe or a sealant, a rubber material such as EPDM rubber, silicone rubber or Byton rubber is preferable.

[0155] It is preferable to add chemicals directly into a processing tank, and to add water, matching the dilution rate, to the processing tank. It is also preferable to automatically execute dissolution and dilution with an automatic preparing device in the replenishing tank, thereby preparing a replenisher.

[0156] The processing materials to be employed in the present invention may be prepared as an individual product form including the processing materials for each step, but are preferably formed as a kit collectively containing the processing materials for the different steps, and, in such case, it is more preferable that the processing materials for the replenisher are formed as a cartridge which can be mounted on and detached from the processor. A container for such processing material may be formed by any material such as paper, plastics or a metal, but, except for the container for the bleach-containing processing material, a plastic material having an oxygen permeation coefficient of 57×10^{-6} $mL/Pa \cdot m^2 \cdot s$ ($50\ mL/m^2 \cdot atm \cdot day$) or less is preferred. The oxygen permeation coefficient can be measured by a method described in N.J. Calyan, "O2 permeation of plastic container, Modem Plastics", December 1968, p.143 - 145.

[0157] Specific examples of the preferred plastic materials include vinylidene chloride (PVDC), nylon (NY), polyethylene (PE), polypropylene (PP), polyester (PES), ethylene-vinyl acetate copolymer (EVA), ethylene-vinyl alcohol copolymer (EVAL), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), and polyethylene terephthalate (PET).

[0158] Except for the container for the bleach-containing processing material, PVDC, NY, PE, EVA, EVAL or PET is preferably employed for the purpose of reducing the oxygen permeability.

[0159] These materials may be employed singly or in a blended state, or used in a molded form, a film-like container or a bottle, or also used in an adhered state of plural types (so-called composite film). Also the container may have various shapes such as a bottle type, a cubic type or a pillow type, but, in the invention, a cubic or similar type is particularly preferable as it is flexible, easy to handle and reducible in volume after use.

[0160] In case of a composite film, following structures are particularly preferable but the invention is not limited to such examples. Examples include: PE/EVAL/PE, PE/aluminum foil/PE, NY/PE/NY, NY/PE/EVAL, PE/NY/PE/WVAL/PE, PE/NY/PE/PE/PE/NY/PE, PE/SiO_2 film/PE, PE/PVDC/PE, PE/NY/aluminum foil/PE, PE/PP/aluminum foil/PE, NY/PE/PVDC/NY, NY/EVAL/PE/EVAL/NY, NY/PE/EVAL/NY, NY/PE/PVDC/NY/EVAL/PE, PP/EVAL/PE, PP/EVAL/PP, NY/EVAL/PE, NY/aluminum foil/PE, paper/aluminum foil/PE, paper/PE/aluminum foil/PE, PE/PVDC/NY/PE, NY/PE/aluminum foil/PE, PET/EVAL/PE, PET/aluminum foil/PE, and PET/aluminum foil/PET/PE.

[0161] The composite film has a thickness of about from 5 to 1,500 micrometers, preferably from 10 to 1,000 micrometers. Also the completed container has a content of from 100 mL to 20 L, preferably from 500 mL to 10 L.

[0162] Such container (cartridge) may have an outer casing of corrugated cardboard or plastics, or may be integrally formed with the outer casing.

[0163] The cartridge of the invention may be filled with various processing solutions, such as a color developer, a monochromatic developer, a bleach solution, a regulating solution, a reversal solution, a fixing solution, a bleach-fix solution, or a stabilizer solution. Particularly a cartridge with a low oxygen permeation coefficient is preferably used for a color developer, a monochromatic developer, a fixing solution and a bleach-fix solution.

[0164] Also prior processing solution containers, such as rigid containers formed of a mono-layered material such as high density polyethylene (HDPE), polyvinyl chloride resin (PVC) or polyethylene terephthalate (PET), or a multi-layered material such as nylon/polyethylene (NY/PE), may be employed.

[0165] Also there may be employed a flexible liquid container, that can be reduced in volume or in the required space, after the container is emptied by discharging the content. As an example, it is preferable to use such flexible container. A specific example of such flexible container is a liquid container in which a hard mouthpiece, protruding upwards from a main body of a flexible container, is opened or closed by a lid member engaging therewith, wherein the mouthpiece and the main body of the container are integrally molded and a bellows portion is provided in at least a part of the main body of the container in a height direction thereof (cf. JP-A-7-5670, Figs. 1 and 2).

[Applicable photosensitive material]

[0166] In the following, a silver halide color photographic photosensitive material (hereinafter also simply called "photosensitive material"), to which the composition of the invention for color developer replenisher is applicable, will be explained.

[0167] The photosensitive material to be employed in the invention includes, as already described in relation to the objects and the background of the invention, a color photographic photosensitive material for image capturing purpose and a color photographic photosensitive material for a color print, and such photosensitive material includes at least a photosensitive layer on a substrate. A typical example is a silver halide photographic photosensitive material including, on a substrate, at least a photosensitive layer formed by plural silver halide emulsion layers which are substantially same in color sensitivity but different in photosensitivity.

[0168] In a multi-layered silver halide color photographic photosensitive material, the photosensitive layer is a unit photosensitive layer having a color sensitivity to a blue light, a green light or a red light, and such unit photosensitive layers are generally arranged in an order, from the side of the substrate, of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer. However, according to the purpose, it is also possible to change the order of arrangement or to adopt an order of arrangement in which a layer of different color sensitivity is sandwiched between layers of a same color sensitivity. A non-photosensitive layer may be provided between the silver halide photosensitive layers, or as an uppermost or lowermost layer. Such layer may contain a coupler, a DIR compound, a color-mixing preventing compound and the like, to be explained later. In the plural silver halide emulsion layers constituting each unit photosensitive layer, it is preferable, as described in DE 1,121,470 or GE 923,045, to arrange a high-sensitivity emulsion layer and a low-sensitivity emulsion layer in such a manner that the sensitivity decreases in succession toward the substrate. It is also possible, as described in JP-A Nos. 57-112751, 62-200350, 62-206541 and 62-206543, to position a low-sensitivity emulsion layer at a side distant from the substrate and a high-sensitivity emulsion layer at a side close to the substrate.

[0169] Also as described in JP-B-49-15495, there may be adopted an arrangement formed by 3 layers of different sensitivities, with a silver halide emulsion layer of a highest sensitivity at an upper layer, a silver halide emulsion layer of a lower sensitivity as a middle layer, and a silver halide emulsion layer of a sensitivity lower than that of the middle layer, as a lower layer, whereby the sensitivity is lowered in succession toward the substrate. Also in case of a structure formed by three layers of different sensitivities, there may be adopted, as described in JP-A-59-202464, an arrangement in the order of medium-sensitivity emulsion layer/high-sensitivity emulsion layer/low-sensitivity emulsion layer from a side distant from the substrate, within the layers of a same color sensitivity.

[0170] In order to improve the color reproducibility, it is preferable, as described in USP Nos. 4,663,271, 4,705,744 and 4,707,436, JP-A Nos. 62-160448 and 63-89850, to position a donor layer (CL) of a layer superposing effect, having a spectral sensitivity distribution different from that of main photosensitive layers such as BL, GL and RL, next to or close to such main photosensitive layers.

[0171] A photosensitive material for color print generally utilizes a reflective substrate, and has a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer often in this order from a side farther from the substrate. As the silver halide emulsion, there is employed a cubic grain emulsion of silver chloride or silver chlorobromide having a high silver chloride content.

[0172] The photosensitive silver halide to be employed in the invention will be explained below. Silver halide in the invention is preferably a cubic grain substantially having a {100} plane, a tetradecahedral crystal grain (which may have rounded apexes and may include higher order planes), an octahedral crystal grain, or a tabular grain of which the principal planes are formed by a {100} or {111} plane and which has an aspect ratio of 2 or higher. The aspect ratio means a value obtained by dividing a diameter of a circle corresponding to a projected area with a thickness of the grain. For the tabular grain having the principal planes formed by a {100} or {111} plane, reference may be made to JP-A-2000-352794, column 33 (p.7) to column 840 (p.8). In the invention, a cubic grain is most preferable. The grain size, in a cube-converted side length, is preferably 0.5 μm or less, and more preferably 0.4 μm or less.

[0173] In the present specification, a cube side length means a length of a side when the volume of each grain is converted into a cube of a same volume, and, in the present specification, a cube-converted side length has a same meaning. The emulsion of the invention is preferably formed by grains having a mono-dispersed gain size distribution. In the invention, all the grains preferably have a variation coefficient of the cube-converted side length of 20 % or less, more preferably 15 % or less and further preferably 10 % or less. The variation coefficient of the cube-converted side length means a standard deviation of the cube-converted side lengths of the individual grains, represented in a percentage to the average of the side lengths. It is also preferable, for the purpose of obtaining a wide latitude, to blend mono-dispersed emulsions above in a single layer, or to coat them in superposed layers.

[0174] The silver halide emulsion to be employed in the invention may contain silver halide grains other than the silver halide grains contained in the silver halide emulsion defined in the invention (namely specified silver halide grains). However, in the silver halide emulsion defined in the invention, it is required that the silver halide grains, defined in the invention, represent 50 % or more of all the projection areas of all the gains, preferably 80 % or more and further preferably 90 % or more.

[0175] The silver halide emulsion to be employed in the invention is an emulsion containing silver halide grains of a specified silver halide content, and, from the standpoint of rapid processability, a content of silver chloride has to be 90 mol% or higher, and is preferably 93 mol% or higher and more preferably 95 mol% or higher. A content in silver bromide is preferably from 0.1 to 7 mol% for a higher contrast and a superior stability of latent image, more preferably from 0.5 to 5 mol%. A content in silver iodide is preferably from 0.02 to 1 mol% for a higher sensitivity by an exposure under a high illumination intensity and for a higher contrast, more preferably from 0.05 to 0.50 mol% and most preferably from 0.07 to 0.40 mol%. The silver halide grains of the present invention are preferably silver iodobromochloride grains, and more preferably silver iodobromochloride grains of the aforementioned halogen composition.

[0176] In the silver halide emulsion to be employed in the invention, the silver halide grains preferably have a silver bromide-containing phase and/or a silver iodide-containing phase. The silver bromide-containing phase or the silver iodide-containing phase means a portion in which silver bromide or silver iodide has a concentration higher than in the periphery thereof. In the silver bromide-containing phase or the silver iodide-containing phase and the periphery thereof, the halogen composition may show a continuous change or a steep change. Such silver bromide-containing phase or silver iodide-containing phase may form, in a certain part of the grain, a layer of a certain width in which the concentration is substantially constant, or may be a maximum point without a spreading. In the silver bromide-containing phase, a local content in silver bromide is preferably 2 mol% or higher, more preferably from 3 to 50 mol% and most preferably from 4 to 20 mol%. In the silver iodide-containing phase, a local content in silver iodide is preferably 0.3 mol% or higher, more preferably from 0.5 to 8 mol% and most preferably from 1 to 5 mol%. Also such silver bromide-containing phase and silver iodide-containing phase each may be present in plurality within a grain, in the form of layers, which may be different in the content of silver bromide or silver iodide, and at least one each of such phases has to be present.

[0177] In the silver halide emulsion to be employed in the invention, it is important that the silver bromide-containing phase or the silver iodide-containing phase is in such a layer form as to surround the grain. In a preferred embodiment, the silver bromide-containing phase or the silver iodide-containing phase, formed in such a layer form as to surround the grain, has a uniform concentration distribution along a circumferential direction of the grain, in each phase. However, the silver bromide-containing phase or the silver iodide-containing phase, formed in such a layer form as to surround the grain, may also include a maximum or minimum point in the concentration of silver bromide or silver iodide, along the circumferential direction of the grain, thereby having a concentration distribution. For example, in the case that the silver bromide-containing phase or the silver iodide-containing phase, formed in such a layer form as to surround the grain, is present in the vicinity of the surface of a grain, a concentration of silver bromide or silver iodide in a corner or an edge of the grain may be different from a concentration in a principal surface. Also separately from the silver bromide-containing phase or the silver iodide-containing phase, formed in such a layer form as to surround the grain, a silver bromide-containing phase or a silver iodide-containing phase, not surrounding the grain, may be present in a completely isolated manner in a specified part on a surface of the grain.

[0178] In the case that the silver halide emulsion to be employed in the invention contains a silver bromide-containing phase, such silver bromide-containing phase is preferably formed as a layer, so as to have a concentration maximum of silver bromide inside the grain. Also in the case that the silver halide emulsion to be employed in the invention contains a silver iodide-containing phase, such silver iodide-containing phase is preferably formed as a layer, so as to have a concentration maximum of silver iodide on a surface of the grain. Such silver bromide-containing phase or the silver iodide-containing phase is preferably formed, for the purpose of elevating the local concentration with a smaller content in silver bromide or silver iodide, with a silver amount of from 3 to 30 % of the grain volume, more preferably with a silver amount of from 3 to 15 %.

[0179] The silver halide emulsion to be employed in the invention preferably include both the silver bromide-containing phase and the silver iodide-containing phase. In such case, the silver bromide-containing phase and the silver iodide-containing phase may be present in a same position of the grain or in different positions, but presence in different positions is preferably in facilitating the control of grain formation. Also the silver bromide-containing phase may contain silver iodide, and the silver iodide-containing phase may contain silver bromide. An iodide, added in the course of grains of a high silver chloride content, oozes out to the gain surface generally more easily than a bromide, so that the silver iodide-containing phase is likely to be formed in the vicinity of the grain surface. Therefore, when the silver bromide-containing phase and the silver iodide-containing phase are present in different positions in the grain, the silver bromide-containing phase is preferably formed more inside than the silver iodide-containing phase. In such case, another silver bromide-containing phase may be provided further outside the silver iodide-containing phase which is present in the vicinity of the grain surface.

[0180] A content of silver bromide or silver iodide, necessary for accomplishing the effects of the invention such as a high sensitivity and a high contrast, may increase as the silver bromide-containing phase or the silver iodide-containing phase is formed more inside the grain, thereby reducing the silver chloride content more than a necessary level and deteriorating the rapid processing property. Therefore, in order to concentrate these functions, for controlling the photographic functions, close to the surface of the grain, the silver bromide-containing phase and the silver iodide-containing phase are preferably present in mutually adjacent manner. In consideration of these points, it is preferable to form the silver bromide-containing phase at any position, measured from inside, of from 50 to 100 % of the grain volume, and to form the silver iodide-containing phase at any position of from 85 to 100 % of the grain volume. It is more preferable to form the silver bromide-containing phase at any position of from 70 to 95 % of the grain volume, and to form the silver iodide-containing phase at any position of from 90 to 100 % of the grain volume.

[0181] Introduction of bromide ion or iodide ion, for including silver bromide or silver iodide in the silver halide emulsion, may be made by adding a solution of a bromide salt or an iodide salt singly, or by adding a solution of a bromide salt or an iodide salt in combination with the additions of a silver salt solution and a high-content chloride salt solution. In the latter case, the bromide salt solution or the iodide salt solution and the high-content chloride solution may be added separately or as a mixed solution. The bromide salt or iodide salt is added as a soluble salt, such as alkali/alkali earth bromide or iodide. Otherwise, the introduction may be made by cleaving a bromide ion or an iodide ion from an organic molecule, described in USP 5,389,508. Also as another source of bromide or iodide ion, minute silver bromide grains or minute silver iodide grains may be utilized.

