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(71) Applicant : **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo (JP)

(72) Inventor : **Yoshimoto, Hiroshi, c/o Konica Corporation**
1, Sakura-machi
Hino-shi, Tokyo (JP)

(74) Representative : **Brock, Peter William et al**
URQUHART-DYKES & LORD 91 Wimpole Street
London W1M 8AH (GB)

(54) Solid processing agent for silver halide photographic light-sensitive material.

(57) A solid processing agent for silver halide photographic light-sensitive material capable of fixation containing at least one kind of thiosulfate, wherein a content of ammonium cations to a total cation content is not more than 50 mol% is disclosed. The material capable of fixation has improved storage stability, improved solubility and increased wear resistance and which is free of color image density reduction after development.

Jouve, 18, rue Saint-Denis, 75001 PARIS

FIELD OF THE INVENTION

The present invention relates to a solid processing agent for silver halide photographic light-sensitive material (hereinafter also referred to as photographic processing agent), more specifically a solid processing agent for silver halide photographic light-sensitive material capable of fixation which is suitable to the working and social environments in that dust scattering is prevented and no plastic bottles are used.

BACKGROUND OF THE INVENTION

The black-and-white developer, fixer, color developer, bleacher, bleach-fixer, stabilizer and other processing solutions used to process silver halide photographic light-sensitive material are supplied to the user in the form of one or more dense part solutions contained in plastic bottles for easy handling. The user dissolves these processing agent kits in water to prepare starting solutions or replenishers before use.

In recent years, small photographic processing laboratories using small-sized automatic processing machines, known as mini-labs, have increased rapidly in the field of photographic processing. Accordingly, there has been rapid increase in the consumption of plastic bottles for processing agents.

In addition to bottles for photographic processing agents, plastics have been widely used for a variety of purposes to make use of their lightness and toughness. The world's annual production of plastics has increased steadily, reaching 100000000 tons in 1988. Meantime, a vast amount of plastics is wasted; for example, about 40% of annual production has been wasted in Japan. Waste plastics deteriorate habitats of marine life when disposed to sea. In Europe, acid rain and other problems arise as a result of incineration of waste plastics in incinerators equipped with poor discharge gas treatment apparatus, provoking major concern.

For this reason, urgent measures have been demanded; in Europe and the Unites States, there has been a trend toward implementing legal regulations, including recycled use of plastics, prohibition of the use of plastics, and obligation of the use of decomposable plastics.

In this situation, it is very undesirable to use large number of plastic bottles for photographic processing agents, though such use is not universal.

Although it may be possible to powder dense solutions of photographic processing agent, this approach has storage-related drawbacks, including solubility deterioration due to caking, and fatigue and coloring due to the presence of moisture and oxygen. Also, there is a high possibility that workers inhale dust scattered at the time of dissolution, which poses a health-related problem, or airborne components can cause troublesome contamination of other photographic processing solutions. Thus, granulation of photographic processing agent to a granular mixture has been proposed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 109042/1990, 109043/1990 and 39735/1991, US Patent No. 2,843,484 and other publications. However, some problems remain unsolved, including the problem in industrial safety and health caused by scattered dust, and hampering of preparation work due to impurity contamination of other kinds of processing solution, caking, in which the photographic processing agent sediments and coagulates on the bottom of container at the time of dissolution, powder coating by the wet film to cause dissolution failure; there is high limitation on the availability of agents suitable for powdering and granulation.

As a preferred form of processing agent making use of such advantages of dryness, tableting is proposed in Japanese Patent O.P.I. Publication No. 61837/1976, Canadian Patent No. 831,928 and other publications.

Meantime, thiosulfate-containing granular fixing agents have been proposed in Japanese Patent O.P.I. Publication Nos. 39735/1991 and 39739/1991.

Although such granular fixing agents produce less dust and have improved water solubility, in comparison with conventional powdery fixing agents, a fixer prepared with a stored fixing agent tends to undergo sulfation in a short time, and when used to develop a color light-sensitive material, it tends to cause photographic performance failures such as color image density reduction due to color reproduction failure and increase in the amount of residual silver in the unexposed portion.

These two are critical to photographic performance, posing the most serious problem if they occur. Thus there has been urgent demand for solutions to these problems.

Through extensive investigations, the present inventors found that these problems are associated with the ratio of ammonium ions to the total cation content in said photographic processing agent. The inventors made further investigations based on this finding, and developed the present invention.

Another finding was that the wear resistance of tablets improved so that dust scattering was prevented and the suitability to the working environment improved. This effect was not expected from previous findings.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a solid processing agent for silver halide photographic light-sensitive material capable of fixation and offering the following features:

1) Saves packing materials (particularly plastic bottles), thus being suitable to the social environment.
2) Solidification offers weight reduction, transportation cost reduction and saves stocking space in laboratories etc.
3) Offers improved storage stability, being free of sulfation-related deterioration and color image density reduction upon development.
4) Freedom of dust scattering makes it suitable to the working environment.
5) Ensures freedom from contamination-related staining.
6) Offers improved solubility for tablet photographic processing agents and mitigates tablet wear.

The object of the present invention has been accomplished by a solid processing agent for silver halide photographic light-sensitive material capable of fixation containing at least one kind of thiosulfate wherein the ratio of ammonium cations to the total cation content is not more than 50 mol%.

It is a preferred mode of embodiment of the present invention that the ratio of ammonium cations to the total cation content in the solid processing agent for silver halide photographic light-sensitive material be not more than 20 mol%, since the effect of the invention is enhanced.

The present invention is hereinafter described in detail.

DETAILED DESCRIPTION OF THE INVENTION

The solid photographic processing agent of the present invention is in a tablet, granule, powder, lump or paste form, with preference given to the tablet form. Tablet processing agents can be produced by ordinary methods such as those described in Japanese Patent O.P.I. Publication Nos. 61837/1976, 155038/1979 and 88025/1977 and British Patent No. 1,213,808. Granular processing agents can be produced by ordinary methods such as those described in Japanese Patent Application Nos. 109042/1990, 109043/1990, 39735/1991 and 39739/1991. Powdery processing agents can be produced by ordinary methods such as those described in Japanese Patent O.P.I. Publication No. 133332/1979, British Patent Nos. 725,892 and 729,862 and German Patent No. 3,733,861.

From the viewpoint of solubility and the desired effect of the present invention, the apparent density of the solid processing agent of the present invention is preferably 0.4 to 0.9 g/cm^3, in a form of granule, and 1.0 to 5.0 g/cm^3 in a tablet form.

When a value of the apparent density excess the upper limit, the solubility tends to lower. And when the value is under the lower limit, a solid strength becomes lower and creates a fine powder which tends to form caking.

The fixing agents used in the solid photographic processing agent capable of fixation of the present invention are thiosulfate and thiocyanate. The amount of thiocyanate added is preferably not less than 0.1 mol/l, more preferably not less than 0.5 mol/l, and still more preferably not less than 1.0 mol/l for processing a color negative film. The amount of thiosulfate added is preferably not less than 0.2 mol/l, more preferably not less than 0.5 mol/l for processing a color negative film. Also, the object of the present invention can be more efficiently accomplished by using a thiocyanate and a thiosulfate in combination.

In addition to these fixing agents, the solid processing agent capable of fixation of the present invention may contain one or more pH regulators comprising various salts. It is also desirable to add a large amount of a re-halogenating agent such as an alkali halide or an ammonium halide, e.g., potassium bromide, sodium bromide, sodium chloride or ammonium bromide. Compounds which are known to be added to fixer or bleach-fixer, such as alkylamines and polyethylene oxides, may be added as appropriate.

In the present invention, a combination of potassium and ammonium salts is preferably selected, and the ratio of ammonium cations to the total cation content in the thiosulfate-containing fixing agent was varied.

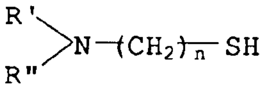
The ratio of ammonium cations to the total cation content in said fixing agent is normally 50 to 0 mol%, preferably 20 to 0 mol%, and more preferably 10 to 0 mol%. Ratios exceeding 50 mol% tend to cause solubility deterioration due to caking, fixer sulfation, color image density reduction upon developing the color light-sensitive material and increase in the amount of residual silver in the unexposed portion.

Ratios exceeding 50 mol% also considerably deteriorate the strength of tablet photographic processing agent. Combined use of thiocyanate enhances the effect of the present invention.

The ratio of ammonium cations to total cation content is not more than 50 mol%, is defined as a solid processing agent for silver halide photographic light-sensitive material of the present invention, is dissolved in a water in a concentration of prefixed rate.

It is preferable to add a compound represented by the following formula FA, specifically one of Example Compounds FA-1 through FA-39, described on page 11 of Japanese Patent Application No. 206120/1990, or a compound in the following group of compounds FB, to the solid photographic processing agent capable of fixation of the present invention, whereby not only the effect of the invention is enhanced but also an additional effect is obtained in that sludge formation in the processing solution capable of fixation is significantly suppressed during prolonged processing of a small amount of light-sensitive material.

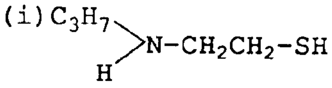
Formula FA



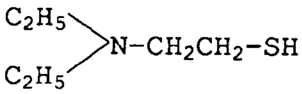
wherein R' and R" independently represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a nitrogen-containing heterocyclic group; n' represents 2 or 3.

Of the Example Compounds FA-1 through FA-39, the following are preferred.

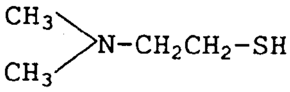
FA-1



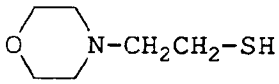
FA-12



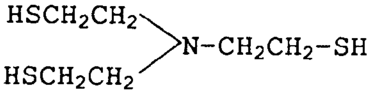
FA-21



FA-32



FA-38



These compounds represented by formula FA can be synthesized by ordinary methods such as those described in US Patent Nos. 3,335,161 and 3,260,718.

The compounds in the compound group FB are as follows:

FB-1: Thiourea

FB-2: Thiocyanocatechol

These compounds represented by formula FA and the compounds in the compound group FB may be used singly or in combination. Preferred combinations include FB-1 and FA-21, FB-1 and FA-12, FA-12 and FA-38, FA-12 and FA-32, and FA-12 and FA-21. Greatest preference is given to FB-1.

Good results are obtained when these compounds represented by formula FA and the compounds in the compound group FB are used in amounts of 0.1 to 300 g, preferably 0.2 to 200 g, and more preferably 0.5 to 150 g per liter of processing solution.

In the present invention, a p-phenylenediamine compound having a water-soluble group is preferably used as a color developing agent in the color developer for the present invention, since it enhances the desired effect of the invention and causes little fogging.

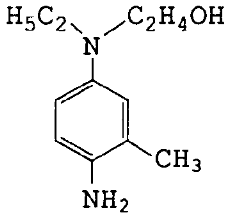
The p-phenylenediamine compounds having a water-soluble group are advantageous over the p-phenylenediamine compounds having no water-soluble group, such as N,N-diethyl-p-phenylenediamine, that they do not contaminate the light-sensitive material and are not irritative to skin upon skin contact.