[0182] The solution of bromide salt or iodide salt may be added in concentrated manner at a timing in the course of grain formation, or over a certain period. An introducing position of iodide ion into a high chloride content emulsion is limited in order to obtain an emulsion of a high sensitivity and a low fog level. The sensitivity increases less as the iodide ion is introduced more inside the emulsion grain. Therefore, the addition of the iodide salt solution is preferably executed at outside of 50 % of the grain volume, more preferably outside of 70 % and most preferably outside of 85 %. Also the addition of the iodide salt solution is preferably terminated at inside of 98 % of the grain volume, and more preferably inside of 96 %. An emulsion of a higher sensitivity and a lower fog level can be obtained by terminating the addition of the iodide salt solution, slightly inside of the grain surface.

[0183] On the other hand, the addition of the bromide salt solution is preferably executed at outside of 50 % of the grain volume, and more preferably outside of 70 %.

[0184] A concentration distribution of the bromide or iodide ion, in the direction of depth in the grain, can be measured by an etching/TOF-SIMS (time of flight-secondary ion mass spectrometry) method, for example with Trift II TOF-SIMS, manufactured by Phi Evans Inc. The TOF-SIMS method is described specifically in The Surface Science Society of Japan, "Surface Analysis Technology, Secondary Ion Mass Spectrometry" (Maruzen, 1999). By an analysis of the emulsion grain with the etching/TOF-SIMS method, it can be observed that the iodide ions ooze out toward the grain surface even when the addition of the iodide salt solution is terminated inside the grain. In the emulsion of the invention, it is preferable, in the etching/TOF-SIMS analysis, that the concentration of iodide ions shows a maximum at the grain surface and decreases toward the interior, and that the concentration of bromide ions shows a maximum in the interior of the grain. The local concentration of silver bromide can also be measured by X-ray diffractometry when the silver bromide content is at a certain high level.

[0185] The silver halide emulsion to be employed in the invention preferably contains iridium. As an iridium compound, there is preferred a 6-coordination complex having 6 ligands and having iridium as a central metal (6-ligand iridium complex), in order to be taken uniformly in the silver halide crystal. As a preferred embodiment of iridium to be employed in the invention, there is preferred a 6-coordination complex having Ir as the central metal and having C1, Br or I as ligands, and; more preferably a 6-coordination complex having Ir as the central metal in which all the six ligands are formed by Cl, Br or I. In such case, Cl, Br and I may be present in mixed manner among six ligands. The 6-coordination complex having Ir as the central metal and having Cl, Br or I as the ligands is particularly preferably contained in the silver bromide-containing phase, for the purpose of obtaining a high contrast gradation under a high intensity exposure.

[0186] In the following there will be shown examples of 6-coordination complex having Ir as the central metal and Cl, Br or I in all the six ligands, but the iridium in the invention is not limited to such examples:

$[IrCl_6]^{2-}$

$[IrCl_6]^{3-}$

$[IrBr_6]^{2-}$

$[IrBr_6]^{3-}$

$[IrI_6]^{3-}$.

[0187] As another preferred embodiment of iridium in the present invention, there is preferred a 6-coordination complex having Ir as the central metal and having at least a ligand other than halogen or cyan, also preferred a 6-coordination complex having Ir as the central metal and having H_2O, OH, O, OCN, thiazole or substituted thiazole as a ligand, and more preferred a 6-coordination complex having Ir as the central metal and having at least one of H_2O, OH, O, OCN, thiazole or substituted thiazole as a ligand, in which remaining ligands are formed by Cl, Br or I.

[0188] In the following there are shown examples of the 6-coordination complex having Ir as the central metal and having at least one of H_2O, OH, O, OCN, thiazole or substituted thiazole as a ligand, in which remaining ligands are formed by Cl, Br or I, but the iridium in the present invention is not limited to such examples:

$[IrCl_5(H_2O)]^{2-}$

$[IrCl_4(H_2O)_2]^{-}$

$[IrCl_5(H_2O)]^{-}$

$[IrCl_4(H_2O)_2]^{0}$

$[IrCl_5(OH)]^{3-}$

$[IrCl_4(OH)_2]^{2-}$

$[IrCl_5(OH)]^{2-}$

$[IrCl_4(OH)_2]^{2-}$

$[IrCl_5(O)]^{4-}$

$[IrCl_4(O)_2]^{5-}$

$[IrCl_5(O)]^{3-}$

$[IrCl_4(O)_2]^{4-}$

$[IrBr_5(H_2O)]^{2-}$

$[IrBr_4(H_2O)_2]^{-}$

$[IrBr_5(H_2O)]^{-}$

$[IrBr_4(H_2O)_2]^{0}$

$[IrBr_5(OH)]^{3-}$

$[IrBr_4(OH)_2]^{2-}$

$[IrBr_5(OH)]^{2-}$

$[IrBr_4(OH)_2]^{2-}$

$[IrBr_5(O)]^{4-}$

$[IrBr_4(O)_2]^{5-}$

$[IrBr_5(O)]^{3}$

$[IrBr_4(O)_2]^{4-}$

$[IrCl_5(OCN)]^{3-}$

$[IrBr_5(OCN)]^{3-}$

$[IrCl_5(\text{thiazole})]^{2-}$

$[IrCl_4(\text{thiazole})_2]^{-}$

$[IrCl_3(\text{thiazole})_3]^{0}$

$[IrBr_5(\text{thiazole})]^{2-}$

$[IrBr_4(\text{thiazole})_2]^{-}$

$[IrBr_3(\text{thiazole})_3]^{0}$

$[IrCl_5(\text{5-methylthiazole})]^{2-}$

$[IrCl_4(\text{5-methylthiazole})_2]^{-}$

$[IrBr_5(\text{5-methylthiazole})]^{2-}$

$[IrBr_4(\text{5-methylthiazole})_2]^{-}$

$[IrCl_5(\text{5-chlorothiazole})]^{2-}$

$[IrCl_4(\text{5-chlorothiazole})_2]^{-}$

$[IrBr_5(\text{5-chlorothiazole})]^{2-}$

$[IrBr_4(\text{5-chlorothiazole})_2]^{-}$.

[0189] The metal complexes mentioned above constitute an anion, and, in case of forming a salt with a cation, the counter cation is preferably easily soluble in water. Specifically there is preferred an alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion or lithium ion, an ammonium ion or an alkylammonium ion. Such metal complex can be used by dissolving in water or in a mixed solvent of water and a suitable water-miscible organic solvent (for example an alcohol, an ether, a glycol, a ketone, an ester or an amide). Such iridium complex is preferably added, in the course of grain formation, in an amount of 1×10^{-10} to 1×10^{-3} moles per 1 mole of silver, most preferably 1×10^{-8} to 1×10^{-5} moles.

[0190] In the invention, the above-mentioned iridium complex is preferably incorporated in the silver halide grain by direct addition to a reaction solution at the formation of the silver halide grains or by addition to an aqueous halide solution for forming the silver halide grains or in another solution thereby realizing addition to the reaction solution for grain formation. It is also preferable to execute a physical ripening with fine particles incorporating the iridium complex in advance thereby achieving incorporation into the silver halide grain. It is furthermore possible to combine these methods to achieve incorporation into the silver halide grain.

[0191] In incorporating such complex into the silver halide grain, it may be uniformly distributed in the interior of the grain, but it is preferable, as disclosed in JP-A Nos. 4-208936, 2-125245 and 3-188437, to distribute the complex only in a surfacial layer of the grain, or also to distribute the complex only in the interior of the grain and to add a complex-free layer on the surface of the grain. It is also preferred, as disclosed in USP Nos. 5,252,451 and 5,256,530, to execute a physical ripening with fine particles incorporating the complex thereby modifying the surfacial phase of the grain. It is also possible to use these methods in combination, or to incorporate plural complexes into a silver halide grain. The halogen composition is not particularly limited in a position where the aforementioned complex is incorporated, but the 6-coordination complex having Ir as the central metal in which all of six ligands are formed by Cl, Br or I is preferably incorporated in a position where silver bromide has a concentration maximum.

[0192] In the invention, a rhodium compound is preferably contained. More preferably, a compound represented by a formula (VI) is employed.

formula (VI) $\mathbf{[RhQ_nL^1{}_{(6-n)}]^m}$

[0193] In the formula (VI), Q represents a halogen atom such as chlorine, bromine or iodine, preferably a bromine atom; L^1 represents an arbitrary ligand different from Br; n represents 3, 4, 5 or 6; and m preferably represents 3-, 2-, 1-, 0 or 1+. L^1 may be an inorganic compound or an organic compound and may be charged or uncharged, but is preferably an inorganic compound. L^1 is preferably Cl, H_2, NO or NS, more preferably H_2O. n is preferably 5 or 6, more preferably 6. m is preferably 3- or 2-, more preferably 3-.

[0194] Preferable specific examples of the metal complex represented by the formula (VI) are shown below, but the present invention is not limited to such examples.

$[RhBr_5Cl]^{3-}$

$[RhBr_6]^{3-}$

$[RhBr_5(H_2O)]^{2-}$

$[RhBr_4(H_2O)_2]^{2-}$.

[0195] In the case that the metal complex represented by the formula (VI) is an anion, and, in the case of forming a salt with a cation, the counter cation is preferably easily soluble in water. Specifically there is preferred an alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion or lithium ion, an ammonium ion or an alkylammonium ion. Such metal complex can be used by dissolving in water or in a mixed solvent of water and a suitable water-miscible organic solvent (for example an alcohol, an ether, a glycol, a ketone, an ester or an amide).

[0196] As to such metal complex, an optimum amount thereof is variable depending for example on a size of the silver halide grains in which it is to be incorporated, but it is preferably used, in the course of grain formation, in an amount of from 5×10^{-10} to 1×10^{-7} moles per 1 mole of silver, more preferably from 2×10^{-10} to 8×10^{-8} moles and particularly preferably from 5×10^{-10} to 5×10^{-8} moles.

[0197] In the invention, other metals than iridium or rhodium may be doped in the interior and/or on the surface of the silver halide grain. The metal ion to be employed is preferably a transition metal ion, among which preferred is iron, ruthenium, osmium, lead, cadmium or zinc. Such metal ion is more preferably employed in the form of a 6-coordination octahedral complex. In the case that an inorganic compound is employed as a ligand, there is preferably employed a cyanide ion, a halide ion, thiocyan, a hydroxide ion, a peroxide ion, an azide ion, a nitrite ion, water, ammonia, a nitrosyl ion, or a thionitrosyl ion. It is also preferable to form a coordination to an ion of the aforementioned metal such as iron, ruthenium, osmium, lead, cadmium or zinc, and it is also preferable to employ ligands of plural kinds within a complex molecule. It is also possible to employ an organic compound as a ligand, and the preferred organic compound can be a linear compound containing 5 or less carbon atoms in a main chain and/or a 5-membered or 6-membered heterocyclic compound. A more preferable organic compound is a compound including a nitrogen atom, a phosphor atom, an oxygen atom or a sulfur atom as a ligand atom to a metal. Particularly preferable is furan, thiophene, oxazole, isooxazole, thiazole, isothiazole, imidazole, pyrazole, triazole, furazane, pyran, pyridine, pyridazine, pyrimidine, or pyrazine, and also preferred are compounds obtained by introducing a substituent into a basic skeleton of these compounds.

[0198] A preferred combination of a metal ion and a ligand is a combination of an iron ion, a ruthenium ion and a cyanide ion. In the invention, it is preferable to employ iridium and such compound in combination. In such compound, the cyanide ions preferably occupy more than half of coordinations to iron or ruthenium constituting the central metal, and remaining coordinations are preferably occupied by thiocyan, ammonia, water, nitrosyl ion, dimethylsulfoxide, pyridine, pyradine or 4,4'-bipyridine. Most preferably all the six coordinations of the central metal are occupied by cyanide ions to form a hexacyano iron complex or a hexacyano ruthenium complex. Such complex having cyanide ions as ligands is preferably added, during the grain formation, in an amount of from 1×10^{-8} to 1×10^{-2} moles per 1 mole of silver, and most preferably from 1 x 10^{-6} to 5 x 10^{-4} moles. In the case that ruthenium or osmium is used as the central metal, it is also preferable to employ a nitroxyl ion, a thionitrosyl ion or a water molecule and a chloride ion as a ligand. More preferably there is formed a pentachloro nitrosyl complex, a pentachloro thionitrosyl complex or a pentachloro aqua complex, and there is also preferred to form a hexachloro complex. Such complex is preferably added, during the grain formation, in an amount of 1 x 10^{-10} to 1 x 10^{-6} moles per 1 mole of silver, more preferably 1 x 10^{-9} to 1 x 10^{-6} moles.

[0199] In the photosensitive silver halide emulsion to be employed in the invention, spectral sensitizing dyes to be used for spectral sensitizations in the green and red regions may be those described for example in F.M. Harmer, Heterocyclic compounds-Cyanine dyes and related compounds (John Wiley & Sons [New York, London], 1964). As specific examples of the compound and the spectral sensitizing method, those described in JP-A-62-215272, page 22, upper right column to page 38 may be employed advantageously. Also as a red-sensitive spectral sensitizing dye particularly for silver halide emulsion grains of a high silver chloride content, a spectral sensitizing dye described in JP-A-3-123340 is very preferable in consideration of stability, adsorption strength and temperature dependence of exposure.

[0200] The silver halide emulsion to be employed in the invention is preferably subjected to a gold sensitization known in the related art. For gold sensitization, there may be utilized various inorganic gold compounds, a gold (I) complex having an inorganic ligand or a gold (I) complex having an organic ligand. As the inorganic gold compound there may be employed for example chloroautic acid or a salt thereof, and, as the gold (I) complex having the inorganic ligand, there may be employed for example a gold dithiocyanate compound such as gold (I) potassium dithiocyanate, or a gold dithiosulfate such as gold (I) trisodium dithiosulfate.

[0201] In addition to gold sensitization, a chalcogen sensitization may be executed also by a same molecule, utilizing a molecule capable of releasing AuCh-, wherein Au represents Au(I), and Ch represents a sulfur atom, a selenium atom, or a tellurium atom. An example of the compound capable of releasing $AuCh^-$ is a gold compound represented by AuCh-L, wherein L represents an atomic group bonded to AuCh to constitute a molecule. Also one or more ligands may be coordinated, in addition to Ch-L, to Au. The gold compound represented by AuCh-L has characteristics, when reacted in a solvent in the presence of silver ions, liable to generate AgAuS, AgAuSe or AgAuTe respectively when Ch is S, Se or Te. Examples of such compound include a compound in which L is an acyl group, and also compounds represented by formulas (AuCh1), (AuCh2) and (AuCh3) shown below.

Formula (AuCH1): **R_1-X-M-ChAu**

wherein Au represents Au(I); Ch represents a sulfur atom, a selenium atom, or a tellurium atom; M represents a substituted or non-substituted methylene group; X represents an oxygen atom, a sulfur atom, a selenium atom or NR_2; R_1 represents an atomic group bonded with X to constitute a molecule (an organic group such as an alkyl group, an aryl group, or a heterocyclic group); and R_2 represents a hydrogen atom or a substituent (an organic group such as an alkyl group, an aryl group, or a heterocyclic group). R_1 and M may be bonded each other to form a ring. In the compound represented by the formula (AuCh1), Ch is preferably a sulfur atom or a selenium atom, X is preferably an oxygen atom or a sulfur atom, and R_1 is preferably an alkyl group or an aryl group. More specific examples of the compound include Au(I) salt of a thiosugar (gold thioglucose such as α-gold thioglucose, gold peracetylthioglucose, gold thiomannose, gold thiogalactose, or gold thioarabinose), Au(I) salt of a selenosugar (such as gold peracetylselenoglucose, or gold peracetylselenomannose), and Au(I) salt of a tellurosugar. The thiosugar, selenosugar or tellurosugar means a compound in which an amoner-hydroxyl group of a sugar is substituted respectively by a SH group, a SeH group or a TeH group.

Formula (AuCH2): **$W_1W_2C{=}CR_3ChAu$**

wherein Au represents Au(I); Ch represents a sulfur atom, a selenium atom, or a tellurium atom; R_3 and W_2 each represents a substituent (such as a hydrogen atom, a halogen atom, or an organic group such as an alkyl group, an aryl group or a heterocyclic group); and W_1 represents an electron-attracting group having a positive Hammett's substituent constant $\sigma\rho$. R_3 and W_1, R_3 and W_2, or W_1 and W_2 may be bonded each other to form a ring.

[0202] In the compound represented by the formula (AuCh2), Ch is preferably a sulfur atom or a selenium atom, R_3 is preferably a hydrogen atom or an alkyl group, and W_1 and W_2 each is preferably an electron-attracting group having a Hammett's substituent constant $\sigma\rho$ of 0.2 or larger. More specific examples of the compound include $(NC)_2C{=}CHSAu$, $(CH_3OCO)_2C{=}CHSAu$, and $CH_3CO(CH_3OCO)C{=}CHSAu$.

Formula (AuCH3): **W_3-E-ChAu**

wherein Au represents Au(I); Ch represents a sulfur atom, a selenium atom, or a tellurium atom; E represents a substituted or non-substituted ethylene group; and W_3 represents an electron-attracting group having a positive Hammett's substituent constant $\sigma\rho$.

[0203] In the compound represented by the formula (AuCh3), Ch is preferably a sulfur atom or a selenium atom, E is preferably an ethylene group having a positive Hammett's substituent constant σρ, and W_3 is preferably an electron-attracting group having a Hammett's substituent constant σρ of 0.2 or larger. The amount of addition of such compounds, being variable over a wide range according to the situation, is generally from 5×10^{-7} to 5×10^{-3} moles per 1 mole of silver halide, and preferably from 3×10^{-6} to 3×10^{-4} moles.

[0204] Also colloidal gold sulfide may be utilized, and a producing method therefor is described for example in Research Disclosure 37154, Solid State Ionics, vo1.79, pp.60 - 66(1995) and Compt. Rend. Hebt. Seances Acad. Sci. Sect., B263, p.1328(1966). The *Research Disclosure* describes a method of utilizing thiocyanate ion in producing colloidal gold sulfide, but it is also possible, instead, to utilize a thioether compound such as methionine or thiodiethanol.

[0205] The colloidal gold sulfide can be used in various sizes, and is preferably used with an average particle size of 50 nm or less, more preferably with an average particle size of 10 nm or less, and further preferably with an average particle size of 3 nm or less. Such particle size can be measured on a TEM photograph. The colloidal gold sulfide may have a composition Au_2S_1 or a sulfur-excessive composition such as Au_2S_1 to Au_2S_2, and a sulfur-excessive composition is preferable. A composition $Au_2S_{1.1}$ to $Au_2S_{1.8}$ is further preferable.

[0206] The composition of such colloidal gold sulfide may be analyzed, for example, by taking out a gold sulfide particle and determining a gold content and a sulfur content respectively for example by ICP and iodometry. Since gold ions or sulfur ions (including hydrogen sulfide and salt thereof), dissolved in liquid phase present in the gold sulfide colloid, affects the compositional analysis of gold sulfide colloid particle, the analysis is executed after separating the gold sulfide particle for example by an ultrafiltration. The amount of addition of gold sulfide colloid may vary within a wide range depending on the situation, but is usually within a range of 5×10^{-7} to 5×10^{-3} moles of gold atoms per 1 mole of silver halide, preferably 5×10^{-6} to 5×10^{-4} moles.

[0207] In the present invention, the gold sensitization may be further combined with another sensitization such as sulfur sensitization, selenium sensitization, tellurium sensitization, reduction sensitization or precious metal sensitization utilizing a compound other than gold compound. In particular, a combination with sulfur sensitization or selenium sensitization is preferable.

[0208] In the invention, a surfactant may be added to the photosensitive material, in view of improving the coating stability of the photosensitive material, preventing generation of electrostatic charge and regulating a charge amount. The surfactant includes an anionic surfactant, a cationic surfactant, a betaine surfactant and a nonionic surfactant, such as those described in JP-A No.5-333492. As the surfactant in the invention, there is preferred a surfactant containing a fluorine atom. In particular, a fluorine atom-containing surfactant can be employed advantageously. Such fluorine atom-containing surfactant may be used singly or in combination with another known surfactant, but is preferably used in combination with another known surfactant. An amount of addition of such surfactant to the photosensitive material is not particularly limited, but is generally within a range from 1×10^{-5} to 1 g/m^2, preferably 1×10^{-4} to 1×10^{-1} g/m^2 and more preferably 1×10^{-3} to 1×10^{-2} g/m^2.

[0209] Furthermore, the photosensitive material to be employed in the invention may contain known additives such as a color coupler, a polymer coupler, a coupler releasing a photographically useful group, a scavenger for an oxidized material of the developing agent, a stain preventing agent, a fading preventing agent, a dye and an ultraviolet absorber, as described in JP-A-2001-183778, a table in paragraph 0100 and paragraphs 0101 to 0119 thereof.

[0210] The photosensitive material to be employed in the present invention can form an image by an exposure step of light irradiation according to image information, and a development step of developing the photosensitive material subjected to the light irradiation.

[0211] A general-purpose printer is used as a printer for preparing a print, by the developing process utilizing the solid processing materials of the invention, but it is usable not only in a print system utilizing an ordinary negative printer but also suitable for a scan exposure method utilizing a cathode ray tube (CRT). The CRT exposure apparatus is simpler, more compact and less expensive in comparison with an apparatus utilizing a laser. Also adjustments of optical axis and colors are easier. In the cathode ray tube employed for image exposure, there are employed various light emitting members showing light emissions in necessary spectral regions. For example, there is employed either one of a red light emitting member, a green light emitting member and a blue light emitting member, or a mixture of two or more thereof. The spectral regions are not limited to red, green and blue mentioned above, but there may also be employed a phosphor emitting light in yellow, orange, purple or infrared region. In particular, there is often employed a cathode ray tube emitting white light by mixing these light emitting members.

[0212] In the case that the photosensitive material includes plural photosensitive layers of different spectral sensitivity distributions and the cathode ray tube has fluorescent members showing light emissions in plural spectral regions, it is possible to expose plural colors at a time, namely to cause light emission from the tube by inputting image signals of plural colors. There may also be adopted a method of inputting image signals of respective colors in succession thereby causing light emissions of respective colors in succession, and executing an exposure through a film that intercepts colors other than an exposed color (field-sequential exposure), and, in general, the field-sequential exposure is preferable for obtaining a higher image quality, since a cathode ray tube of a higher resolution can be employed in such method.

[0213] For the photosensitive material, there is preferably employed a digital scan exposure method utilizing a monochromic high-density light of a gas laser, a light emitting diode, a semiconductor laser, or a second harmonic generating light source (SHG) formed by a combination of a semiconductor laser or a solid-state laser utilizing a semiconductor laser as an exciting light source and a non-linear optical crystal. For obtaining a compact and inexpensive system, it is preferable to use a semiconductor laser, or a second harmonic generating light source (SHG) formed by a combination of a semiconductor laser or a solid-state laser utilizing a semiconductor laser as an exciting light source and a non-linear optical crystal. In particular, for designing a compact, inexpensive apparatus of a long service life and a high stability, there is preferred the use of a semiconductor laser, and it is preferable to use a semiconductor laser in at least one of the exposure light sources.

[0214] The photosensitive material is preferably subjected to an imagewise exposure by a coherent light of a blue laser having a light emission wavelength range of from 420 to 460 nm. Among such blue lasers, there is particularly preferred a blue semiconductor laser.

[0215] As specific examples of the laser light source, there can be preferably employed a blue semiconductor laser of a wavelength of from 430 to 450 nm (announced by Nichia Corp. in March 2001, at 48th Applied Physics United Symposium, a blue laser of a wavelength of about 470 nm, taken out from a semiconductor laser (oscillation wavelength: about 940 nm) by a wavelength conversion in an $LiNbO_3$ SHG crystal having a waveguide-shaped inversion domain structure, a green laser of a wavelength of about 530 nm, taken out from a semiconductor laser (oscillation wavelength: about 1060 nm) by a wavelength conversion in an $LiNbO_3$ SHG crystal having a waveguide-shaped inversion domain structure, a red semiconductor laser of a wavelength of about 685 nm (Hitachi Type No. HL6738MG), and a red semiconductor laser of a wavelength of about 650 nm (Hitachi Type No. HL6501MG).

[0216] In case of utilizing such scan exposure light source, a spectral sensitivity peak wavelength of the photosensitive material of the invention can be arbitrarily selected according to the wavelength of the scan exposure light source to be used. A blue light or a green light can be obtained from am SHG light source, formed by combining a solid state laser utilizing a semiconductor laser as an excitation light source or a semiconductor laser, and a non-linear optical crystal, as it can halve the oscillation wavelength of the laser. Consequently, the spectral sensitivity peaks of the photosensitive material can be provided in the ordinary three wavelength regions of blue, green and red. An exposure time in such scan exposure, defined as a time exposing a pixel size at a pixel density of 300 dpi, is preferably 10^{-4} sec or less, more preferably 10^{-6} sec or less. Also for the purpose of avoiding an unauthorized copying of the photosensitive material, subjected to the processing of the invention, a latent image of microdot patterns may be formed on the photosensitive material. Such method is described in JP-A-9-226227.

[0217] The silver halide color photographic photosensitive material to be employed in the invention can be advantageously used in combination with an exposure or development system described in following related references. Examples of such system include an automatic print and development system described in JP-A-10-333253, a photosensitive material transporting apparatus described in JP-A-2000-10206, a recording system including an image reading apparatus described in JP-A-11-215312, an exposure system utilizing a color image recording method described in JP-A-11-88619 and JP-A-10-202950, a digital photoprint system including a remote diagnostic method described in JP-A-10-210206, and a photoprint system including an image recording apparatus described in JP-A-2000-310822.

[0218] The preferable scan exposure method applicable to the invention is explained in detail in the patent references described in the foregoing table. Also for processing the photosensitive material of the invention, preferably employable are processing material and processing methods described in JP-A-2-207250, p.26, lower right column, line 1 to p.34, upper right column, line 9, and in JP-A-4-97355, p.5, upper left column, line 17 to p.18, lower right column, line 20.

[0219] In the following, the present invention will be clarified in more detail by examples, but the scope of the invention is not at all restricted by such examples.

[Example 1-1]

(Preparation of concentrated bleach composition)

[0220] Samples Nos. 1 to 17 of concentrated bleach composition were prepared with formulations shown in Table 3. Amounts in the table indicate those per 1 L of the composition.

<Concentrated bleach composition>

water	400 ml
ethylenediaminetetraacetic acid iron(III) ammonium (EDTAFe(III))	cf. Table 3
ethylenediaminetetraacetic acid (EDTA)	cf. Table 3
m-carboxybenzenesulfinic acid	20.0 g
nitric acid	38.0g

(continued)

<Concentrated bleach composition>

succinic acid	cf. Table 3
ammonia water (27 %)	25.0 g
water to make	1000 ml
pH (25˚C/adjusted with ammonia or nitric acid)	cf. Table 3

Table 3

No.	EDTAFe(III) concentration (mol/L)	EDTA concentration (mol%)	succinic acid concentration (mol/L)	pH	remarks
1	1.00	0.3	0.4	2.5	comp. example
2	0.70	0.3	0.4	2.5	comp. example
3	0.50	0.3	0.4	2.0	comp. example
4	0.40	0.1	0.5	2.0	comp. example
5	0.42	0.1	0.4	2.5	comp. example
6	0.42	0.5	0.2	3.0	invention
7	0.40	5.0	0.1	3.5	invention
8	0.40	2.0	0.3	2.5	invention
9	0.35	3.0	0.3	2.5	invention
10	0.35	10.0	0.3	2.5	invention
11	0.20	5.0	0.3	2.0	invention
12	0.20	15.0	0.3	2.5	invention
13	0.15	20.0	0.3	2.5	invention
14	0.10	30.0	0.4	2.0	invention
15	0.05	40.0	0.3	2.5	comp. example
16	0.35	0.3	0.2	3.0	comp. example
17	0.35	5.0	0.01	5.2	comp. example

[0221] In Table 3, Comparative Examples 1, 2 and 3 correspond to Nos. 11, 3 and 17 in JP-A-2004-53921, Example 1, Table 2.

(Evaluation of performances and characteristics)

[0222] On thus prepared samples Nos. 1 to 17 of concentrated bleach composition, a stability was evaluated, and following running tests were executed with the concentrated bleach compositions to evaluate a sulfurization resistance, a desilvering property and a silver recovery efficiency.

<Running test conditions>

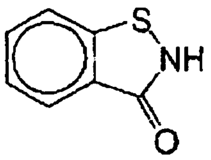
1-1. Preparation of photosensitive material sample

[0223] A photosensitive material to be employed in the continuous processing test was prepared in the following manner (Preparation of emulsion BH-1 for blue-sensitive layer)

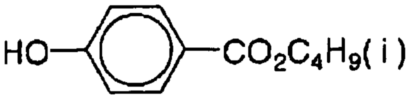
[0224] Cubic grains of a high silver chloride content were prepared by a method of simultaneously adding and mixing silver nitrate and sodium chloride in agitated deionized distilled water containing deionized gelatin. In the course of preparation, over a period where the addition of silver nitrate proceeded from 60 % to 80 %, $Cs_2[OsCl_5(NO)]$ was added. Over a period where the addition of silver nitrate proceeded from 80 % to 90 %, potassium bromide (1.5 mol% per 1 mole of silver halide to be formed) and $K_4[Fe(CN)_6]$ were added. Over a period where the addition of silver nitrate proceeded from 83 % to 88 %, $K_2[IrCl_6]$ was added. Over a period where the addition of silver nitrate proceeded from 92 % to 98 %, $K_2[IrCl_5(H_2O)]$ and $K[IrCl_4(H_2O)2]$ were added. At a point where the addition of silver nitrate proceeded by 94 %, potassium iodide (0.27 mole% per 1 mole of silver halide to be formed) was added under vigorous mixing. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.54 μm and a variation coefficient of 8.5 %. The emulsion, after being subjected to a deposition-desalting process, was subjected to additions of gelatin, compounds Ab-1, Ab-2 and Ab-3 and calcium nitrate, and was re-dispersed.