The p-phenylenediamine compound for the present invention has at least one water-soluble group as described above on the amino group or benzene nucleus thereof. Preferred water-soluble groups include $-(CH_2)_nCH_2OH$, $-(CH_2)_mNHSO_2(CH_2)_nCH_3$, $-(CH_2)_mO(CH_2)_nCH_3$, $-(CH_2CH_2O)_nC_mH_{2m+1}$ (m and n independently represent an integer of not less than 0), a -COOH group and a $-SO_3H$ group.

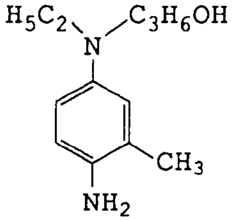
Examples of color developing agents preferably used for the present invention are C-1 through C-16 described on pages 26 through 31 of Japanese Patent Application No. 203169/1990, and 4-amino-3-methyl-N-(3-hydroxypropyl)aniline.

The following compounds Dev-1 through Dev-3 are more preferably used color developing agents.

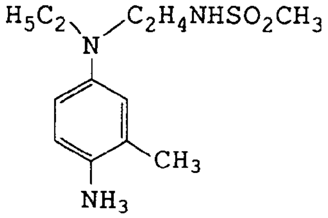
Dev-1



Dev-2



Dev-3

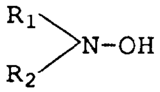


The color developing agents described above are used normally in the form of a salt such as hydrochloride, sulfate or p-toluenesulfonate.

The above-mentioned color developing agents may be used singly or in combination, and may be used in combination with black-and-white developing agents such as phenidone, 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrrazolidone and Metol as desired.

It is a preferred mode of embodiment of the present invention to add compounds represented by the following formula A and B to the color developer relating to the present invention, whereby not only the desired effect of the invention is enhanced but also an additional effect is obtained in which fogging in the unexposed portion is suppressed.

Formula A

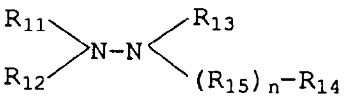


$$R_1R_2N\text{-}OH$$

wherein R_1 and R_2 independently represent an alkyl group, an aryl group, an R_3CO- group or a hydrogen atom, provided that R_1 and R_2 do not represent a hydrogen atom concurrently. R_1 and R_2 may bind together to form a ring.

With respect to formula A, the alkyl groups represented by R_1 and R_2 may be identical or different, each of which preferably has 1 to 3 carbon atoms. These alkyl groups may have a carboxyl group, a phosphate group, a sulfonate group or a hydroxyl group. R_3 represents an alkoxy group, an alkyl group or an aryl group. The alkyl groups and aryl groups for R_1, R_2 and R_3 include those having a substituent. R_1 and R_2 may bind together to form a ring, such as a heterocyclic ring like piperidine, pyridine, triazine or morpholine.

Formula B



$$R_{11}R_{12}N\text{-}N(R_{13})\text{-}(R_{15})_n\text{-}R_{14}$$

wherein R_{11}, R_{12} and R_{13} independently represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{14} represents a hydroxyl group, a hydroxyamino group, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a carbamoyl group or an amino group. The heterocyclic group is a 5- or 6-membered ring comprising C, H, O, N, S and halogen atoms, whether saturated or unsaturated. R_{15} represents a divalent group selected from the group comprising -CO-, $-SO_2-$ and -C(=NH)-; n represents 0 or 1. Provided that n is 0, R_{14} represents a group selected from an alkyl group, an aryl group and a heterocyclic group; R_{13} and R_{14} may cooperate to form a heterocyclic group. The alkyl groups, aryl groups and heterocyclic groups represented by R_{11}, R_{12}, R_{13} and R_{14} include those having a substituent.

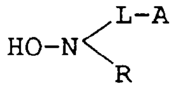
Examples of the hydroxylamine compound represented by formula A are given in US Patent Nos. 3,287,125, 3,329,034 and 3,287,124 and other publications. Particularly preferable compounds are compound Nos. A-1 through A-39 described on pages 36 through 38 of Japanese Patent Application No. 203169/1990, compound Nos. 1 through 53 described on pages 3 through 6 of Japanese Patent O.P.I. Publication No. 33845/1991 and compound Nos. 1 through 52 described on pages 5 through 7 of Japanese Patent O.P.I. Publication No. 63646/1991.

Examples of the compound represented by formula B are compound Nos. B-1 through B-33 described on pages 40 through 43 of Japanese Patent Application No. 203169/1990 and compound Nos. 1 through 56 described on pages 4 through 6 of Japanese Patent O.P.I. Publication No. 33846/1991.

These compounds represented by formula A or B are used normally in the forms of free amine, hydrochloride, sulfate, p-toluenesulfonate, oxalate, phosphate, acetate and others.

The hydroxylamine compound represented by the following formula A' is also preferably used as a preservative for color developers.

Formula A'



$$HO\text{-}N(L\text{-}A)(R)$$

wherein L represents an alkylene group which may have a substituent; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphino group, a hydroxyl group, an amino group, ammonium group, carbamoyl group or sulfamoyl group which may have a substituent alkyl group; R represents a hydrogen atom or an alkyl group which may have a substituent.

The compound represented by formula A' is exemplified by compound Nos. 1 through 54 described in the lower left column on page 4 through the lower right column on page 6 of Japanese Patent O.P.I. Publication No. 184044/1991, with preference given to the following compounds 1 and 7:

1: $HON(CH_2COOH)_2$
7: $HON(CH_2CH_2SO_3H)_2$

The compound represented by formula A' is prepared by alkylating a commercially available hydroxylamine. It can be synthesized in accordance with the methods described in West German Patent No. 1,159,634 and on pages 101 through 108 of Inorganica Chimica Acta, 93 (1984).

The color developer used for the present invention may incorporate a trace amount of sulfite as a preservative. Examples of such sulfites include sodium sulfite, potassium sulfite, sodium bisulfite and potassium bisulfite.

The color developer used for the present invention must contain a buffer. Examples of buffers include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (boric acid), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate) and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate).

Examples of developing accelerators which can be added as necessary include thioether compounds such as those disclosed in Japanese Patent Examined Publication Nos. 16088/1962, 5987/1962, 7826/1963, 12380/1969 and 9019/1970 and US Patent No. 3,813,247, p-phenylenediamine compounds such as those disclosed in Japanese Patent O.P.I. Publication Nos. 49829/1977 and 15554/1975, quaternary ammonium salts such as those disclosed in Japanese Patent Examined Publication No. 30074/1969 and Japanese Patent O.P.I. Publication Nos. 137726/1975, 156826/1981 and 43429/1977, the p-aminophenols disclosed in US Patent Nos. 2,610,122 and 4,119,462, the amine compounds disclosed in US Patent Nos. 2,494,903, 3,128,182, 4,230,796, 3,253,919, 2,482,546, 2,596,926 and 3,582,346 and Japanese Patent Examined Publication No. 11431/1966, polyalkylene oxides such as those disclosed in Japanese Patent Examined Publication Nos. 16088/1962, 25201/1967, 11431/1966 and 23883/1967 and US Patent Nos. 3,128,183 and 3,532,501, and 1-phenyl-3-pyrrazolidones, hydrozines, meso-ionic compounds, ionic compounds and imidazoles.

For the prevention of fogging and other purposes, chlorine ions and bromine ions may be present in the color developer. In the present invention, it is preferable that chlorine ions be contained at 1.0×10^{-2} to 1.5×10^{-1} mol, more preferably 3.5×10^{-2} to 1.0×10^{-1} mol per liter of color developer. Chlorine ion concentrations exceeding 1.5×10^{-1} mol/l are undesirable for rapidly reaching the maximum density because development is retarded. Chlorine ion concentrations of less than 3.5×10^{-2} mol/l are also undesirable because staining occurs and fluctuations in photographic properties (especially minimum density) in continuous processing widen.

In the present invention, the color developer preferably contains bromine ions at a concentration of 3.0×10^{-5} to 1.0×10^{-3} mol/l, more preferably 5.0×10^{-5} to 5×10^{-4} mol/l, and still more preferably 1×10^{-4} to 3×10^{-4} mol/l. Bromine ion concentrations exceeding 1×10^{-3} mol/l and those lower than 3.0×10^{-5} mol/l are undesirable because development is retarded and the maximum density and sensitivity lower in the former case and because staining occurs and fluctuations in photographic properties (especially minimum density) occur in continuous processing in the latter case.

Provided that chlorine ions are added directly to the color developer, examples of chlorine ion sources include sodium chloride, potassium chloride, ammonium chloride, nickel chloride, magnesium chloride, manganese chloride, calcium chloride and cadmium chloride, with preference given to sodium chloride and potassium chloride.

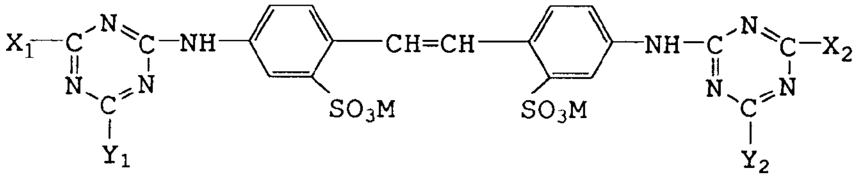
Chlorine ions may also be supplied in the form of a counterpart salt of the brightening agent added to color developer.

Examples of bromine ion sources include sodium bromide, potassium bromide, ammonium bromide, lithium bromide, calcium bromide, magnesium bromide, manganese bromide, nickel bromide, cadmium bromide, cerium bromide and thallium bromide, with preference given to potassium bromide and sodium bromide.

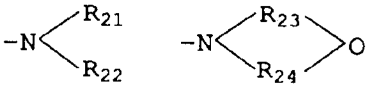
In addition to chlorine ions and bromine ions, the color developer used for the present invention may incorporate antifogging agents which are optionally selected as necessary. Antifogging agents which can be used include alkali metal halides such as potassium iodide and organic antifogging agents. Typical examples of organic antifogging agents include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolizine and adenine.

From the viewpoint of background brightening, it is preferable to add a triazinylstylbene brightening agent to the color developer used for the present invention. Said brightening agent is preferably represented by the following formula E.

Formula E



wherein X_1, X_2, Y_1 and Y_2 independently represent a hydroxyl group, a chlorine atom, a bromine atom or another halogen atom, an alkyl group, an aryl group,



or $-OR_{25}$, wherein R_{21} and R_{22} independently represent a hydrogen atom, an alkyl group which may be substituted or an aryl group which may be substituted; R_{23} and R_{24} each represent an alkylene group which may be substituted; R_{25} represents a hydrogen atom, an alkyl group which may be substituted or an aryl group which may be substituted; M represents a cation.