[0225] The re-dispersed emulsion was dissolved at 40°C, and sensitizing dyes S-1, S-2 and S-3 of the invention were so added as to obtain optimum spectral sensitizations. Then sodium benzenethiosulfate, triethylthiourea as a sulfur sensitizer and a compound-1 as a gold sensitizer were added, and the emulsion was ripened to an optimum chemical sensitization. Thereafter, 1-(5-methylureidophenyl)-5-mercaptotetrazole, a compound-2, a compound principally formed by 2 or 3 repeating units represented by a compound -3 (terminal ends X_1 and X_2 being hydroxyl groups), a compound-4 and potassium bromide were added to terminate the chemical sensitization. The emulsion thus obtained was taken as an emulsion BH-1.

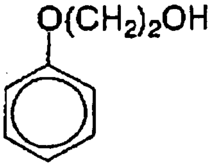
(Ab-1) antiseptic



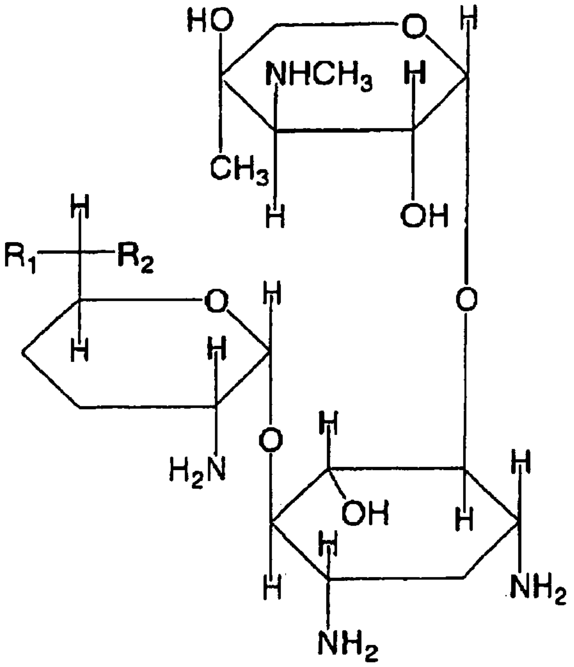
(Ab-2) antiseptic



(Ab-3) antiseptic



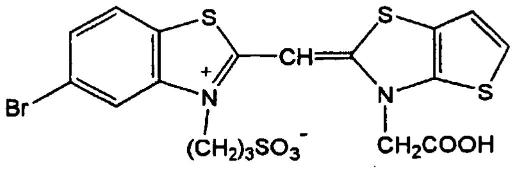
(Ab-4) antiseptic



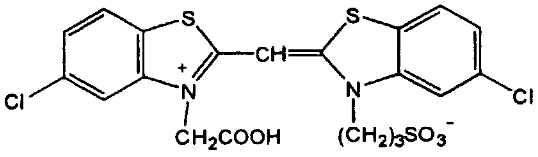
	R_1	R_2
a	$-CH_3$	$-NHCH_3$
b	$-CH_3$	$-NH_2$
c	$-H$	$-NH_2$
d	$-H$	$-NHCH_3$

1:1:1:1 mixture (molar ratio) of a, b, c and d

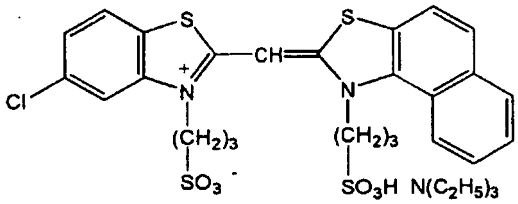
sensitizer S-1



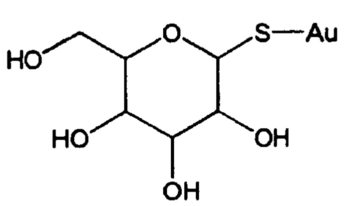
sensitizer S-2



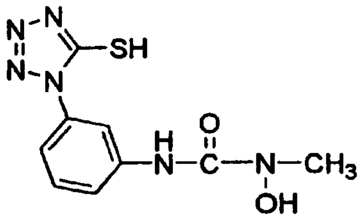
sensitizer S-3



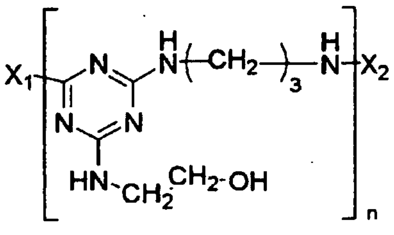
compound-1



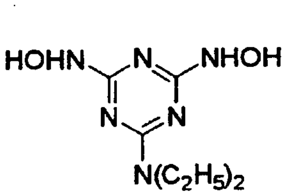
compound-2



compound-3



compound-4



(Preparation of emulsion BL-1 for blue-sensitive layer)

[0226] Emulsion grains were obtained in the same manner as in the preparation of emulsion BH-1, except that the temperature and the adding speed were changed in the step of simultaneously adding and mixing silver nitrate and sodium chloride, and that the amounts of metal complexes, added in the course of addition of silver nitrate and sodium chloride, were changed. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.44 μm and a variation coefficient of 9.5 %. After the emulsion was re-dispersed, an emulsion BL-1 was prepared in the same manner except that the amounts of the various added compounds were changed from those in BH-1.

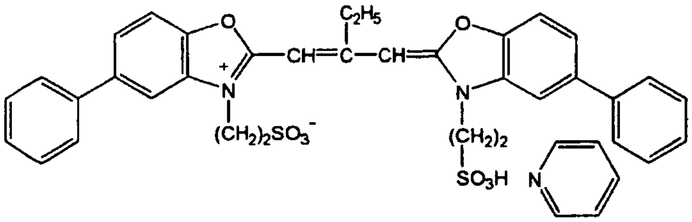
(Preparation of emulsion GH-1 for green-sensitive layer)

[0227] Cubic grains of a high silver chloride content were prepared by a method of simultaneously adding and mixing silver nitrate and sodium chloride in agitated deionized distilled water containing deionized gelatin. In the course of preparation, over a period where the addition of silver nitrate proceeded from 80 % to 90 %, $K_4[Ru(CN)_6]$ was added. Over a period where the addition of silver nitrate proceeded from 80 % to 100 %, potassium bromide (2 mol% per 1 mole of silver halide to be formed) was added. Over a period where the addition of silver nitrate proceeded from 83 %

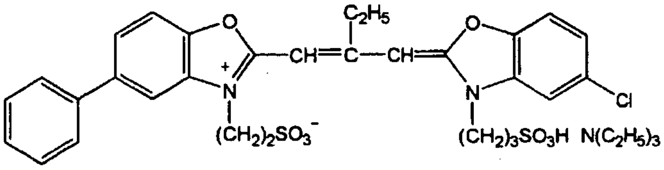
to 88 %, $K_2[IrCl_6]$ and $K_2[RhBr_5(H_2O)]$ were added. At a point where the addition of silver nitrate proceeded by 90 %, potassium iodide (0.1 mol% per 1 mole of silver halide to be formed) was added under vigorous mixing. Also over a period where the addition of silver nitrate proceeded from 92 % to 98 %, $K_2[IrCl_5(H_2O)]$ and $K[IrCl_4(H_2O)_2]$ were added. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.42 μm and a variation coefficient of 8.0 %. The emulsion was subjected to a deposition-desalting process, and re-dispersion.

[0228] The emulsion was dissolved at 40°C, and sodium benzenethiosulfonate, p-glutaramidephenyl disulfide, sodium thiosulfate pentahydrate as a sulfur sensitizer and bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)aurate(I) tetrafluoroborate as a gold sensitizer were added, and the emulsion was so ripened as to obtain an optimum chemical sensitization. Thereafter, 1-(3-acetamidephenyl)-5-mercaptotetrazole, 1-(5-methylureidophenyl)-5-mercaptotetrazole, a compound-2, a compound-4 and potassium bromide were added. Also in the course of emulsion preparation process, sensitizing dyes S-4, S-5, S-6 and S-7 were added for spectral sensitization. The emulsion thus obtained was taken as an emulsion GH-1.

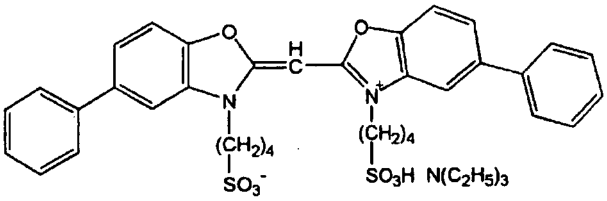
sensitizing dye S-4



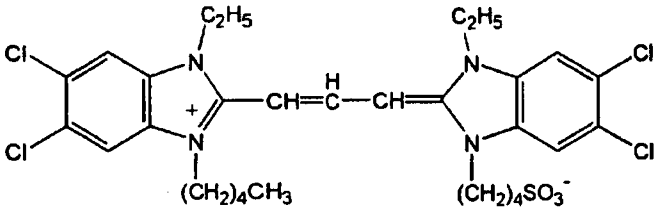
sensitizing dye S-5



sensitizing dye S-6



sensitizing dye S-7



(Preparation of emulsion GL-1 for green-sensitive layer)

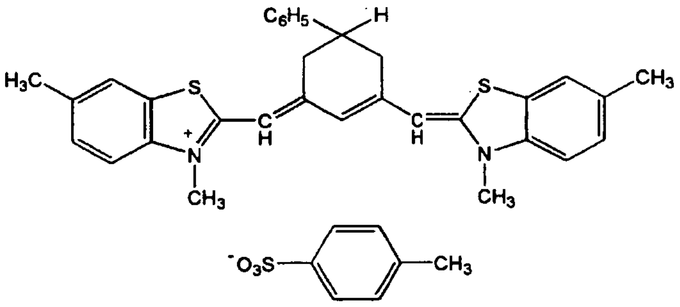
[0229] Emulsion grains were obtained in the same manner as in the preparation of emulsion GH-1, except that the temperature and the adding speed were changed in the step of simultaneously adding and mixing silver nitrate and sodium chloride, and that the amounts of metal complexes, added in the course of addition of silver nitrate and sodium chloride, were changed. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.35 μm and a variation coefficient of 9.8 %. After the emulsion was re-dispersed, an emulsion GL-1 was prepared in the same manner except that the amounts of the various added compounds were changed from those in GH-1.

(Preparation of emulsion RH-1 for red-sensitive layer)

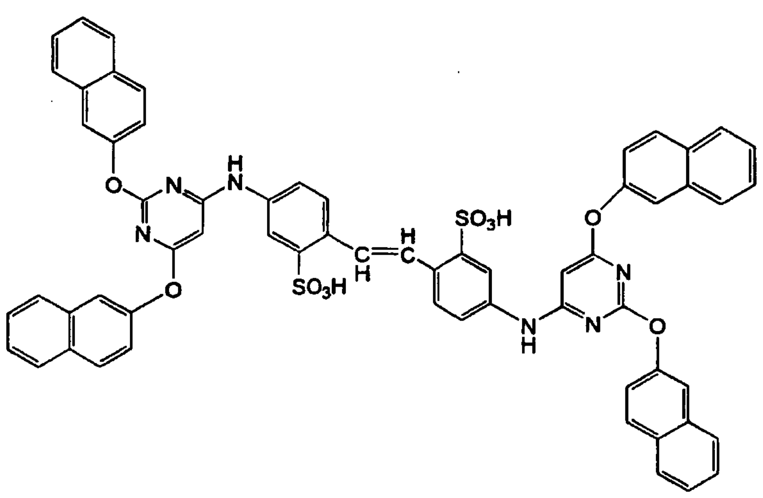
[0230] Cubic grains of a high silver chloride content were prepared by a method of simultaneously adding and mixing silver nitrate and sodium chloride in agitated deionized distilled water containing deionized gelatin. In the course of preparation, over a period where the addition of silver nitrate proceeded from 60 % to 80 %, $Cs_2[OsCL_5(NO)]$ was added. Over a period where the addition of silver nitrate proceeded from 80 % to 90 %, $K_4[Ru(CN)_6]$ was added. Over a period where the addition of silver nitrate proceeded from 80 % to 100 %, potassium bromide (1.3 mol% per 1 mole of silver halide to be formed) was added. Over a period where the addition of silver nitrate proceeded from 83 % to 88 %, $K_2[IrCl_5(5\text{-methylthiazole})]$ was added. At a point where the addition of silver nitrate proceeded by 88 %, potassium iodide (an amount corresponding to 0.05 mol% of silver iodide per 1 mole of silver halide to be formed) was added under vigorous mixing. Also over a period where the addition of silver nitrate proceeded from 92 % to 98 %, $K_2[IrCl_5(H_2O)]$ and $K[IrCl_4(H_2O)_2]$ were added. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.39 μm and a variation coefficient of 10 %. The emulsion was subjected to a deposition-desalting process, and re-dispersion, as described above.

[0231] The emulsion was dissolved at 40°C, and a sensitizing dye S-8, a compound-5, triethylthiourea as a sulfur sensitizer and a compound-1 as a gold sensitizer were added, and the emulsion was so ripened as to obtain an optimum chemical sensitization. Thereafter, 1-(3-acetamidephenyl)-5-mercaptotetrazole, 1-(5-methylureidophenyl)-5-mercaptotetrazole, a compound-2, a compound-4 and potassium bromide were added. The emulsion thus obtained was taken as an emulsion RH-1.

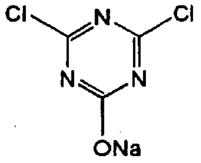
sensitizing dye S-8



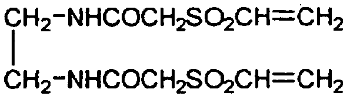
compound-5



(H-1) hardener

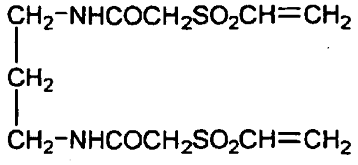


(H-2) hardener



$$\begin{array}{l} CH_2\text{-}NHCOCH_2SO_2CH=CH_2 \\ | \\ CH_2\text{-}NHCOCH_2SO_2CH=CH_2 \end{array}$$

(H-3) hardener



$$\begin{array}{l} CH_2\text{-}NHCOCH_2SO_2CH=CH_2 \\ | \\ CH_2 \\ | \\ CH_2\text{-}NHCOCH_2SO_2CH=CH_2 \end{array}$$

(Preparation of emulsion RL-1 for red-sensitive layer)

[0232] Emulsion grains were obtained in the same manner as in the preparation of emulsion RH-1, except that the temperature and the adding speed were changed in the step of simultaneously adding and mixing silver nitrate and sodium chloride, and that the amounts of metal complexes, added in the course of addition of silver nitrate and sodium chloride, were changed. The obtained emulsion grains were mono-dispersion cubic silver iodobromochloride grains having a side length of 0.29 μm and a variation coefficient of 9.9 %. After the emulsion was subjected to a deposition-desalting process and a re-dispersion, an emulsion RL-1 was prepared in the same manner except that the amounts of the various added compounds were changed from those in RH-1.

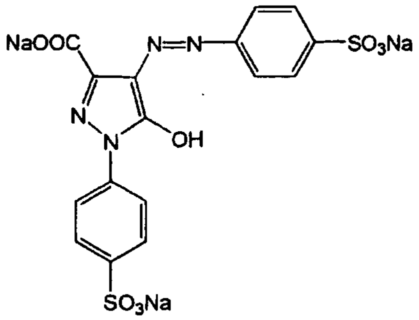
Preparation of first layer coating liquid

[0233] 34 g of a yellow coupler (Ex-Y), 1 g of a color image stabilizer (Cpd-1), 1 g of a color image stabilizer (Cpd-2), 8 g of a color image stabilizer (Cpd-8), 1 g of a color image stabilizer (Cpd-18), 2 g of a color image stabilizer (Cpd-19), 15 g of a color image stabilizer (Cpd-20), 1 g of a color image stabilizer (Cpd-21), 15 g of a color image stabilizer (Cpd-23), 0.1 g of an additive (ExC-1), and 1 g of a color image stabilizer (UV-A) were dissolved in 23 g of a solvent (Solv-4), 4 g of a solvent (Solv-6), 23 g of a solvent (Solv-9), and 60 ml of ethyl acetate, and the obtained solution was emulsified in 270 g of a 20 mass% aqueous gelatin solution, containing 4 g of sodium dodecylbenzenesulfonate, by a high-speed agitating emulsifier (Dissolver), and water was added to obtain 900 g of an emulsified dispersion A.

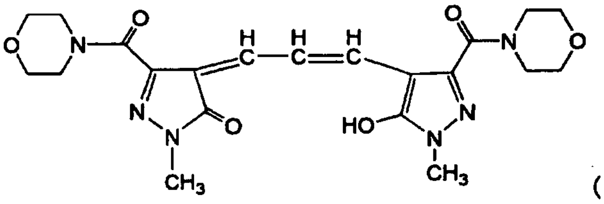
[0234] Then, the emulsified dispersion A and the emulsions BH-1, BL-1 were mixed and dissolved to prepare a first layer coating liquid of a composition to be shown below. A coating amount of the emulsion is shown in a coating amount converted to a silver amount.

[0235] Coating liquids for second to seventh layers were prepared in a similar manner as the coating liquid for the first layer. (H-1), (H-2) and (H-3) were used as gelatin hardeners in each layer. In each layer, Ab-1, Ab-2, Ab-3 and Ab-4 were also added so as to obtain total amounts respectively of 14.0 mg/m^2, 62.0 mg/m^2, 5.0 mg/m^2, and 10.0 mg/m^2.

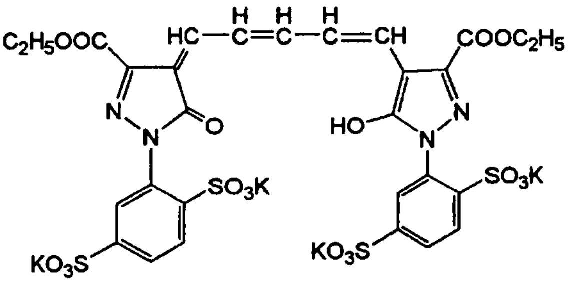
[0236] 1-(3-methylureidophenyl)-5-mercaptotetrazole was added in the second, fourth and sixth layers so as to obtain respective amounts of 0.2 mg/m^2, 0.2 mg/m^2, and 0.6 mg/m^2. In the blue-sensitive emulsion layer and the green-sensitive emulsion layer, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added so as to obtain respective amounts of 1 x 10^{-4} moles and 2 x 10^{-4} moles per 1 mole of silver halide. In the red-sensitive emulsion layer, a methacrylic acid-butyl acrylate copolymer latex (mass ratio 1:1, average molecular weight 200,000 to 400,000) was added so as to obtain an amount of 0.05 g/m^2. In the second, fourth and sixth layers, disodium catechol-3,5-disulfonate was added so as to obtain respective amounts of 6 mg/m^2, 6 mg/m^2, and 18 mg/m^2. Also sodium polystyrenesulfonate was added, if necessary in each layer, for regulating the viscosity of the coating liquid. Also for preventing irradiation, following dyes (parenthesized number indicating coating amount) were added.



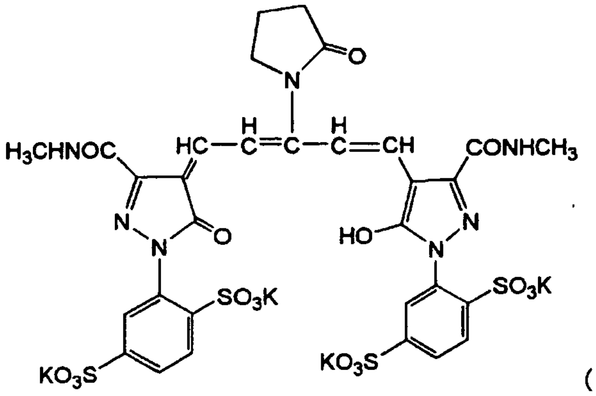
(2mg／m^2)



(3mg／m^2)



(10mg／m^2)



(16mg/m²)

(Layer structure)

[0237] Formulation of each layer is shown below, in which a number indicates a coating amount (g/m^2), and, for the silver halide emulsion, the coating amount is shown by a coating amount converted into a silver amount.

Substrate

[0238] polyethylene resin-laminated paper [polyethylene resin at the side of the first layer containing a white pigment (TiO$_2$ content: 16 mass%, ZnO content: 4 mass%), a fluorescent whitening agent (4,4'-bis(5-methylbenzoxazolyl)stilbene (content: 0.03 mass%) and a blue dye (ultramarine, content: 0.33 mass%), amount of polyethylene resin being 29.2 g/m^2]

First layer (blue-sensitive emulsion layer) emulsion (5:5 mixture (in silver molar ratio) of BH-1 and BL-1)	0.16
gelatin	1.35
yellow coupler (Ex-Y)	0.36
color image stabilizer (Cpd-1)	0.01
color image stabilizer (Cpd-2)	0.01
color image stabilizer (Cpd-8)	0.08
color image stabilizer (Cpd-18)	0.01
color image stabilizer (Cpd-19)	0.02
color image stabilizer (Cpd-20)	0.15
color image stabilizer (Cpd-21)	0.01
color image stabilizer (Cpd-23)	0.15
additive (ExC-1)	0.002
color image stabilizer (UV-A)	0.01
solvent (Solv-4)	0.23
solvent (Solv-6)	0.04
solvent (Solv-9)	0.23
Second layer (color-mixing preventing layer)	
gelatin	0.80
color-mixing preventing agent (Cpd-4)	0.05
color-mixing preventing agent (Cpd-12)	0.01
color image stabilizer (Cpd-3)	0.01
color image stabilizer (Cpd-5)	0.006
color image stabilizer (Cpd-6)	0.05
color image stabilizer (UV-A)	0.06
color image stabilizer (Cpd-7)	0.006

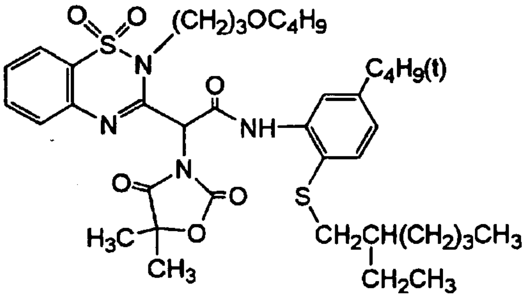
(continued)

Second layer (color-mixing preventing layer)	
solvent (Solv-1)	0.06
solvent (Solv-2)	0.06
solvent (Solv-5)	0.07
solvent (Solv-8)	0.07
Third layer (green-sensitive emulsion layer) emulsion (1:3 mixture (in silver molar ratio) of GH-1 and GL-1)	0.10
gelatin	0.93
magenta coupler (ExM)	0.12
ultraviolet absorber (UV-A)	0.03
color image stabilizer (Cpd-2)	0.01
color image stabilizer (Cpd-6)	0.08
color image stabilizer (Cpd-7)	0.005
color image stabilizer (Cpd-8)	0.01
color image stabilizer (Cpd-9)	0.01
color image stabilizer (Cpd-10)	0.005
color image stabilizer (Cpd-11)	0.0001
color image stabilizer (Cpd-20)	0.01
solvent (Solv-3)	0.06
solvent (Solv-4)	0.12
solvent (Solv-6)	0.05
solvent (Solv-9)	0.16
Fourth layer (color-mixing preventing layer)	
gelatin	0.63
color-mixing preventing agent (Cpd-4)	0.04
color-mixing preventing agent (Cpd-12)	0.01
color image stabilizer (Cpd-3)	0.01
color image stabilizer (Cpd-5)	0.005
color image stabilizer (Cpd-6)	0.04
color image stabilizer (UV-A)	0.05
color image stabilizer (Cpd-7)	0.005
solvent (Solv-1)	0.05
solvent (Solv-2)	0.05
solvent (Solv-5)	0.06
solvent (Solv-8)	0.06
Fifth layer (red-sensitive emulsion layer) emulsion (4:6 mixture (in silver molar ratio) of RH-1 and RL-1)	0.10
gelatin	1.12
cyan coupler (ExC-1)	0.10
cyan coupler (ExC-2)	0.02
cyan coupler (ExC-3)	0.02
color image stabilizer (Cpd-1)	0.03
color image stabilizer (Cpd-7)	0.01
color image stabilizer (Cpd-9)	0.04
color image stabilizer (Cpd-10)	0.001
color image stabilizer (Cpd-14)	0.001
color image stabilizer (Cpd-15)	0.18

(continued)

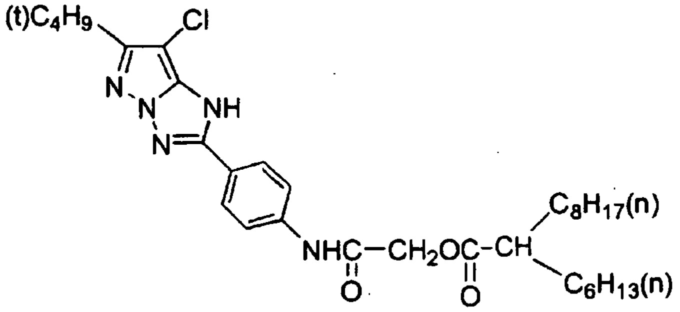
Fifth layer (red-sensitive emulsion layer) emulsion (4:6 mixture (in silver molar ratio)	
color image stabilizer (Cpd-16)	0.002
color image stabilizer (Cpd-17)	0.001
color image stabilizer (Cpd-18)	0.05
color image stabilizer (Cpd-19)	0.04
color image stabilizer (UV-5)	0.10
solvent (Solv-5)	0.19
Sixth layer (ultraviolet absorbing layer)	
gelatin	0.34
ultraviolet absorber (UV-B)	0.24
compound (S1-4)	0.0015
solvent (Solv-7)	0.11
Seventh layer (protective layer) gelatin	0.80
additive (Cpd-22)	0.03
liquid paraffin	0.02
surfactant (Cpd-13)	0.02

(Ex-Y) yellow coupler

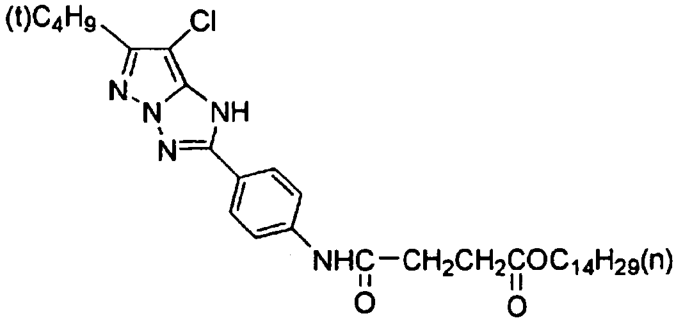


(Ex-M) magenta coupler

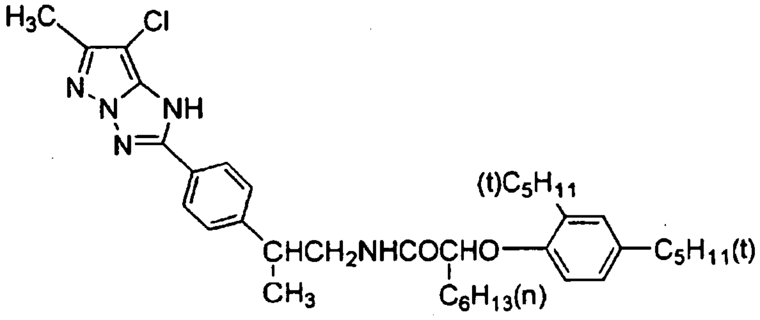
40:40:20 mixture (molar ratio) of



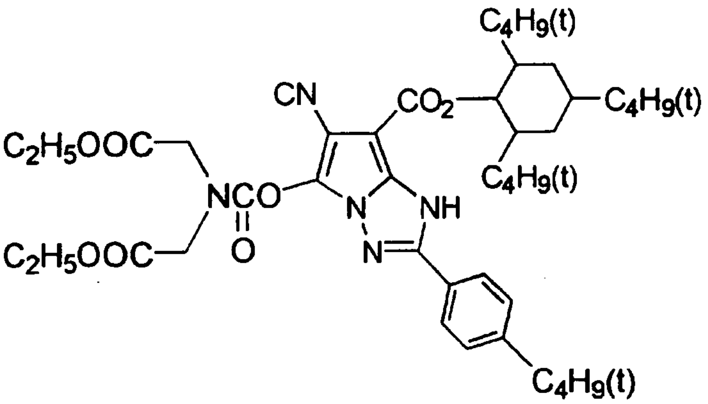
,



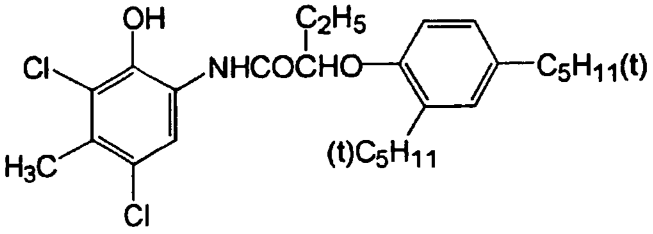
and



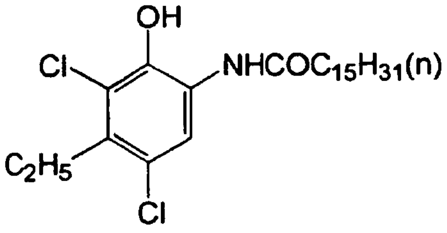
(ExC-1) cyan coupler



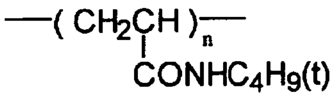
(ExC-2) cyan coupler



(ExC-3) cyan coupler



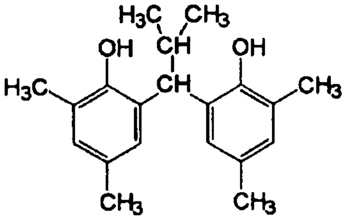
(Cpd-1) color image stabilizer



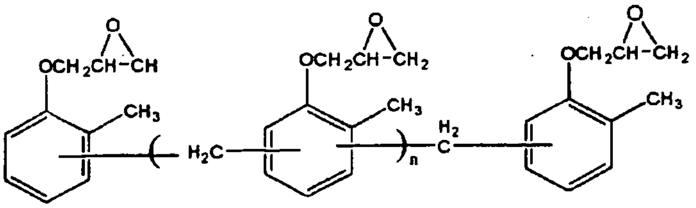
$$-\!\!\left(\underset{\displaystyle CONHC_4H_9(t)}{CH_2\underset{|}{C}H}\right)_n\!\!-$$

average molecular weight 60,000

(Cpd-2) color image stabilizer

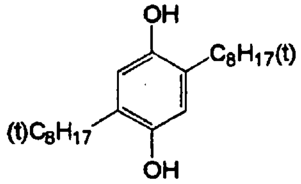


(Cpd-3) color image stabilizer

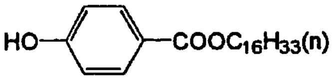


n = 7 - 8 (average)