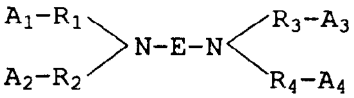
Details of the groups in formula E and substituents therefor are the same as those described from the 8th line from bottom of page 62 through the 3rd line from the bottom of page 64 of Japanese Patent Application No. 240400/1990. Example compounds E-1 through E-45 are specified on pages 65 through 67 of the same application, with preference given to E-4, E-24, E-34, E-35, E-36, E-37 and E-41. The amount of these compounds added is preferably in the range of 0.2 to 10 g, more preferably 0.4 to 5 g per liter of color developer.

An auxiliary developing agent may be used in combination with the principal developing agent. Examples of such auxiliary developing agents include N-methyl-p-aminophenol hexasulfate (Metol), phenidone, N,N-diethyl-p-aminophenol hydrochloride and N,N,N',N'-tetramethyl-p-phenylenediamine hydrochloride. The amount of their addition is preferably 0.01 to 1.0 g/l.

It is also possible to use various additives such as an antistaining agent, an anti-sludge agent and a lamination effect enhancer.

It is preferable to add a chelating agent represented by the following formula K and Example compound Nos. K-1 through K-22, described from the 9th line on page 69 through page 75 of Japanese Patent Application No. 240400/1990.

Formula K



wherein E represents an alkylene group, a cycloalkylene group, a phenylene group (these three groups may have a substituent), $-R_5OR_5-$, $-R_5OR_5OR_5-$ or $-R_5ZR_5-$; R_1 through R_5 independently represent an alkylene group which may have a substituent; Z represents $=N-R_5-A_5$ or $=N-A_5$; A_1 through A_5 independently represent a hydrogen atom, a hydroxyl group, a $-CO_2M$ group or a $-PO_3(M)_2$ group; M represents a hydrogen atom or an atom of alkali metal.

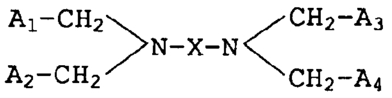
Of these chelating agents, K-2, K-9, K-12, K-13, K-17 and K-19 are preferably used, with greater preference given to K-2 and K-9, which enhances the effect of the present invention when added to the color developer.

The amount of these chelating agents added is preferably in the range of 0.1 to 20 g, more preferably from 0.2 to 8 g per liter of color developer.

The color developer may contain a surfactant, whether anionic, cationic, amphoteric or nonionic. Various surfactants such as alkylsulfonic acid, arylsulfonic acid, aliphatic carboxylic acid and aromatic carboxylic acid may be added as necessary.

The bleaching agent for the bleacher used for the present invention is a ferric complex salt of organic acid represented by the following formula L.

Formula L



$$\begin{matrix} A_1-CH_2 \\ A_2-CH_2 \end{matrix} \!\!> N-X-N < \!\! \begin{matrix} CH_2-A_3 \\ CH_2-A_4 \end{matrix}$$

wherein A_1 through A_4, whether identical or not, independently represent $-CH_2OH$, -COOH or $-PO3M_1M_2$ (M, M_1 and M_2 independently represent a hydrogen atom, an atom of alkali metal or ammonium); X represents an alkylene group having 3 to 6 carbon atoms, which alkylene group may have a substituent.

The groups represented by A_1 through A_4 are not described in detail herein, since they are identical to those represented by A_1 through A_4 described on the 15th line on page 12 through the 3rd line on page 15, of Japanese Patent Application No. 260628/1989.

Examples of preferred compounds represented by Formula L are given below.

L-1 : 1,3-propanediaminetetraacetic acid
L-2 : 2-hydroxy-1,3-propanediaminetetraacetic acid
L-3 : 2,3-propanediaminetetraacetic acid
L-4 : 1,4-butanediaminetetraacetic acid
L-5 : 2-methyl-1,3-propanediaminetetraacetic acid
L-6 : N-(2-hydroxyethyl)-1,3-propanediaminetriacetic acid
L-7 : 1,3-propanediaminetetrakismethylenephosphonic acid
L-8 : 2-hydroxy-1, 3-propanediaminetetrakismethylenephosphonic acid
L-9 : 2,2-dimethyl-1,3-propanediaminetetraacetic acid
L-10: 2,4-butanediaminetetraacetic acid
L-11: 2,4-pentanediaminetetraacetic acid
L-12: 2-methyl-2,4-pentanediaminetetraacetic acid

Sodium salts, potassium salts and ammonium salts of these ferric complex salts of these compounds L-1 through L-12 can be used optionally, with preference given to ammonium salts of these ferric complex salts from the viewpoint of the desired effect of the present invention and solubility.

Of these compounds, L-1, L-3, L-4, L-5 and L-9 are particularly preferable for the invention, with greater preference given to L-1.

In the present invention, the bleacher may contain a ferric complex salt of one of the following compounds in addition to an iron complex salts of the compound represented by formula L above as a bleaching agent.

L'-1 : Ethylenediaminetetraacetic acid
L'-2 : Trans-1,2-cyclohexanediaminetetraacetic acid
L'-3 : Dihydroxyethylglycinic acid
L'-4 : Ethylenediaminetetrakismethylenephosphonic acid
L'-5 : Nitrilotrimethylenephosphonic acid
L'-6 : Diethylenetriaminepentakismethylenephosphonic acid
L'-7 : Diethylenetriaminepentaacetic acid
L'-8 : Ethylenediaminediorthohydroxyphenylacetic acid
L'-9 : Hydroxyethylethylenediaminetriacetic acid
L'-10: Ethylenediaminedipropionic acid
L'-11: Ethylenediaminediacetic acid
L'-12: Hydroxyethyliminodiacetic acid
L'-13: Nitrilotriacetic acid
L'-14: Nitrilotripropionic acid
L'-15: Triethylenetetraminehexaacetic acid
L'-16: Ethylenediaminetetrapropionic acid

The amount of ferric complex salt of organic acid added is preferably in the range of 0.1 to 2.0 mol, more preferably 0.15 to 1.5 mol per liter of bleacher.

Bleaching is accelerated by adding the imidazole derivative described in Japanese Patent O.P.I. Publication No. 295258/1989 or at least one kind of compound represented by formulas I through IX described in the same publication.

In addition to these accelerators, the example compounds described on pages 51 through 115 of Japanese Patent O.P.I. Publication No. 123459/1987, the example compounds described on pages 22 through 25 of Japanese Patent O.P.I. Publication No. 17445/1988 and the compounds described in Japanese Patent O.P.I. Publication Nos. 95630/1978 and 28426/1978 can also be used for the same purpose.

In addition to the above additives, the bleacher may contain halides such as ammonium bromide, potassium bromide and sodium bromide, various brightening agents, antifoaming agents and surfactants.

In the present invention, it is preferable to add a chelating agent having a ferric ion chelate stability constant of over 8 to the stabilizer. Here, the chelate stability constant is the constant which is well known in "Stability Constants of Metal Ion Complexes", L. G. Sillen and A. E. Martell, The Chemical Society, London (1964), "Organic Sequestering Agents", S. Chaberek and A. E. Martell Wiley (1959) and other publications.

Examples of chelating agents having a ferric ion chelate stability constant of over 8 include those described in Japanese Patent Application Nos. 234776/1990 and 324507/1989. The amount of these chelating agents used is preferably 0.01 to 50 g, more preferably 0.05 to 20 g per liter of stabilizer, in which good results in content range are obtained.

Ammonium compounds are preferably added to the stabilizer, which are supplied by ammonium salts of various inorganic compounds. The amount of ammonium compound added is preferably 0.001 to 2.0 mol, more preferably 0.002 to 1.0 mol per liter of stabilizer. It is also preferable to add a sulfite to the stabilizer.

The stabilizer preferably contains a metal salt in combination with the chelating agent described above. Examples of such metal salts include salts of Ba, Ca, Ce, Co, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al and Sr, and it can be supplied as an inorganic salt such as halide, hydroxide, sulfate, carbonate, phosphate or acetate, or a water-soluble chelating agent. The amount of its addition is preferably 1×10^{-4} to 1×10^{-1} mol, more preferably 4×10^{-4} to 2×10^{-2} mol per liter of stabilizer.

The stabilizer may contain an organic salt such as citrate, acetate, succinate, oxalate or benzoate, and a pH regulator such as malate, borate, hydrochloride or sulfate.

In the present invention, one or more fungicides can be added, whether singly or in combination, as long as the effect of the invention is not degraded.

The light-sensitive material to which the processing agent of the present invention is applied is described below.

When the light-sensitive material is for taking pictures, a silver iodobromide or silver iodochloride having an average silver iodide content of not less than 3 mol% is used for silver halide grains, with preference given to a silver iodobromide containing 4 to 15 mol% silver iodide. The average silver iodide content is preferably 5 to 12 mol%, and ideally 8 to 11 mol%.

In the light-sensitive material to be processed with the photographic processing agent of the present invention, the silver halide emulsions described in Research disclosure No. 308119 (hereinafter referred to as RD308119) can be used. The following table shows where the additives are described.

Item	Pages in RD308119
Iodine structure	993, I-Term A
Production method	993, I-Term A and 994, Term E
Crystal habit: Normal crystal	993, I-Term A
Twin crystal	993, I-Term A
Epitaxial	993, I-Term A
Halogen composition: Uniform	993, I-Term B
Not uniform	993, I-Term B
Halogen conversion	994, I-Term C
Halogen substitution	994, I-Term C
Metal content	994, I-Term D
Monodispersion	995, I-Term F
Solvent addition	995, I-Term F
Site where latent images are formed : Surface	995, I-Term G
: Core	995, I-Term G
Applicable light-sensitive materials : Negative films	995, I-Term H
Positive films: (containing core fogging grains)	995, I-Term H
Emulsion mixture	995, I-Term J
Desalinization	995, II-Term A

In the present invention, the silver halide emulsion is used after physical ripening, chemical ripening and spectral sensitization. Additives used in these processes are described in Research Disclosure Nos. 17643, 18716 and 308119 (hereinafter referred to as RD17643, RD18716 and RD308119, respectively). The following table shows where the additives are described.

Item	Page in RD308119	RD17643	RD18716
Chemical sensitizer	996, III-Term A	23	648
Spectral sensitizer	996, IV-Terms A, B, C, D, E, H, I, J	23-24	648-649
Supersensitizer	996, IV-Terms A, E, J	23-24	648-649
Antifogging agent	998 VI	24-25	649
Stabilizer	998, VI	24-25	649

Known photographic additives which can be used for the present invention are also described in the above Research Disclosure numbers. The following table shows where they are described.

Item	Page in RD308119	RD17643	RD18716
Antistaining agent	1002, VII-Term I	25	650
Dye image stabilizer	1001, VII-Term J	25	
Brightening agent	998, V	24	
Ultraviolet absorbent	1003, VIII-Term C, XIII-Term C	25-26	
Light absorbent	1003, VIII	25-26	
Light scattering agent	1003, VIII		
Filter dye	1003, VIII	25-26	
Binder	1003, IX	26	651
Antistatic agent	1006, XIII	27	650
Hardener	1004, X	26	651
Plasticizer	1006, XII	27	650
Lubricant	1006, XII	27	650
Activator, coating aid	1005, XI	26-27	650
Matting agent	1007, X, VI		
Developing agent (contained in the light-sensitive material)	1011, XX-Term B		

The light-sensitive material to be processed with the photographic processing agent of the present invention may incorporate various couplers. Examples thereof are described in the above Research Disclosure Numbers. The following table shows where they are described.