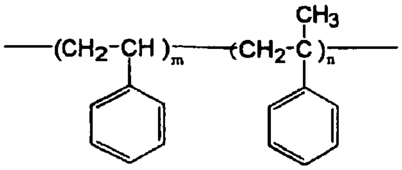
(Cpd-4) color image stabilizer



(Cpd-5) color image stabilizer



(Cpd-6) color image stabilizer

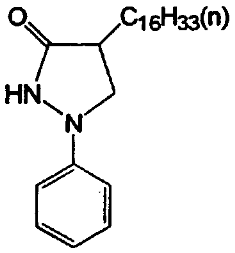


number-average molecular weight 600,

m/n = 10/90

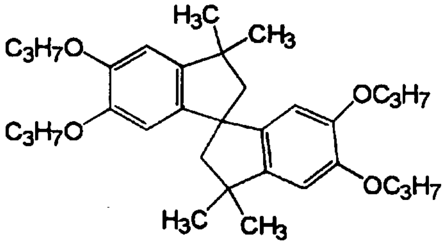
(Cpd-7)

color image stabilizer



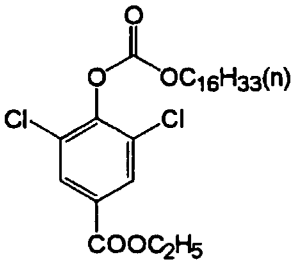
(Cpd-8)

color image stabilizer



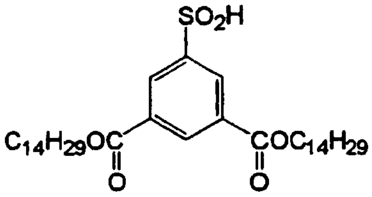
(Cpd-9)

color image stabilizer

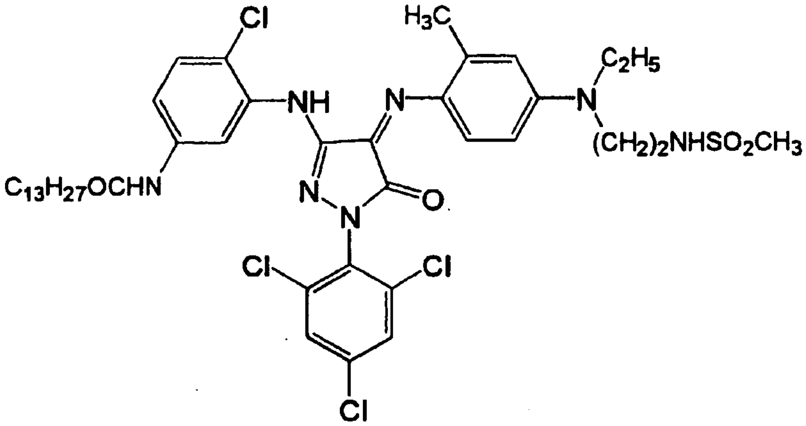


(Cpd-10)

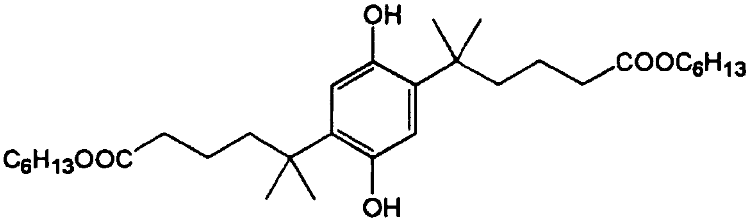
color image stabilizer



(Cpd-11)

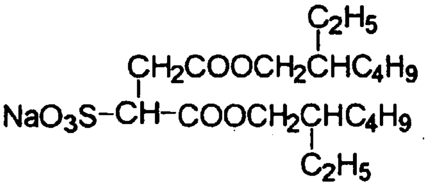

Cl
H3C
C2H5
NH
N
N
(CH2)2NHSO2CH3
C13H27OCHN
N
N
O
Cl
Cl
Cl

(Cpd-12)


OH
COOC6H13
C6H13OOC
OH

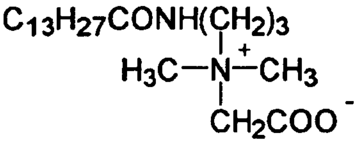
(Cpd-13) 6:2:2 mixture of (a)/(b)/(c) (molar ratio)

(a)



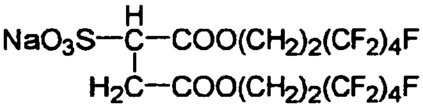
$$NaO_3S-CH(CH_2COOCH_2CH(C_2H_5)C_4H_9)-COOCH_2CH(C_2H_5)C_4H_9$$

(b)



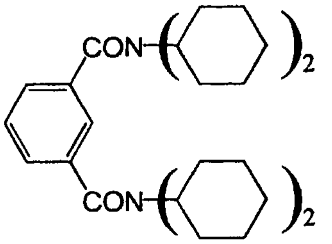
$$C_{13}H_{27}CONH(CH_2)_3-N^{+}(CH_3)_2-CH_2COO^{-}$$

(c)

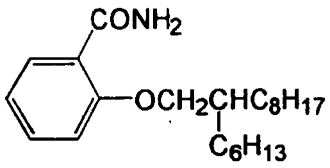


$$NaO_3S-CH(COO(CH_2)_2(CF_2)_4F)-H_2C-COO(CH_2)_2(CF_2)_4F$$

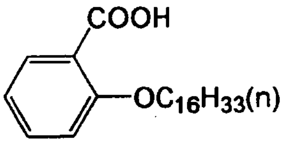
(Cpd−14)



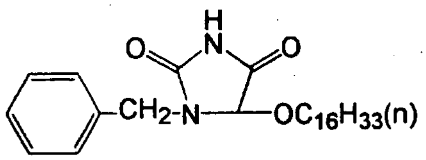
(Cpd−15)



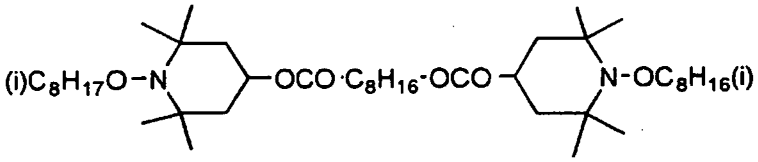
(Cpd−16)



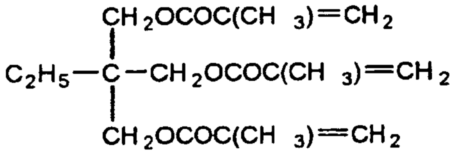
(Cpd−17)



(Cpd−18)

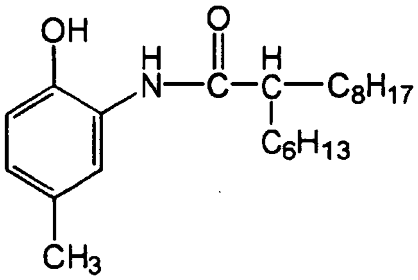


(Cpd−19)

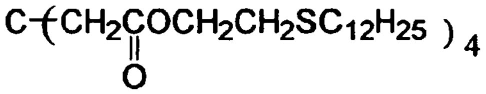


$$\begin{array}{l} \qquad\quad \mathrm{CH_2OCOC(CH_3){=}CH_2} \\ \qquad\quad | \\ \mathrm{C_2H_5{-}C{-}CH_2OCOC(CH_3){=}CH_2} \\ \qquad\quad | \\ \qquad\quad \mathrm{CH_2OCOC(CH_3){=}CH_2} \end{array}$$

(Cpd−20)

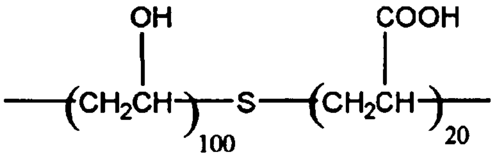


(Cpd−21)



$$\mathrm{C}\!\left(\mathrm{CH_2}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{OCH_2CH_2SC_{12}H_{25}}\right)_4$$

(Cpd−22)



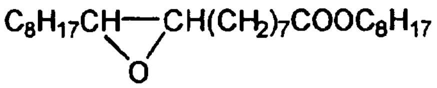
$$-\left(CH_2\overset{OH}{\overset{|}{CH}}\right)_{100}-S-\left(CH_2\overset{COOH}{\overset{|}{CH}}\right)_{20}-$$

(mass ratio)

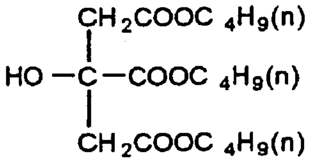
(Cpd-23)

KAYARAD DPCA-30, manufactured by Nippon Kayaku Co.

(Solv-1)

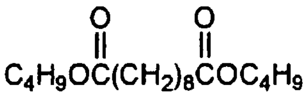


(Solv-2)



$$\begin{array}{c} CH_2COOC_4H_9(n) \\ | \\ HO-C-COOC_4H_9(n) \\ | \\ CH_2COOC_4H_9(n) \end{array}$$

(Solv-3)

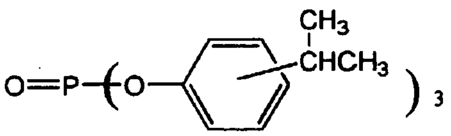


$$C_4H_9O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OC_4H_9$$

(Solv-4)

$O=P-(OC_6H_{13}(n))_3$

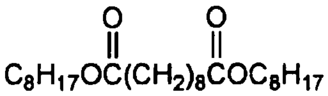
(Solv-5)



(Solv-6)

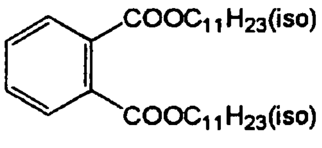
$C_8H_{17}CH=CHC_8H_{16}OH$

(Solv-7)

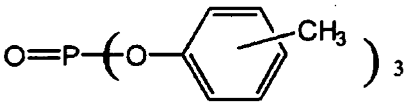


$$C_8H_{17}O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OC_8H_{17}$$

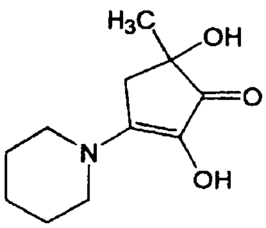
(Solv-8)



(Solv-9)



(S1-4)



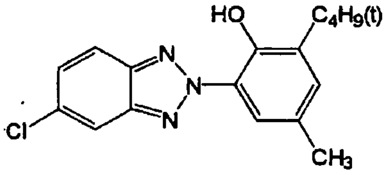
UV-A: 1/7/2 mixture (mass ratio) of

(UV-1)/(UV-4)/(UV-5)

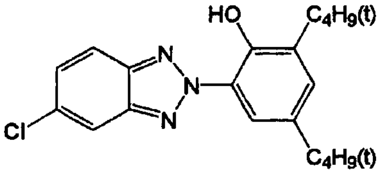
UV-B: 1/1/2/3/3 mixture (mass ratio) of

(UV-1)/(UV-2)/(UV-3)/(UV-4)/(UV-5)

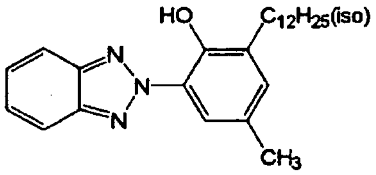
(UV−1)



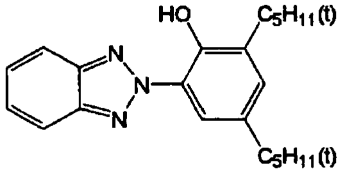
(UV−2)



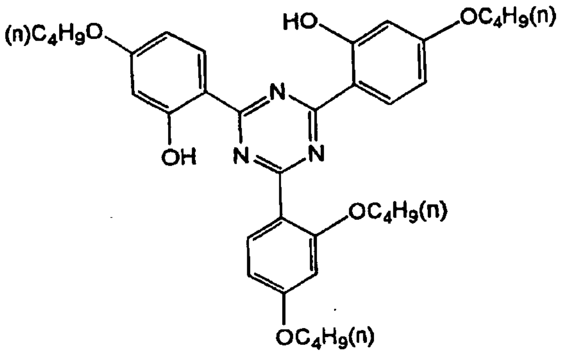
(UV−3)



(UV−4)



(UV−5)



[0239] The sample prepared as described above was used.

1-2. Development process

[0240] The sample described above was continuously processed, on a minilab printer-processor Frontier 330 manufactured by Fuji Photo Film Co., with following processing steps and following processing compositions, until the solution in the color development tank was replenished by a triple amount (3 rounds). The running test was conducted by printing standard negatives of the sample that provide an average visual density of 0.6 on the prints, and conducted with a process amount of one round per week.

<Development process conditions>

Process step	Temp.	Time	Replenish amt.
color development	38.5˚C	45 sec.	45 ml/m^2
bleach-fix	38.0˚C	25 sec.	A: 17.5 ml/m^2 B: 17.5 ml/m^2
rinse (1)	38.0˚C	20 sec.	-
rinse (2)	38.0˚C	20 sec.	-
rinse (3)	38.0˚C	20 sec.	-
rinse (4)	38.0˚C	20 sec.	175 ml/m^2
drying	80˚C	20 sec.	

* replenishing amount: amount per 1 m^2 of photosensitive material

** A rinse cleaning system RC-50D, manufactured by Fuji Photo Film Co. was mounted in Rinse 3. The rinse solution taken out from Rinse 3 was supplied by a pump to a reverse osmosis module (RC50D). A transmitted water therefrom was supplied to Rinse 4, and a concentrated solution was returned to Rinse 3. The pump pressure was so regulated that the amount of water to the reverse osmosis unit was maintained at from 50 to 300 mL/min, and the circulation was conducted under temperature control, for 10 hours per day. The rinse from 1 to 4 was conducted by a 4-tank countercurrent system.