Item	Page in RD308119	RD17643
Yellow coupler	1001, VII-Term D	VII-Terms C-G
Magenta coupler	1001, VII-Term D	VII-Terms C-G
Cyan coupler	1001, VII-Term D	VII-Terms C-G
DIR coupler	1001, VII-Term F	VII-Term F
BAR coupler	1002, VII-Term F	
Other couplers which release a useful residue	1001, VII-Term F	
Alkali-soluble coupler	1001, VII-Term E	

The additives used for the present invention can be added by dispersion as described in RD308119 XIV and by other methods.

In the present invention, the supports described in RD17643, p. 28, RD18716, pp. 647-648 and RD308119 XIX.

The light-sensitive material may be provided with auxiliary layers such as filter layers and intermediate layers as described in RD308119, VII-Term K. The light-sensitive material of the present invention can have various layer configurations such as the ordinary, reverse and unit structures described in RD308119, VII-Term K.

Color light-sensitive materials to which the photographic processing agent of the present invention is preferably applicable are described below.

It is preferable to use silver halide grains based mainly on silver chloride wherein the silver chloride content is at least 80 mol%, more preferably at least 90 mol%, still more preferably at least 95 mol%, and ideally at least 99 mol%.

Said silver halide emulsion based mainly on silver chloride may contain silver bromide and/or silver iodide in addition to silver chloride in the silver halide composition. In this case, the silver bromide content is preferably not more than 20 mol%, more preferably not more than 10 mol%, and still more preferably not more than 3 mol%. When silver iodide is contained, its content is preferably not more than 1 mol%, more preferably not more than 0.5 mol%, and ideally zero. Such silver halide grains based mainly on silver chloride having a silver chloride content of not less than 50 mol% are added to at least one silver halide emulsion layer, but it is preferable to add them to all light-sensitive silver halide emulsion layers.

The crystal configuration of the silver halide grains may be normal crystal, twin crystal or any other crystal, and any ratio of the [1.0.0] plane and the [1.1.1] plane is usable. With respect to the crystal structure of these silver halide grains, it may be uniform from core to outer portion and may be of the core/shell type wherein the core and the outer portion are of different layer (phase) structures. These silver halides may be of the type wherein latent images are formed mainly on the surface or the type wherein latent images are formed mainly inside the grains. Moreover, tabular grains of silver halide such as those described in Japanese Patent O.P.I. Publication No. 113934/1983 and Japanese Patent Application No. 170070/1984 may be used. Also usable are the silver halides described in Japanese Patent O.P.I. Publication Nos. 26837/1989, 26838/1989 and 77047/1989.

The silver halide grains may be prepared by any of the acid method, neutral method, ammoniacal method and other methods. It is also possible to use the method in which seed grains are formed by the acid method and are grown to a given size by the ammoniacal method, which offers rapid grain growth. In growing silver halide grains, it is preferable to control the pH, pAg and other factors in the reactor and to sequentially and simultaneously add and mix silver ions and halide ions in an amount according to the rate of growth of silver halide grains as described in Japanese Patent O.P.I. Publication No. 48521/1979.

When the light-sensitive material processed with the photographic processing agent of the present invention is for color photography, the silver halide emulsion layer contains color couplers.

The red-sensitive layer may contain a non-diffusible color coupler which forms a cyan color image, normally a phenol or α-naphthol coupler.

The green-sensitive layer may contain at least one non-diffusible color coupler which forms a magenta color image, normally a 5-pyrazolone coupler and or a pyrazolotriazole coupler. The blue-sensitive layer may contain at least one non-diffusible color coupler which forms a yellow color image, normally a color coupler having an open chain ketomethylene group. These color couplers may be 6-, 4- or 2-equivalent couplers, for instance.

A 2-equivalent coupler is particularly preferred for the color light-sensitive material to which the photographic processing agent of the present invention is applied.

Appropriate couplers are disclosed in the following publications: W. Pelz, "Color Coupler" (Farbkuppler) in MitteilungInausden Forschungslaboratorien der Agfa, Leverkusen/Munchen, Vol. III, p. 111 (1961); K. Venkataraman, "The Chemistry of Synthetic Dyes", Vol. 4, pp. 341-387, Academic Press; "The Theory of the Photographic Processes", 4th edition, pp. 353-362; Research Disclosure No. 17643, Section VII.

From the viewpoint of enhancement of the desired effect of the invention, it is preferable to use the magenta coupler represented by formula M-1 described on page 26 of Japanese Patent O.P.I. Publication No. 106655/1988 (exemplified by Magenta Coupler Nos. 1 through 77 described on pages 29 through 34 of the same publication), the cyan coupler represented by formula C-I or C-II described on page 34 of the same publication (exemplified by Cyan Coupler Nos. C'-1 through C'-82 and C''-1 through C''-36 described on pages 37 through 42 of the same publication) and the rapid yellow coupler described on page 20 of the same publication (exemplified by Yellow Coupler Nos. Y'-1 through Y'-39 described on page 21 through 26 of the same publication).

EXAMPLES

The present invention is hereinafter described in more detail by means of the following examples, which are not to be construed as limitative on the embodiment of the invention.

Example 1

Using a commercially available powder mixer, the following color printing paper fixing agents were thoroughly mixed to yield a powder processing agent for 10 liters. Powder processing agent (fixing agent) for 10 liters

Thiosulfate (potassium salt, ammonium salt)	See Table 3.
Thiocyanate (potassium salt, ammonium salt)	See Table 3.
Anhydrous sodium bisulfite	20 g
Sodium metabisulfite	4.0 g
Disodium ethylenediaminetetraacetate	1.0 g

Sample Nos. 1-1 through 1-16 were prepared with the ratio of ammonium ions to the total cation content in the fixing agent changed by adjusting the ratio of thiosulfate (potassium salt, ammonium salt) and thiocyanate (potassium salt, ammonium salt) as appropriate.

Each processing agent sample was placed in a polyethylene bag, which was sealed tight, and was stored in an autoclave containing 2.0 kg/cm^3 oxygen at 45°C and 65% RH for 1 month. Then, the packing material was cut, and the sample was dissolved in water in a chemical mixer. The caking condition was observed visually. Next, a color printing paper sample was prepared as follows:

Color printing paper

Layers with the compositions shown in Tables 1 and 2 were coated on a paper support laminated with polyethylene on one face and titanium-oxide-containing polyethylene on the first layer on the opposite face, to yield a color printing paper sample. The coating solutions were prepared as follows:

First layer coating solution

26.7 g of a yellow coupler Y-1, 10.0 g of a dye image stabilizer ST-1, 6.67 g of another dye image stabilizer ST-2, 0.67 g of an additive HQ-1 and 6.67 g of a high boiling organic solvent DNP were dissolved in 60 ml of ethyl acetate. This solution was emulsified and dispersed in 220 ml of a 10% aqueous solution of gelatin containing 7 ml of 20% surfactant SU-1 using an ultrasonic homogenizer to yield a yellow coupler dispersion. This dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the following conditions, to yield a first layer coating solution.

Second through seventh layer coating solutions were prepared in the same manner as the first layer coating solution.

Hardeners H-1 and H-2 were added to layers 2 and 4 and layer 7, respectively. Surfactants SU-2 and SU-3, as coating aids, were added to adjust surface tension.

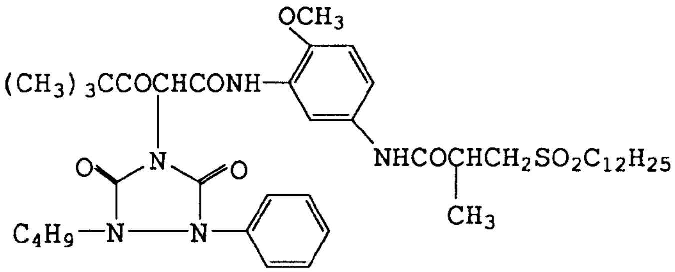
Table 1

Layer	Composition	Amount of addition (g/m^2)
Layer 7: Protective layer	Gelatin	1.00
Layer 6: Ultraviolet absorbing layer	Gelatin	0.40
	UV absorbent UV-1	0.10
	UV absorbent UV-2	0.04
	UV absorbent UV-3	0.16
	Antistaining agent HQ-1	0.01
	DNP	0.20
	PVP	0.03
	Anti-irradiation dye AI-2	0.02
Layer 5: Red-sensitive layer	Gelatin	1.30
	Red-sensitive silver chlorobromide emulsion Em-R	0.21*
	Cyan coupler C-1	0.17
	Cyan coupler C-2	0.25
	Dye image stabilizer ST-1	0.20
	Antistaining agent HQ-1	0.01
	HBS-1	0.20
	DOP	0.20
Layer 4: Ultraviolet absorbing layer	Gelatin	0.94
	UV absorbent UV-1	0.28
	UV absorbent UV-2	0.09
	UV absorbent UV-3	0.38
	Antistaining agent HQ-1	0.03
	DNP	0.40

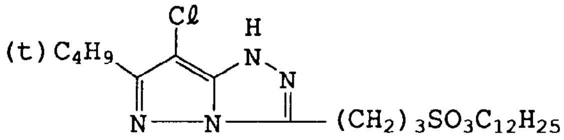
Table 2

Layer	Composition	Amount of addition (g/m^2)
Layer 3: Green-sensitive layer	Gelatin	1.40
	Green-sensitive silver chlrorobromide emulsion Em-G(as silver)	0.19
	Magenta coupler M-1	0.35
	Dye image stabilizer ST-3	0.15
	Dye image stabilizer ST-4	0.15
	Dye image stabiliser ST-5	0.15
	DNP	0.20
	Anti-irradiation dye AI-1	0.01
Layer 2: Intermediate layer	Gelatin	1.20
	Antistaining agent HQ-2	0.12
	DIDP	0.15
Layer 1: Blue-sensitive layer	Gelatin	1.20
	Blue-sensitive silver chlorobromide emulsion Em-A (as silver)	0.26
	Yellow coupler Y-1	0.80
	Dye image stabilizer ST-1	0.30
	Dye image stabilizer ST-2	0.20
	Antistaining agent HQ-1	0.02
	Anti-irradiation dye AI-3	0.01
	DNP	0.20
Support	Polyethylene-laminated paper	

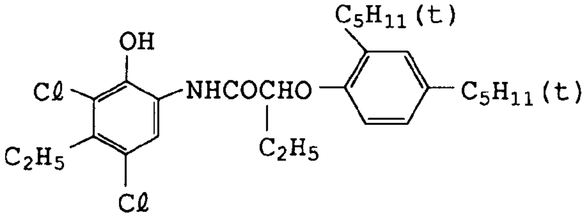
Y-1



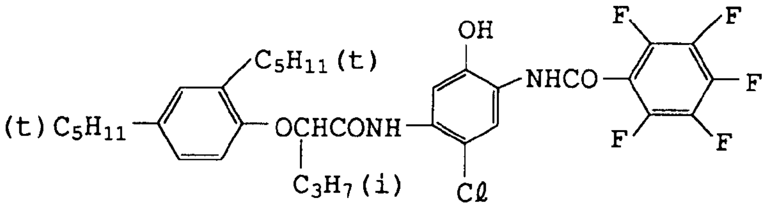
M-1



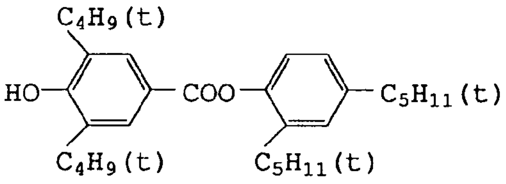
C-1



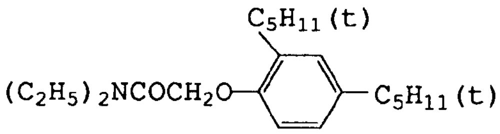
C-2



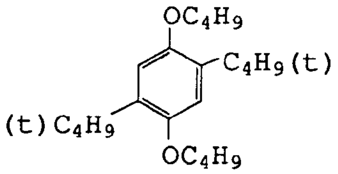
ST-1



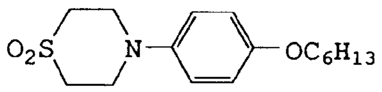
ST-2



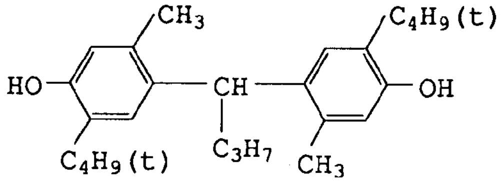
ST-3



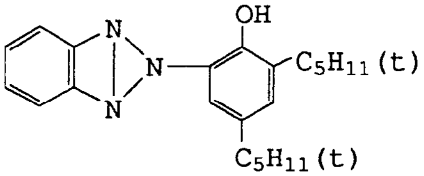
ST-4



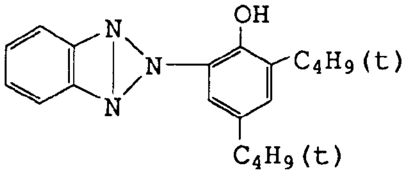
ST-5



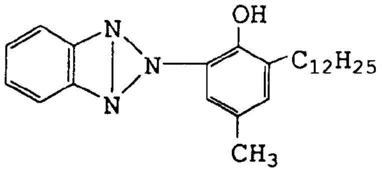
UV-1



UV-2

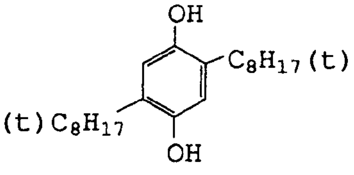


UV-3

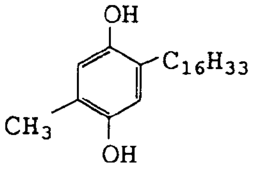


DOP: Dioctyl phthalate
DNP: Dinonyl phthalate
DIDP: Diisodecyl phthalate
PVP: Polyvinylpyrrolidone

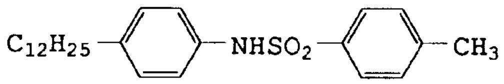
HQ-1



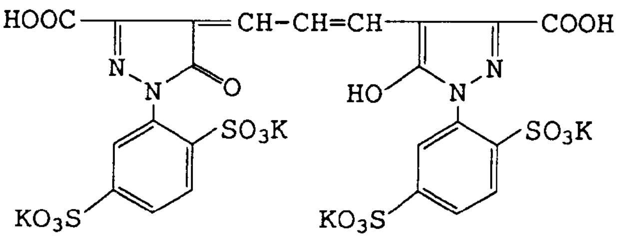
HQ-2



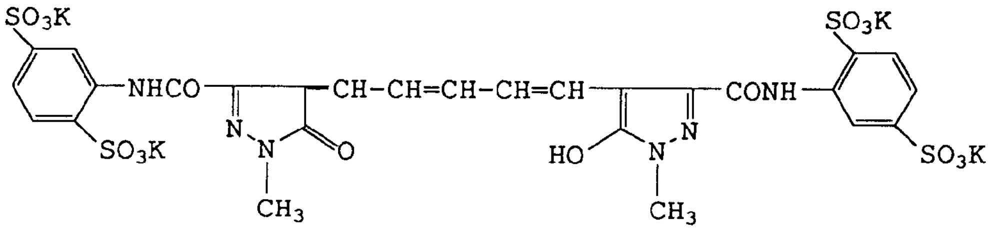
HBS-1



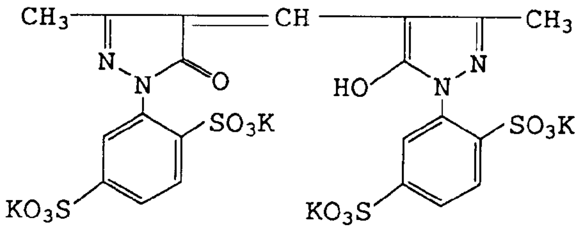
AI-1



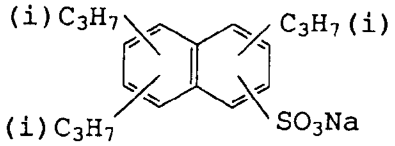
AI-2



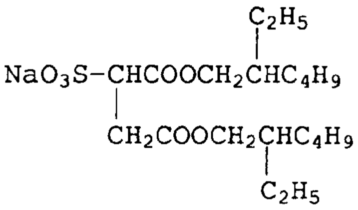
AI-3



SU-1

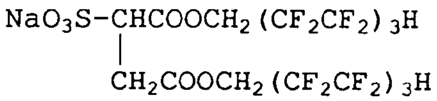


SU-2



$$NaO_3S-\underset{\displaystyle CH_2COOCH_2\underset{\displaystyle C_2H_5}{CH}C_4H_9}{CH}COOCH_2\overset{\displaystyle C_2H_5}{CH}C_4H_9$$

SU-3

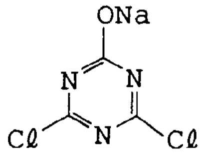


$$NaO_3S-\underset{\displaystyle CH_2COOCH_2(CF_2CF_2)_3H}{CHCOOCH_2}(CF_2CF_2)_3H$$

H-1

$(CH_2{=}CHSO_2CH_2)_4C$

H-2



Preparation of blue-sensitive silver halide emulsion

To 1000 ml of a 2% aqueous solution of gelatin incubated at 40°C, the following solutions A and B were simultaneously added over a period of 30 minutes while maintaining a pAg of 6.5 and a pH of 3.0, after which the following solutions C and D were simultaneously added over a period of 180 minutes while maintaining a pAg of 7.3 and a pH of 5.5. pAg was regulated by the method described in Japanese Patent O.P.I. Publication No. 45437/1984, and pH was regulated using an aqueous solution of sulfuric acid or sodium hydroxide.

Solution A

Sodium chloride	3.42 g
Potassium bromide	0.03 g

Water was added to make a total quantity of 200 ml.

Solution B

Silver nitrate	10 g

Water was added to make a total quantity of 200 ml.

Solution C

Sodium chloride	102.7 g
Potassium bromide	1.0 g

Water was added to make a total quantity of 600 ml.

Solution D

Silver nitrate	300 g

Water was added to make a total quantity of 600 ml.

After completion of the addition, the mixture was desalinized with a 5% aqueous solution of Demol N, a product of Kao Atlas, and a 20% aqueous solution of magnesium sulfate, and was then mixed with an aqueous solution of gelatin to yield a monodispersed emulsion EMP-1 comprising cubic grains having an average grain size of 0.85 μm, a coefficient of variance of 0.07 and a silver chloride content of 99.5 mol%.

The emulsion EMP-1 was chemically ripened with the following compounds at 50°C for 90 minutes to yield a blue-sensitive silver halide emulsion Em-B.

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX

Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye BS-1	4×10^{-4} mol/mol AgX
Sensitizing dye BS-2	1×10^{-4} mol/mol AgX

Preparation of green-sensitive silver halide emulsion

A monodispersed emulsion EMP-2 comprising cubic grains having an average grain size of 0.43 μm, a coefficient of variance of 0.08 and a silver chloride content of 99.5 mol% was prepared in the same manner as EMP-1 except that the addition time for Solutions A and B and the addition time for Solutions C and D were changed.

The emulsion EMP-2 was chemically ripened with the following compounds at 65°C for 120 minutes to yield a green-sensitive silver halide emulsion Em-G.

Sodium thiosulfate	1.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye GS-1	4×10^{-4} mol/mol AgX

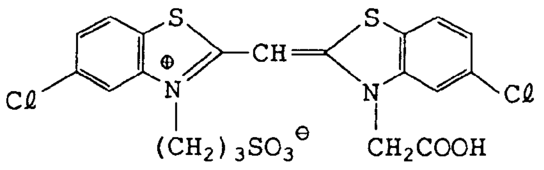
Preparation of red-sensitive silver halide emulsion

A monodispersed emulsion EMP-3 comprising cubic grains having an average grain size of 0.50 μm, a coefficient of variance of 0.08 and a silver chloride content of 99.5 mol% was prepared in the same manner as EMP-1 except that the addition time for Solutions A and B and the addition time for Solutions C and D were changed.

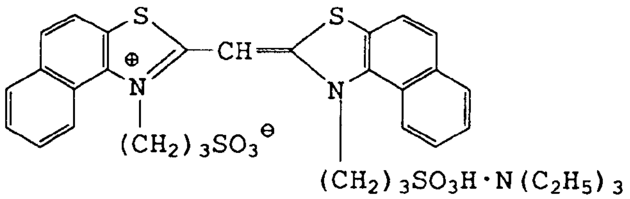
The emulsion EMP-3 was chemically ripened with the following compounds at 60°C for 90 minutes to yield a red-sensitive silver halide emulsion Em-R.

Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye RS-1	4×10^{-4} mol/mol AgX

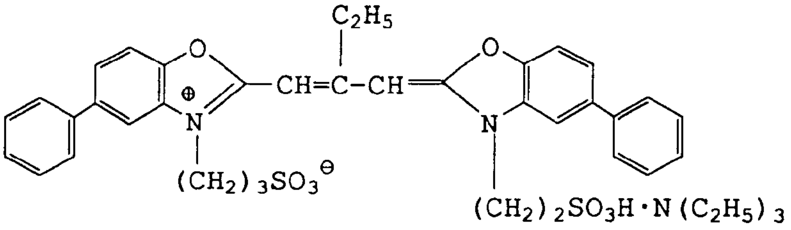
BS-1



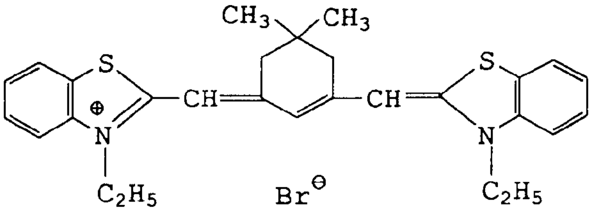
BS-2



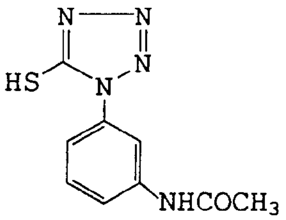
GS-1



RS-1



STAB-1



The samples thus obtained were subjected to exposure through an optical wedge in accordance with a conventional method, after which they were subjected to running processing using the following procedures and processing solutions.

Procedure	Temperature (°C)	Treatment time (sec)	replenishing rate (ml/m^2)
Color development	38	20	70
Bleaching	38	20	50
Fixation	30	20	40
Stabilization	30	(first tank) 20	120
Drying	60 to 80	(second tank) 30	-
		30	

The first and second stabilizing tanks were of the counter current type, and the replenisher was added to the second tank.

The processing solutions used in the respective procedures are as follows:

Color developer

Water	800 ml
Potassium bromide	0.02 g
Potassium chloride	3.3 g
Potassium carbonate	25 g
Potassium sulfite	0.2 g
Sodium diethylenetriaminepentaacetate	3.0 g
1-(N-ethyl-N-methanesulfonamidoethyl)-3-methyl-p-phenylenediamine·3/2H_2SO_4·H_2O (CD-3)	4.5 g
Sodium hydrogen carbonate	3.1 g
Diethylhydroxylamine oxalate	6.5 g
Tinopal SFP (produced by Ciba-Geigy)	2.5 g

Water was added to make a total quantity of 1 l, and pH was adjusted to 10.00.

Bleacher

Sodium ferric pentaethylenediaminetetraacetate	0.35 mol
Potassium bromide	170 g
Maleic acid	30 g
Succinic acid	30 g
Disodium ethylenediaminetetraacetate	1.0 g

Water was added to make a total quantity of 1 l, and pH was adjusted to 4.3.

Fixer

The previously prepared powdery fixing agent sample was dissolved in water, and the resulting processing solution was stored at 38°C for 10 days before use.

Stabilizer

Water	800 ml
1,2-benzoisothiazolin-3-one	0.1 g
1-hydroxyethylidene-1,1-diphosphonic acid	5.0 g
Ethylenediaminetetraacetic acid	1.0 g
Tinopal SFP (produced by Ciba-Geigy)	2.0 g
Ammonium sulfate	2.5 g
Zinc chloride	1.0 g
Magnesium chloride	0.5 g
o-phenylphenol	1.0 g
Sodium sulfite	2.0 g

Water was added to make a total quantity of 1 l, and 50% sulfuric acid or 25% aqueous ammonia was added to obtain a pH of 8.0.

After three rounds of running processing, the reflective red color density in the maximum density portion and the amount of residual silver in the exposed portion in the processed color printing paper sample were measured. Also, 1 liter of the fixer tank solution was placed in a beaker with an opening area ratio of 50 cm^2/l and stored at 38°C to obtain the number of days required for sulfation.

Table 3 gives data on the ratio of ammonium cations in the fixer, caking condition, reflective red color density in the maximum density portion, the amount of residual silver in the exposed portion and days required for sulfation.

Table 3

No.	Thiosulfate* (mol)	Thiocyanate* (mol)	Ratio of ammonium cations (mol%) in the fixer	Caking condition	Reflective red color density in the maximum density portion	Amount of residual silver (mg/dm^2) in the unexposed portion	Days until sulfation	Remark
1-1	0.30	-	5	A	2.58	0.5	26	Inventive
1-2	0.40	-	5	A	2.58	0.4	27	Inventive
1-3	0.50	-	5	A	2.58	0.4	28	Inventive
1-4	0.30	0.10	5	A	2.58	0.2	30	Inventive
1-5	0.30	0.20	5	A	2.58	0.2	31	Inventive
1-6	0.30	0.35	5	A	2.58	0.0	33	Inventive
1-7	0.30	0.40	5	A	2.58	0.0	33	Inventive
1-8	0.30	0.30	5	A	2.58	0.0	32	Inventive
1-9	0.30	0.30	0	A	2.58	0.0	33	Inventive
1-10	0.30	0.30	10	A	2.58	0.0	32	Inventive
1-11	0.30	0.30	20	B	2.57	0.2	30	Inventive
1-12	0.30	0.30	30	B-C	2.52	0.4	25	Inventive
1-13	0.30	0.30	40	C	2.51	0.4	25	Inventive
1-14	0.30	0.30	50	C	2.50	0.4	24	Inventive
1-15	0.30	0.30	60	D	2.40	1.0	20	Comparative
1-16	0.30	0.30	70	E	2.38	1.1	18	Comparative

* Potassium salt, ammonium salt.

The evaluation criteria for caking condition are as follows:

A: No caking.

B: Very slight caking seen, no problem in solubility.

C: Caking seen in some portions, but no problem in solubility.

D: Caking poses a problem in solubility.,

As the number of "D" marks increases, the degree of caking increases and the solubility decreases.

From Table 3, it is seen that the ratio (mol%) of ammonium cations in the fixer is preferably not more than 50 mol%, more preferably not more than 20 mol% for the desired effect of the present invention, with better results obtained by using a thiocyanate (potassium salt, ammonium salt) in combination with a thiosulfate (potassium salt, ammonium salt).

In addition, the use of the photographic processing agent of the present invention eliminates the need for conventionally used plastic bottles containing dense solutions of photographic processing agent; plastic consumption decreased by a factor of about 1/5 to 1/30, with the packing material alone needed. The processing agent kit volume decreased by a factor of 1/3 to 1/10.

Example 2

The fixing agent used in Example 1 was granulated in accordance with the method described in Japanese Patent O.P.I Publication No. 109042/1990, using a commercially available fluidized bed spray granulator, to yield a granular processing agent, which was tested in the same manner as in Example 1 and thus found to have improved caking condition, with storage stability (days required for sulfation) improved by 20 to 30%.

Example 3

The fixing agent mixture used in Example 1 was tableted using a solid processing agent tableting machine made by modifying the Tough Press Correct 1527HU, produced by Kikusui Seisakusho, to yield tablet processing agent sample Nos. 3-1 through 3-16, which were tested in the same manner as in Example 1 and thus found to have improved caking condition, with storage stability (days required for sulfation) improved by 30 to 45%. A tablet strength improving effect was also noted. Data on tablet strength are summarized in Table 4. Tablet strength was evaluated by visual observation after allowing the tablet sample to fall freely from a height of 1.2 m.

The results are given in Table 4.

Table 4

Sample No.	Thiosulfate* (mol)	Thiocyanate* (mol)	Ratio of ammonium cations (mol%) in the fixer	Tablet strength	Remark
3-1	0.30	-	5	A	Inventive
3-2	0.40	-	5	A	Inventive
3-3	0.50	-	5	A	Inventive
3-4	0.30	0.10	5	A	Inventive
3-5	0.30	0.20	5	A	Inventive
3-6	0.30	0.35	5	A	Inventive
3-7	0.30	0.40	5	A	Inventive
3-8	0.30	0.30	5	A	Inventive
3-9	0.30	0.30	0	A	Inventive
3-10	0.30	0.30	10	A	Inventive
3-11	0.30	0.30	20	B	Inventive
3-12	0.30	0.30	30	B-C	Inventive
3-13	0.30	0.30	40	C	Inventive
3-14	0.30	0.30	50	C	Inventive
3-15	0.30	0.30	60	D	Comparative
3-16	0.30	0.30	70	E	Comparative

* Potassium salt, ammonium salt.

The evaluation criteria for tablet strength are as follows:
A: High strength, with no disintegration.
B: Slight disintegration in the edge (incidence 2%).
C: Slight disintegration in the edge (incidence 10%)
D: Edge disintegration.
As the number of "D" marks increases, the degree of disintegration increases.

As seen from Table 4, it is preferable that the ammonium cation ratio be not more than 50 mol%, more preferably not more than 20 mol% for sufficient tablet strength.

Example 4

The following color negative film fixing agent components were thoroughly mixed to yield a powdery processing agent for 10 liters. Using a tableting machine, this powdery processing agent was tableted by the ordinary method described herein to yield sample Nos. 4-1 through 4-16, each of which comprised 80 tablets.

Tablet fixing agent for 10 liters

Thiosulfate (potassium salt, ammonium salt)	See Table 5.
Thiocyanate (potassium salt, ammonium salt)	See Table 5.
Sodium sulfite	20 g
Sodium ethylenediaminetetraacetate	5 g
Sodium metabisulfite	5 g

The ratio of ammonium ions to the total cation content in the fixing agent was changed as shown in Table 5, by adjusting the ratio of thiosulfate (potassium salt, ammonium salt) and thiocyanate (potassium salt, ammonium salt) as appropriate.

Tablet strength was evaluated as described in Example 3.

Next, a color negative film sample was prepared as follows:

Figures for the amount of addition in the silver halide photographic light-sensitive material are expressed in grams per m^2, unless otherwise stated. Figures for silver halide and colloidal silver are expressed as the amount of silver.

A triacetyl cellulose film support (50 μm thickness) was subbed on one face (surface), and layers with the following compositions were formed on the opposite face (back face) from the support side.

First backing layer

Alumina Sol AS-100 (aluminum oxide, produced by Nissan Chemical Industries, Ltd.)	0.8 g

Second backing layer

Diacetyl cellulose	100 mg
Stearic acid	10 mg
Fine grains of silica (average grain size 0.2 μm)	50 mg

Next, layers with the compositions shown below were sequentially formed on the subbed surface from the support side to yield a multiple-layered color photographic light-sensitive material.