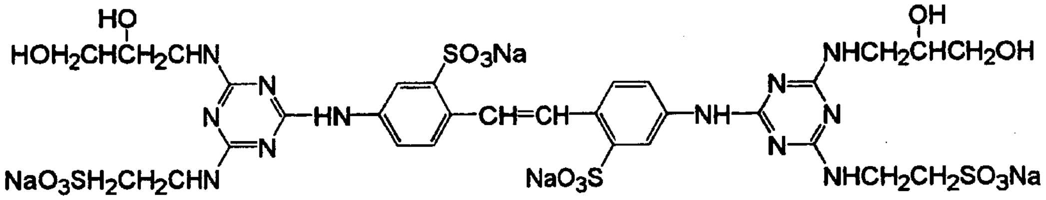
<Color developing solution>

[Color developer]	[tank soln.]	[replenisher]
water	800 mL	800 mL
silicone KF351A (manufactured by Shin-etsu Chemical Co.	0.05 g	0.05 g
potassium hydroxide	3.0 g	6.0 g
sodium hydroxide	3.0 g	6.0 g
fluorescent whitening agent (FL-1)	0.5 g	0.5 g
fluorescent whitening agent (FL-2)	0.8 g	0.8 g
fluorescent whitening agent (FL-3)	1.0 g	1.0 g
polyethylene glycol (average molecular weight: 300)	10.0 g	10.0 g
diethylene glycol	10.0 g	10.0 g
ethylenediaminetetraacetic acid	4.0 g	4.0 g
sodium sulfite	0.10 g	0.10 g
potassium chloride	10.0 g	-
sodium 4,5-dihydroxybenzene-1,3-disulfonate	0.50 g	0.50 g
disodium-N,N-bis(sulfonatethyl)hydroxylamine	4.0 g	8.0 g

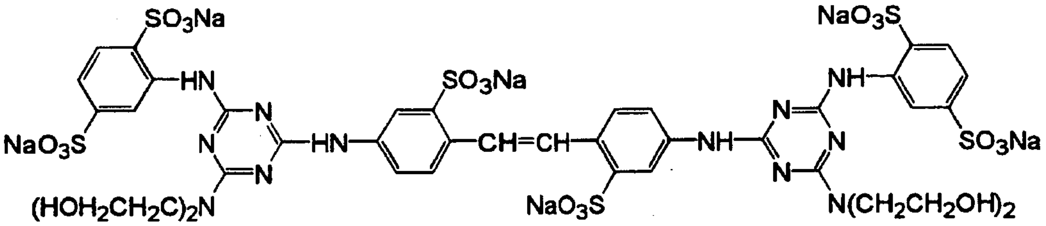
(continued)

[Color developer]	[tank soln.]	[replenisher]
m-carboxybenzenesulfinic acid	1.5 g	2.5 g
4-amino-3-methyl-N-ethyl-N-(β-methanesulfon-amidethyl)analine·3/2 sulfate salt·monohydrate	4.0 g	12.0 g
potassium carbonate	26.3 g	26.3 g
water to make	1000 mL	1000 mL
pH (25°C, regulated with sulfuric acid and KOH)	10.20	12.55

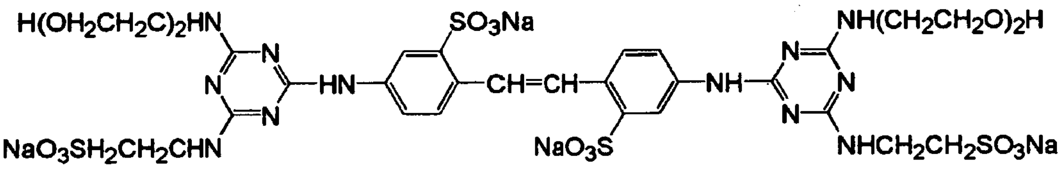
FL−1



FL−2



FL−3



[0241] The color developer replenisher was prepared in advance as a concentrate of 3.84 times, which was set on the Frontier 330 and automatically diluted with water to prepare the replenisher described above.

<Bleach-fix solution>

[0242] Each of the concentrated bleach-fix compositions above and a following concentration fixing composition were prepared in the following manner. The replenisher A and the replenisher B were respectively directly replenished to the bleach-fix tank solution for processing.

<Concentrated fixing composition>

water	70 mL
ammonium thiosulfate (750 g/L)	500.0 mL
ammonium bisulfite solution (65 %)	250.0 g
ethylenediaminetetraacetic acid	15.0 g
ammonia water (27 %)	45.0 g
water to make	1000 mL
pH (25˚C, adjusted with ammonia and nitric acid)	5.75

	<tank solution>	<replenisher A>	<replenisher B>
concentrated bleach composition	250 mL	670 mL	-
concentrated fixing composition	250 mL	-	670 mL
water to make	1000 mL	1000 mL	1000 mL

<Rinse> (Replenisher being same as the tank solution)

chlorinated sodium isocyanurate	0.02 g
deionized water (conductivity: 5 μs/cm or less)	1000 mL

[0243] In the Frontier 330 employed for evaluation, each of the concentred color developer composition, the concentrated bleach composition and the concentrated fixing composition, when set in an exclusive 1.3L container, is automatically introduced into a replenishing tank and diluted with water to the aforementioned composition for use in the processing.

<Stability of concentrated bleach composition>

[0244] 1300 mL of the prepared concentrated bleach composition were placed in a 1300-mL polyethylene container and were stored, in a stoppered state, for 3 months at 50˚C or - 5˚C. After 3 months, the composition was taken out and visually inspected for presence/absence of deposition in the sample and for state of turbidity. Results are shown in Table 4. One month at 50˚C corresponds to an accelerated condition for one year at the room temperature, and the test was conducted at the above-mentioned conditions in order to ensure a three-year long-term guarantee. States of deposition were evaluated in following criteria:

+: no abnormality such as deposition;
±: slight turbidity observed;
-: deposition present;
--: deposition present in a large amount.

<Sulfurization resistance>

[0245] After each of the concentrated bleach compositions above was subjected to a running test of 3 rounds according to the processing method described above, the tank solution of rinse (1) was extracted, placed in a 100-mL transparent polyvinyl chloride bottle and, with a holed stopper, let to stand under a condition of 40˚C, and a period until the liquid became turbid by sulfurization was evaluated as follows:

+: no sulfurization after 4 weeks;
±: sulfurization in 4 weeks;
-: sulfurization in 3 weeks;
-: sulfurization in 2 weeks.

<Desilvering property>

[0246] After each of the concentrated bleach compositions above was subjected to a running test of 3 rounds according to the processing method described above, a solid black sample was prepared with the photosensitive material above and a remaining silver amount was measured by fluorescent X-ray analysis. A high remaining silver amount means an undesirably insufficient desilvering.

<Silver recovery efficiency>

[0247] An overflow liquid from the bleach-fix tank solution was recovered after 2 rounds, then 1L of the liquid was placed in a beaker, 500 g of steel wool were immersed in the liquid and the liquid was recovered after 1 hour. A silver concentration in the liquid was measured by atomic absorption on the liquid after steel wool immersion and on the liquid without steel wool immersion, and a percentage of silver decrease was determined. A higher percentage means a higher silver recovery rate and is therefore preferable.

[0248] Obtained results are summarized in Table 4.

Table 4

No.	stability of concentrated composition		sulfurization resistance	desilvering property (μg/cm²)	silver recovery efficiency (%)	remarks
	50˚C	-5˚C				
1	-	+	-	1.0	75	comp. example
2	-	+	-	1.2	70	comp. example
3	--	+	-	1.2	70	comp. example
4	-	-	±	8.3	80	comp. example
5	--	-	±	6.5	80	comp. example
6	±	+	+	1.5	85	invention
7	+	+	+	1.2	87	invention
8	+	+	+	1.3	80	invention
9	+	+	+	1.2	82	invention
10	+	+	+	1.0	80	invention
11	+	+	+	1.5	80	invention
12	+	+	+	1.2	85	invention
13	+	+	+	1.6	85	invention
14	+	+	+	1.8	78	invention
15	+	-	+	18.4	70	comp. example
16	-	+	±	10.2	70	comp. example
17	+	-	-	25.0	35	comp. example

[0249] These results indicate that the present invention achieves an improvement in the concentrated bleach composition, also significant improvements in the sulfurization resistance and silver recovery efficiency in the running process utilizing the concentrated bleach composition, and a sufficient desilvering property, thus providing a satisfactory photographic quality.

[0250] The invention of JP-A-2004-53921 is insufficient, as the deposition is generated in a prolonged standing at a high temperature (Nos. 1 to 3). Also a succinic acid concentration, higher than that in the invention, results in a deposition of succinic acid in a low-temperature storage of the concentrate (No. 4). In a low-concentration range of EDTAFe(III), the concentrated composition is liable to be frozen, and, once frozen, it is estimated that succinic acid becomes very easily deposited.

[0251] Also in a running test conducted with a concentrated composition having an EDTAFe(III) concentration lower than that in the invention of JP-A-2004-53921 (less than 0.5 g/L), a deterioration in the desilvering property is observed

(Nos. 4, 5 and 16). However, such deterioration in the desilvering property can be solved by utilizing the free EDTA within the concentration ratio of the invention.

[0252] In the visual observation, edge stain and bleach fog were not observed in any of Examples of the invention.

[Example 1-2]

[0253] Concentrated solutions were prepared in the same manner as the concentrated bleach composition No. 9 in Example 1-1 except that succinic acid was respectively replaced by maleic acid, malonic acid and glutaric acid, and the stability of the concentrates was investigated in the same manner as in Example 1-1. As a result, the concentrated compositions were satisfactory in all the evaluation items of stability, sulfurization resistance, desilvering property and silver recovery efficiency, and, in the visual observation, edge stain and bleach fog were not observed in any of Examples of the invention. It was found that succinic acid was most preferable among these Examples.

[Example 1-3]

[0254] The concentrated bleach compositions Nos. 9 and 11 of Example 1-1 were used in the processing in the same manner as in Example 1-1, except that Frontier 340E, manufactured by Fuji Photo Film Co. was used and that the processing conditions were changed as follows.

<Development process conditions>

Process step	Temp.	Time	Replenish amt.
color development	45.0˚C	25 sec.	45 ml/m^2
bleach-fix	40.0˚C	25 sec.	A: 17.5 ml/m^2 B: 17.5 ml/m^2
rinse (1)	40.0˚C	7 sec.	-
rinse (2)	40.0˚C	4 sec.	-
rinse (3)	40.0˚C	4 sec.	-
rinse (4)	40.0˚C	7 sec.	175 ml/m^2
drying	80˚C	20 sec.	

[0255] As a result, it was found that, despite of a rapid processing with a bleach-fix time of 25 seconds, the desilvering property was not deteriorated and satisfactory photographic performance. Also by modifying the Frontier 340 in such a manner that the linear speed thereof can be varied, the bleach-fix time was changed for investigating the permissible time for the desilvering property, and was found to be reducible to 10 seconds. It was found that the present invention, operating in a low concentration range of EDTAFe(III), provided a low cost and was also capable of a rapid processing. Also in the visual observation, edge stain and bleach fog were not observed.

[Example 2-1]

(Preparation of concentrated composition for color developer replenisher)

[0256] Samples #1 - #6 of the concentrated composition for color developer replenisher were prepared with the compositions shown in Table 5. Amounts in the table are those for 1L of the composition. CBS, DSHA, PTS.Na, TIPA, DEG, and PEG300 respectively represent m-carboxybenzenesulfinic acid, disodium-N,N-bis(sulfonatethyl)hydroxylamine, sodium p-toluenesulfonate, triisopropanolamine, diethylene glycol, and polyethylene glycol having an average molecular weight of 300. The developing agent is 4-amino-3-methyl-N-ethyl-N-(β-methanesulfonamidethyl)aniline·3/2 sulfate salt-monohydrate.

Table 5

	#1	#2	#3	#4	#5	#6
KOH	21 g	21 g	25 g	25 g	25 g	25 g
NaOH	25 g	25 g	25 g	25 g	25 g	25 g
EDTA	20 g	20 g	20 g	20 g	20 g	20 g
Tiron	2g	2g	2g	2g	2g	2g

(continued)

	#1	#2	#3	#4	#5	#6
sodium sulfite	1g	1g	1g	1g	1g	1g
fluorescent whitening agentIV-13	10 mmol	10 mmol	10 mmol	10 mmol	10 mmol	10 mmol
fluorescent whitening agent III-5	5 mmol	5 mmol	5 mmol	5 mmol	5 mmol	5 mmol
CBS	0.08 mol	0.08 mol	0.08 mol	0.08 mol	0.08 mol	0.08 mol
DSHA	0.15 mol	0.15 mol	0.15 mol	0.15 mol	0.15 mol	0.15 mol
PTS.Na	0.28 mol	0.28 mol	0.28 mol	none	none	none
DEG	none	none	none	0.3 mol	none	0.3 mol
PEG300	none	none	none	none	0.15 mol	0.15 mol
developing agent	0.13 mol	0.13 mol	0.11 mol	0.11 mol	0.11 mol	0.11 mol
potassium carbonate	100 g	100 g	100 g	100 g	100 g	100 g
TIPA	30 g	none	none	none	none	none
water to make	1000 ml	1000 ml	1000 ml	1000 ml	1000 ml	1000 ml
pH when diluted 3.84 times with water	12.30	12.30	12.60	12.60	12.60	12.60
remarks	comp. example	comp. example	comp. example	invention	invention	invention

(Evaluation of concentrated composition)

[0257] The prepared samples #1 to #6 of the concentrated composition were subjected to evaluations for stability of concentrated composition, creep-up preventing ability of the developer replenisher, photographic properties and edge stain.

<Deposition in concentrated composition>

[0258] Each sample was prepared in an amount of 400 mL, of which 200 mL were placed in a 200-mL transparent polyvinyl chloride bottle and were stored, in a stoppered state, for 2 weeks at 0˚C or -5˚C. After 2 weeks, the sample was taken out and visually inspected for presence/absence of deposition in the sample and for state of turbidity. Results are shown in Table 6.

<Creep-up preventing property of developer replenisher>

[0259] 260 mL of each of the samples #1 to #6 of the concentrated composition were diluted with water to prepare 1L of developer replenisher (3.84 times dilution). 1L of each replenisher was placed in a container of hard polyvinyl chloride resin, having a square internal size of 10 x 10 cm and a height of 15 cm, and a floating lid of a foamed polyvinyl chloride resin, having a size of 9.7 mm x 9.7 mm and a thickness of 3 mm, thereby reducing the aperture area. This was to simulate the developer replenishing tank. After a storage in this state for 2 weeks at the room temperature (about 20 to 25˚C), presence/absence of deposition around the floating lid was inspected visually. Results are also shown in Table 6.

<Photographic performance>

2-1. Preparation of photosensitive material sample

[0260] As the photosensitive material to be employed in the continuous processing, a sample prepared in the same manner as in 1-1 was used.

2-2. Development process

[0261] The sample described above was continuously processed, on a minilab printer-processor Frontier 330 manufactured by Fuji Photo Film Co., with following processing steps and following processing compositions, until the solution in the color development tank was replenished by a triple amount (3 rounds). The running test was conducted by printing standard negatives of the sample that provide an average visual density of 0.6 on the prints, and conducted with a process amount of one round per week.

<Development process conditions>

Process step	Temp.	Time	Replenish amt.
color development	38.5°C	45 sec.	45 ml/m^2
bleach-fix	38.0°C	25 sec.	A: 17.5 ml/m^2 B: 17.5 ml/m^2
rinse (1)	38.0°C	20 sec.	-
rinse (2)	38.0°C	20 sec.	-
rinse (3)	38.0°C	20 sec.	-
rinse (4)	38.0°C	20 sec.	175 ml/m^2
drying	80°C	20 sec.	

* replenishing amount: amount per 1 m^2 of photosensitive material

** A rinse cleaning system RC-50D, manufactured by Fuji Photo Film Co. was mounted in Rinse 3. The rinse solution taken out from Rinse 3 was supplied by a pump to a reverse osmosis module (RC50D). A transmitted water therefrom was supplied to Rinse 4, and a concentrated solution was returned to Rinse 3. The pump pressure was so regulated that the amount of water to the reverse osmosis unit was maintained at from 50 to 300 mL/min, and the circulation was conducted under temperature control, for 10 hours per day. The rinse from 1 to 4 was conducted by a 4-tank countercurrent system.

<Color developing solution>

Replenisher:

[0262] Each of separately prepared samples #1 to #6 of the concentrated color developer composition was diluted 3.84 times with water to obtain a color developer replenisher.

Tank solution:

[0263] The developing tank solution was prepared by mixing 300 mL of the developer replenisher with 100 mL of CP-47L P1-S solution, manufactured by Fuji Photo Film Co., and 600 mL of water.