Layer 1: Anti-halation layer HC

Black colloidal silver	0.15 g
UV absorbent UV-4	0.20 g
Colored cyan coupler CC-1	0.02 g
High boiling solvent Oil-1	0.20 g
High boiling solvent Oil-2	0.20 g
Gelatin	1.6 g

Layer 2: Intermediate layer IL-1

Gelatin	1.3 g

Layer 3: Low speed red-sensitive emulsion layer RL

Silver iodobromide emulsion having an average grain size of 0.3 μm	0.40 g
Silver iodobromide emulsion having an average grain size of 0.4 μm	0.30 g
Sensitizing dye S-1	3.2 × 10^{-4} mol/mol silver
Sensitizing dye S-2	3.2 × 10^{-4} mol/mol silver
sensitizing dye S-3	0.2 × 10^{-4} mol/mol silver
Cyan coupler C-3	0.50 g
Cyan coupler C-4	0.13 g
Colored cyan coupler CC-1	0.07 g
DIR compound D-1	0.006 g
DIR compound D-2	0.01 g
High boiling solvent Oil-1	0.55 g
Gelatin	1.0 g

Layer 4: High speed red-sensitive emulsion layer RH

Silver iodobromide emulsion having an average grain size of 0.7 μm	0.90 g
Sensitizing dye S-1	1.7×10^{-4} mol/mol silver
Sensitizing dye S-2	1.6×10^{-4} mol/mol silver
Sensitizing dye S-3	0.1×10^{-4} mol/mol silver
Cyan coupler C-4	0.23 g
Colored cyan coupler CC-1	0.03 g
DIR compound D-2	0.02 g
High boiling solvent Oil-1	0.25 g
Gelatin	1.0 g

Layer 5: Intermediate layer IL-2

Gelatin	0.8 g

Layer 6: Low speed green-sensitive emulsion layer GL

Silver iodobromide emulsion having an average grain size of 0.4 μm	0.6 g
Silver iodobromide emulsion having an average grain size of 0.3 μm	0.2 g
Sensitizing dye S-4	6.7×10^{-4} mol/mol silver
Sensitizing dye S-5	0.8×10^{-4} mol/mol silver
Magenta coupler M-2	0.17 g
Magenta coupler M-3	0.43 g
Colored magenta coupler CM-1	0.10 g
DIR compound D-3	0.02 g
High boiling solvent Oil-2	0.7 g
Gelatin	1.0 g

Layer 7: High speed green-sensitive emulsion layer GH

Silver iodobromide emulsion having an average grain size of 0.7 µm	0.91 g
Sensitizing dye S-6	1.1×10^{-4} mol/mol silver
Sensitizing dye S-7	2.0×10^{-4} mol/mol silver
Sensitizing dye S-8	0.3×10^{-4} mol/mol silver
Magenta coupler M-2	0.30 g
Magenta coupler M-3	0.13 g
Colored magenta coupler CM-1	0.04 g
DIR compound D-3	0.004 g
High boiling solvent Oil-2	0.35 g
Gelatin	1.0 g

Layer 8: Yellow filter layer YC

Yellow colloidal silver	0.1 g
Additive HS-1	0.07 g
Additive HS-2	0.07 g
Additive SC-1	0.12 g
High boiling solvent Oil-2	0.15 g
Gelatin	1.0 g

Layer 9: Low speed blue-sensitive emulsion layer BL

Silver iodobromide emulsion having an average grain size of 0.3 µm	0.25 g
Silver iodobromide emulsion having an average grain size of 0.4 µm	0.25 g
Sensitizing dye S-9	5.8×10^{-4} mol/mol silver
Yellow coupler Y-2	0.6

Yellow coupler Y-3	0.32 g
DIR compound D-1	0.003 g
DIR compound D-2	0.006 g
High boiling solvent Oil-2	0.18 g
Gelatin	1.3 g

Layer 10: High speed blue-sensitive emulsion layer BH

Silver iodobromide emulsion having an average grain size of 0.8 μm	0.5 g
Sensitizing dye S-10	3.0×10^{-4} mol/mol silver
Sensitizing dye S-11	1.2×10^{-4} mol/mol silver
Yellow coupler Y-2	0.18 g
Yellow coupler Y-3	0.10 g
High boiling solvent Oil-2	0.05 g
Gelatin	1.0 g

Layer 11: First protective layer PRO-1

Silver iodobromide emulsion having an average grain size of 0.08 μm	0.3 g
UV absorbent UV-4	0.07 g
UV absorbent UV-5	0.10 g
Additive HS-1	0.2 g
Additive HS-2	0.1 g
High boiling solvent Oil-1	0.07 g
High boiling solvent Oil-3	0.07 g
Gelatin	0.8 g

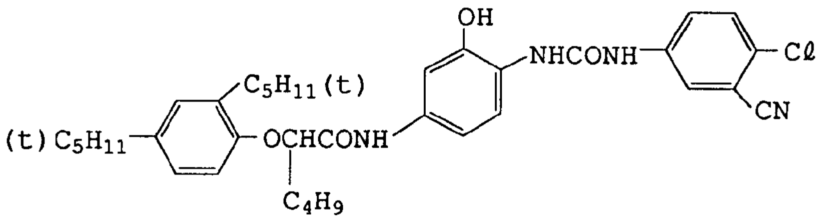
Layer 12: Second protective layer PRO-2

Lubricant WAX-1	0.04 g

Surfactant SU-1	0.004 g
Polymethyl methacrylate (average grain size 3 μm)	0.02 g
Copolymer of methyl methacrylate:ethyl methacrylate:methacrylic acid = 3:3:4 (by weight) (average grain size 3 μm)	0.13 g

In addition to these compositions, the color negative film contains compounds SU-1 and SU-4, a viscosity regulator, hardeners H-1 and H-2, a stabilizer STAB-2, antifogging agents AF-1 and AF-2 (weight-average molecular weights of 10000 and 1100000, respectively), dyes AI-4 and AI-5, and compound DI-1 (9.4 mg/m^2).

C-3



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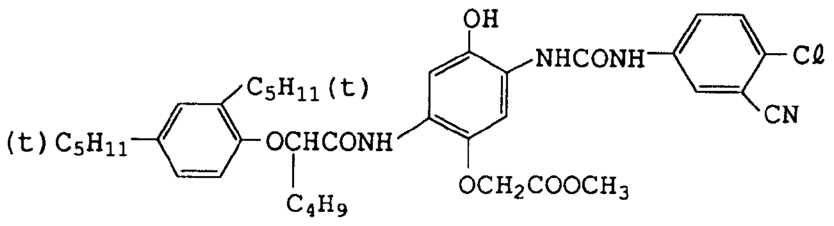

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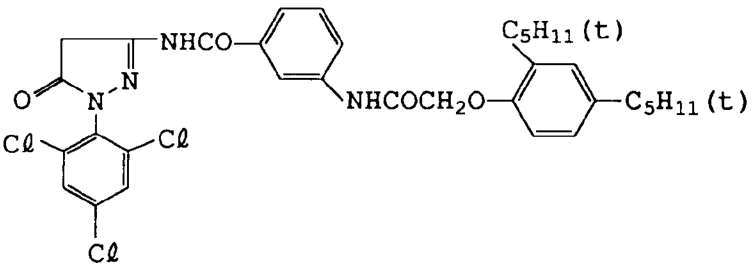

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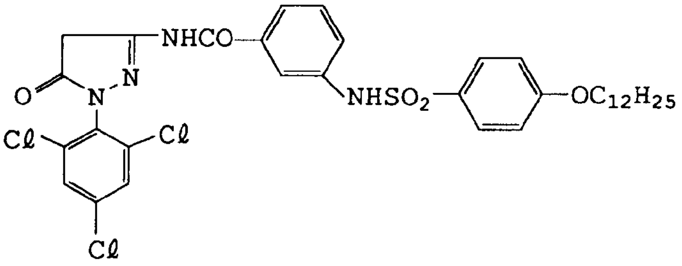
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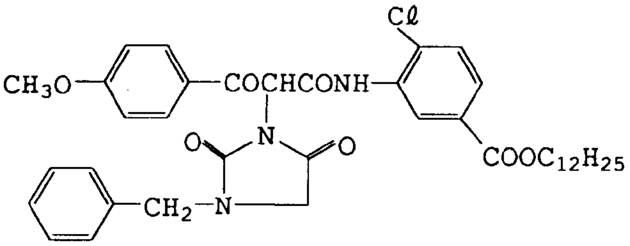
Y-2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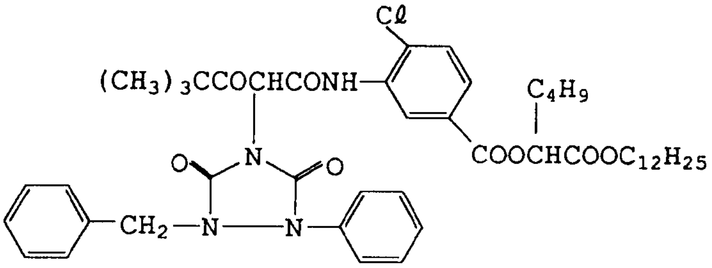
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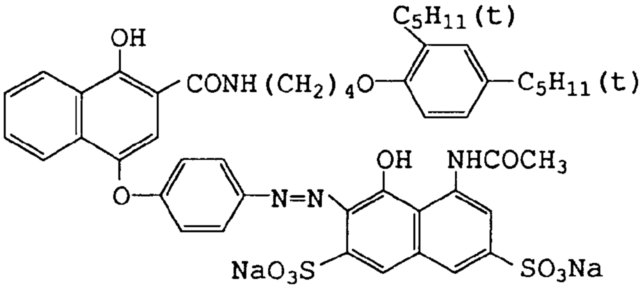
CC-1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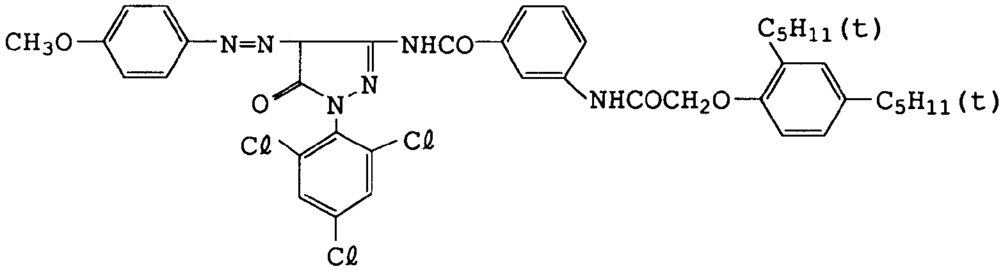
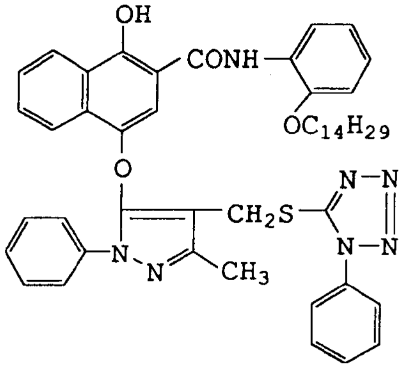
CM-1



D-1



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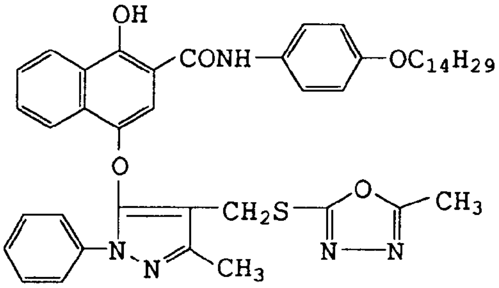