<Bleach-fix solution>

	tank solution	replenisher A	replenisher B
water	650 mL	300 mL	300 mL
ammoniu thiosulfate (750 g/L)	97.0 mL	-	376.0 mL
ammonium bisulfite solution (65 %)	50.0 g	-	185.5 g
ethylenediaminetetraacetic acid iron (III) ammonium	30.0 g	94.0 g	-
ethylenediaminetetraacetic acid	3.0 g	2.0 g	10.0 g
m-carboxybenzenesulfinic acid	5.0 g	15.0 g	-

(continued)

	tank solution	replenisher A	replenisher B
nitric acid	5.2 g	25.0 g	-
succinic acid	-	20.0 g	-
ammonia water (27 %)	8.0 g	15.0 g	36.0 g
water to make	1000 mL	1000 mL	1000 mL
pH (25˚C, regulated with ammonia and nitric acid)	5.9	2.5	5.75

<Rinse> (Replenisher being same as the tank solution)

chlorinated sodium isocyanurate	0.02 g
deionized water (conductivity: 5 μs/cm or less)	1000 mL

[0264] The replenishers A and B of bleach-fix were prepared by respectively diluting the parts A and B of the concentrated bleach-fix compositions by 1.5 times with water.

[0265] In the Frontier 330 employed for evaluation, each of the concentrated color developer composition, and parts A and B of the concentrated bleach-fix composition, when set in an exclusive 1.3L container, is automatically introduced into a replenishing tank and diluted with water to the aforementioned composition for use in the processing.

(Evaluation of photographic performance: GL sensitivity)

[0266] Each of the concentrated color developer compositions #1 to #6 above was subjected to a running test of 3 rounds according to the processing method described above. Subsequently a sample, subjected to a gray imagewise exposure, was processed, then a magenta density was determined at an exposure amount providing a magenta density of 0.6 in #1, and a density difference (ΔD(GL)) was calculated, as shown in Table 6. A negative difference means a sensitivity loss while a positive difference means a sensitivity increase. A larger value is preferable as it indicates absence of sensitivity loss.

(Evaluation of edge stain)

[0267] After the evaluation of photographic performance on the concentrated color developer compositions #1 to #6 above, 20 L-sized unexposed samples were processed, and an edge stain (stain on four edges of the substrate) was visually evaluated, and a level of stain is shown in Table 6.

Table 6

	#1	#2	#3	#4	#5	#6
deposition of concentrated liquid (0˚C/2 weeks)	slightly present	none	none	none	none	none
deposition of concentrated liquid (-5˚C/2 weeks)	evidently present	present	present	slightly present	none	none
crystal deposition by creep-up of replenisher	present	slightly present	none	slightly present	slightly present	none
photographic performance (ΔD(GL))	0.00 (reference)	-0.04	-0.06	0.00	0.01	0.01

(continued)

	#1	#2	#3	#4	#5	#6
edge stain	very bad	slightly present	slightly present	none	none	none
remarks	comp. example	comp. example	comp. example	invention	invention	invention

[0268] Based on these results, it is rendered possible, by the present invention, to provide a processing material capable of improving the deposition of in the concentrated liquid (particularly deposition of fluorescent whitening agent), not aggravating the crystal deposition by the creep-up of the replenisher, improving the photographic performance without a sensitivity loss even with a reduced concentration of the color developing agent, and completely free from the edge stain. It is also possible to provide an inexpensive processing material by reducing the concentration of the color developing agent and by not using PTS.Na and TIPA. Furthermore, most preferable effects can be accomplished by employing DEG and PEG300 in combination.

[Example 2-2]

[0269] Concentrated color developer compositions were prepared in the same manner as #6 in Example 2-1, except that PEG300 therein was replaced by PEG200, PEG600 or PEG1000, and the depositing property and the creep-up property were evaluated. Satisfactory results were obtained in all the cases, but PEG 300 was most preferably, then PEG200 and PEG600 provided next preferable results, while PEG1000 could not provide much effects.

[Example 2-3]

[0270] #6 of Example 2-1 was subjected to a pH regulation by a change in the amount of KOH and to changes in the amounts of the color developing agent and DSHA, and evaluations were made in the same manner as in Example 2-1. As a result, it was confirmed that the results were made even better with the aforementioned preferable amounts of addition of the invention. Also a concentrated liquid, prepared in the same manner as #6 of Example 2-1 except that DSHA therein was replaced by a same molar amount of diethylhydroxylamine, showed a deposition.

[Comparative Example]

[0271] On #6 of Example 2-1, it was found that an addition TIPA in an amount of 30 g/L significantly aggravated the deposition of the concentrated liquid and the edge stain, whereby the effects of the invention could not be obtained.

[Example 2-4]

[0272] #6 of Example 2-1 was processed in the same manner as in Example 2-1, except that Frontier 340E, manufactured by Fuji Photo Film Co. was used and that the processing conditions were changed as follows.

<Development process conditions>

Process step	Temp.	Time	Replenish amt.
color development	45.0˚C	25 sec.	45 ml/m^2
bleach-fix	40.0˚C	25 sec.	A: 17.5 ml/m^2 B: 17.5 ml/m^2
rinse (1)	40.0˚C	7 sec.	-
rinse (2)	40.0˚C	4 sec.	-
rinse (3)	40.0˚C	4 sec.	-
rinse (4)	40.0˚C	7 sec.	175 ml/m^2
drying	80˚C	20 sec.	

[0273] As a result, it was found that satisfactory photographic performance was obtained and the edge stain was not generated at all.

[0274] While the present invention has been described in detail with reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the present invention.

[0275] This application claims the benefit of Japanese Patent Application No. 2004-135681, filed April 30, 2004, and Japanese Patent Application No. 2004-135684, filed April 30, 2004, which are incorporated by reference herein in their entirety.

INDUSTRIAL APPLICABILITY

[0276] Field of photographic technology.

Claims

1. A concentrated bleach composition for a silver halide color photographic photosensitive material, which comprises a single liquid satisfying following compositional conditions (A) to (D):

    (A) an ethylenediaminetetraacetic acid-iron (III) complex salt as a bleaching agent is contained in an amount of from 0.10 to 0.42 mol/L;
    (B) an uncomplexed ethylenediaminetetraacetic acid is contained in an amount of from 0.5 to 30 mol% with respect to the bleaching agent;
    (C) a dibasic acid having a pKa of from 2.0 to 5.0 is contained in an amount of from 0.10 to 0.40 mol/L; and
    (D) a pH value is from 2.0 to 3.5.

2. The concentrated bleach composition according to claim 1,
wherein an azole compound is not contained.

3. The concentrated bleach composition according to claim 1 or 2,
wherein the concentrated bleach composition is used after dilution of from 1.2 to 5.0 times with water.

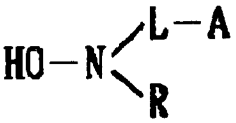
4. A processing method for a silver halide color photographic photosensitive material, which comprises:

    replenishing a bleach-fix tank with a water-diluted solution of a concentrated bleach composition according to any of claims 1 to 3 and a water-diluted solution of a concentrated fixing composition containing a thiosulfate salt in an amount of from 1.0 to 3.0 mol/L in a ratio of 1:1, in which a water-dilution ratio of each of the water-diluted solutions is from 1.2 to 5.0 times,
    wherein the silver halide photographic photosensitive material is immersed for a period of from 10 to 30 seconds in a solution in the bleach-fix tank.

5. A concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material, which satisfies following compositional conditions:

    (A) a p-phenylenediamine color developing agent is contained in an amount of from 0.08 to 0.12 mol/L;
    (B) a substituted hydroxyamine derivative represented by formula (I) is contained in an amount of from 0.06 to 0.16 mol/L:

Formula (I)



$$HO-N(L-A)(R)$$

wherein L represents an alkylene group that may be substituted;
A represents a carboxyl group, a sulfo group, a phosphono group, a hydroxyl group or an amino group that

may be substituted with an alkyl; and
R represents a hydrogen atom or an alkyl group that may be substituted;
(C) an ethylene glycol compound is contained in an amount of from 0.05 to 1.0 mol/L;
(D) a pH value is from 12.5 to 12.8 when the composition is diluted to 3.84 times with water; and
(E) an alkanolamine is not substantially contained.

6. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material according to claim 5,
wherein the ethylene glycol compound comprises at least a combination of diethylene glycol and polyethylene glycol having a molecular weight of from 200 to 600.

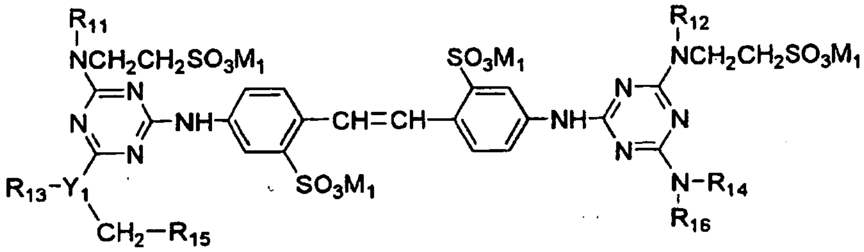
7. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material according to claim 5 or 6, which comprises a sulfinic acid compound represented by formula (II) in an amount of from 0.01 to 0.2 mol/L:

Formula (II) **RSO_2M**

wherein R represents an alkyl group, a cycloalkyl group, an alkenyl group, an alkinyl group, an aralkyl group or an aryl group; and
M represents a hydrogen atom or an alkali metal atom.

8. The concentrated one-part composition for a color developer replenisher for a color photographic photosensitive material according to any of claims 5 to 7, which comprises a diaminostilbene derivative represented by formula (III) and/or formula (IV) in an amount of from 1 to 50 mmol/L:

Formula (III)



wherein R_{11} and R_{12} each independently represents a hydrogen atom or an alkyl group;
R_{13} and R_{14} each independently represents a hydrogen atom, an alkyl group or an aryl group;
R_{15} represents an alkyl group containing at least one asymmetric carbon or a group represented by formula (I-a);
R_{16} represents an alkyl group containing at least one asymmetric carbon or a group represented by formula (I-b); and
M_1 represents a hydrogen atom or an alkali metal atom; provided that R_{13} and R_{15}, or R_{14} and R_{16} may be bonded each other to form a ring:

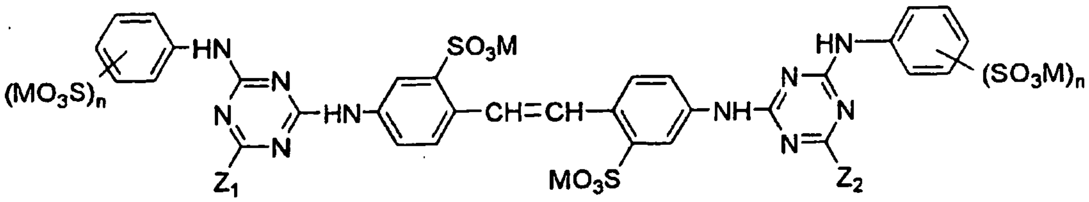
Formula (I-a) **-CH2O (CH2CH2O)n11H**

wherein n_{11} represents an integer of from 1 to 3;

Formula (I-b) **-(CH2CH2O) n12H**

wherein n_{12} represents an integer of from 2 to 4;

Formula (IV)



wherein Z_1 and Z_2 may be mutually same or different, and each represents an amino group containing from 2 to 3 carbon atoms which is substituted with a hydroxyl group or a sulfonic acid group; and M represents a hydrogen atom or an alkali metal atom.

9. A processing method for a color photographic photosensitive material, which comprises:

utilizing a concentrated one-part composition for a color developer replenisher according to any of claims 5 to 8 with a dilution of from 3 to 6 times with water as a replenisher.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/008045

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 G03C7/42, 7/407, 7/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 G03C7/42, 7/407, 7/44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004-53921 A (Fuji Photo Film Co., Ltd.), 19 February, 2004 (19.02.04), Claims 1 to 3; Par. Nos. [0004] to [0005], [0012] to [0031]; examples 1 to 4 & US 2004/0023167 A1 & EP 1383002 A1	1-4
X	JP 2003-140311 A (Eastman Kodak Japan Ltd.), 14 May, 2003 (14.05.03), Claims 1 to 2; Par. Nos. [0010], [0012], [0019], [0022], [0024], [0027], [0032]; examples & US 2003/0190560 A1 & EP 1308778 A1	1-2

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 25 July, 2005 (25.07.05)	Date of mailing of the international search report 09 August, 2005 (09.08.05)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/008045

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 3-188443 A (Konica Corp.), 16 August, 1991 (16.08.91), Claims 1, 4, 5; official gazette; page 3, upper right column, line 6 to lower left column, line 15; page 4, upper left column, line 15 to lower right column, line 7; page 8, upper left column, lines 4 to 6; page 9, lower left column, lines 1 to 3; page 20, lower left column, lines 5 to 13; examples 3; page 21, lower left column, lines 10 to 15; table 3 (Family: none)	1-2
Y	JP 7-159957 A (Fuji Photo Film Co., Ltd.), 23 June, 1995 (23.06.95), Example 1; Par. No. [0155] (Family: none)	1-4
Y	JP 6-3788 A (Konica Corp.), 14 January, 1994 (14.01.94), Claim 1; Par. Nos. [0016] to [0017], [0021] to [0028], [0162] to [0186] (Family: none)	1-4
X Y	JP 2004-70199 A (Konica Minolta Holdings Kabushiki Kaisha), 04 March, 2004 (04.03.04), Claim 1; Par. Nos. [0036] to [0040], [0073], [0075], [0081]; examples 1 to 5 & US 2004/0067458 A1 & EP 1388756 A1	5,8,9 6,7
Y	JP 2003-66570 A (Fuji Photo Film Co., Ltd.), 05 March, 2003 (05.03.03), Claims 1, 2; Par. Nos. [0019], [0067] to [0070], [0077], [0080], [0090] to [0091], [0207] to [0222] & US 2003/0148230 A1	6
Y	JP 2001-100382 A (Agfa-Gevaert N.V.), 13 April, 2001 (13.04.01), Claims 1, 3, 4, 8; Par. Nos. [0011] to [0019] & US 6413703 B1 & EP 1085375 A1 & DE 10005498 A1	6
Y	JP 2002-258451 A (Fuji Photo Film Co., Ltd.), 11 September, 2002 (11.09.02), Claims 1 to 3; Par. Nos. [0005], [0023]; examples 1, 2; Par. No. [0172] & US 2002/0164550 A1	7
P,X	JP 2005-99767 A (Konica Minolta Holdings Kabushiki Kaisha), 14 April, 2005 (14.04.05), Full text (Family: none)	5,9

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/008045

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-4 relate to a bleach concentrate composition and a process of processing with the composition, while claims 5-9 relate to a one-part type concentrate composition for replenishment color developers and a process of processing with the composition.

A group of inventions of claims 1-4 and a group of inventions of claims 5-9 have in common only a concentrate composition for the processing of silver halide color photographic materials. However, use of a concentrate composition in processing silver halide color photographic materials is well known.

(continued to extra sheet)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/008045

Continuation of Box No.III of continuation of first sheet(2)

Thus, there is no feature common to all of claims 1-9,and claims 1-9 do not satisfy the requirement of unity of invention.

Form PCT/ISA/210 (extra sheet) (January 2004)

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