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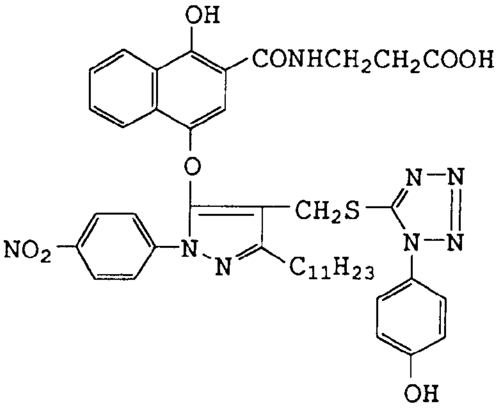

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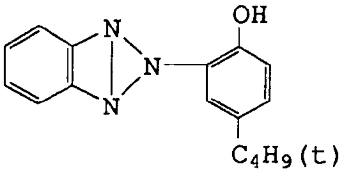

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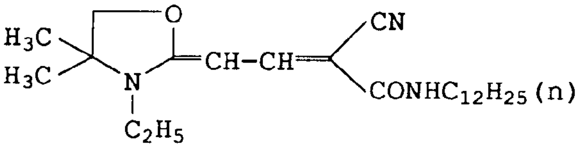
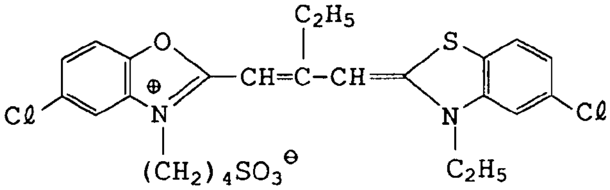


S-1



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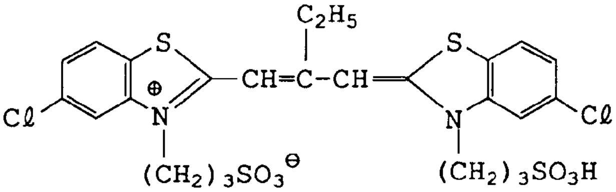

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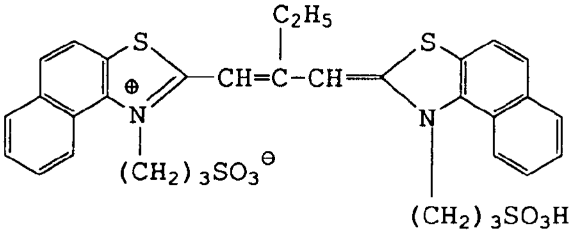

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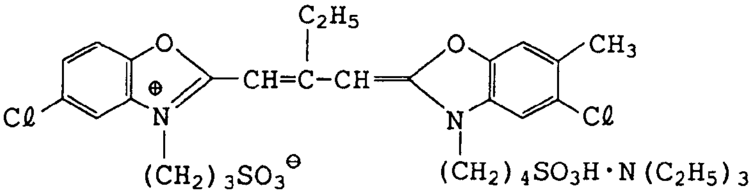

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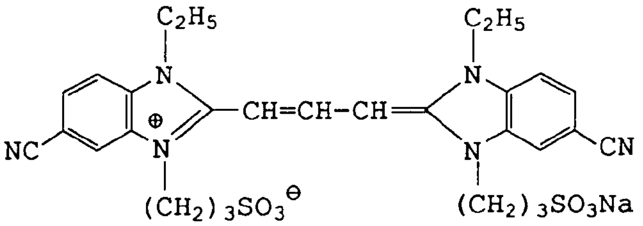

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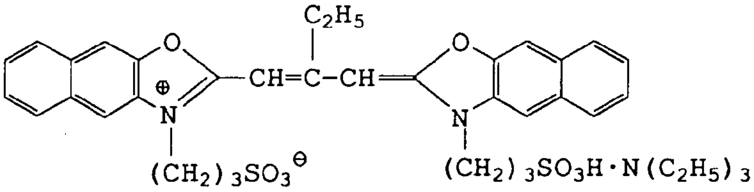

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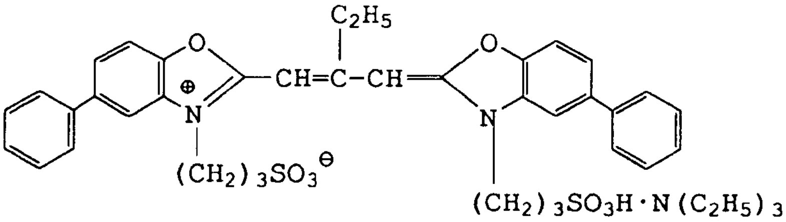
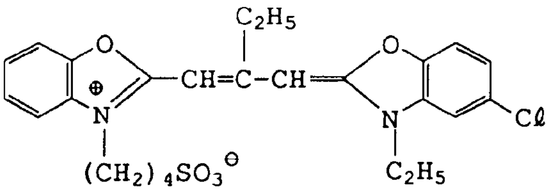
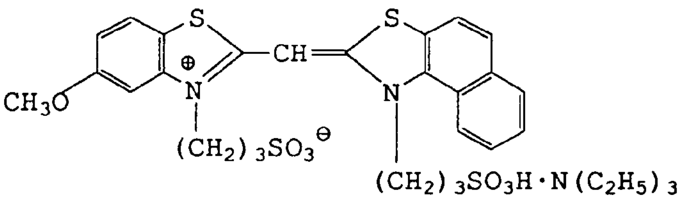


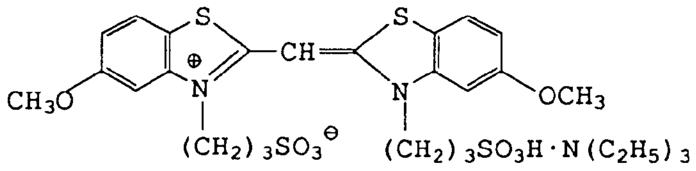
S-8



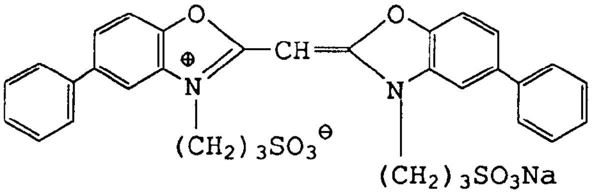
S-9



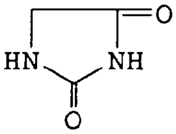
S-10



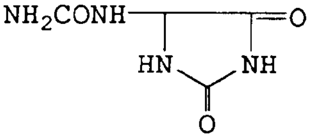
S-11



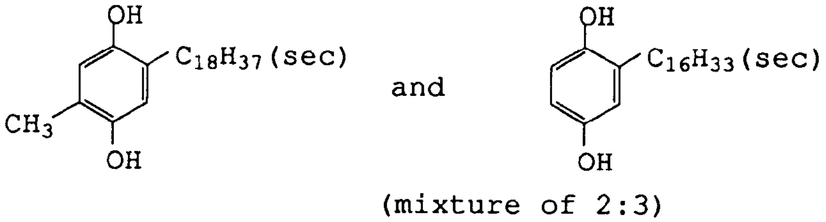
HS-1



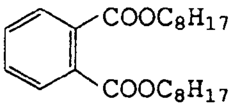
HS-2



SC-1



Oil-1



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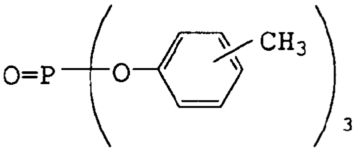

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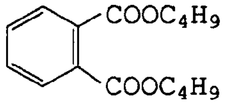
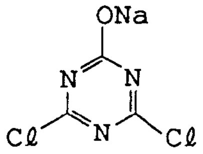


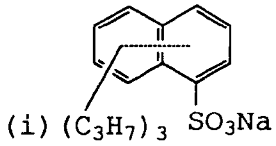
H-1



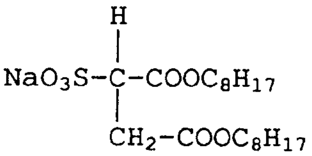
H-2

$(CH_2{=}CHSO_2CH_2)_2O$

SU-1

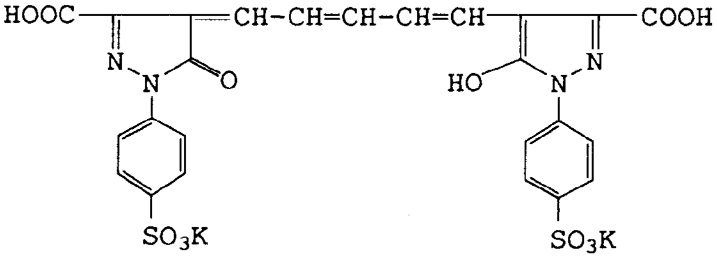


SU-4

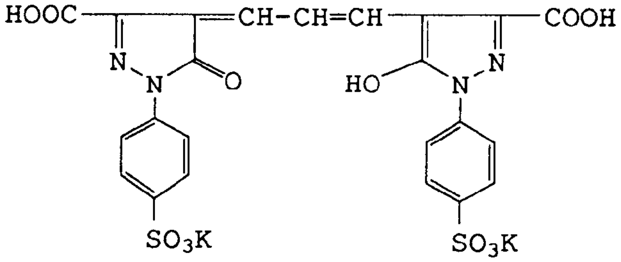


$NaO_3S-\overset{H}{\underset{CH_2-COOC_8H_{17}}{C}}-COOC_8H_{17}$

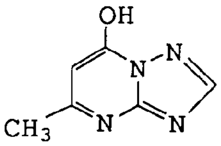
AI-4



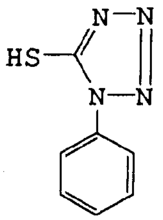
AI-5



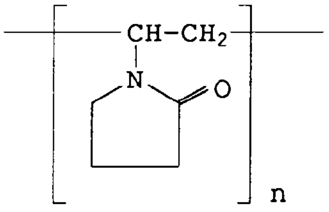
STAB-2



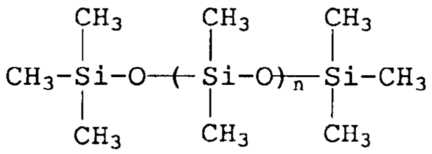
AF-1



AF-2

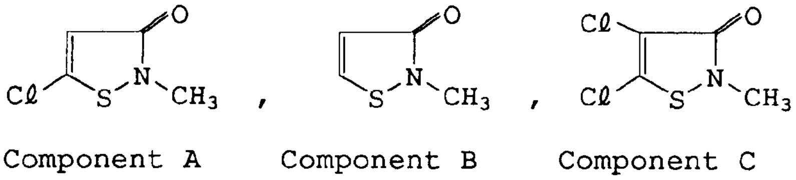


WAX-1



Weight-average molecular weight = 30,000

DI-1 (mixture of the following three components)


Component A Component B Component C

A:B:C = 50:46:4 (molar ratio)

Preparation of emulsion

The silver iodobromide emulsion used in layer 10 was prepared as follows:

Using monodispersed silver iodobromide grains having an average grain size of 0.33 μm and a silver iodide content of 2 mol% as seed crystals, a silver iodobromide emulsion was prepared by the double jet method.

While keeping solution G-1 at a temperature of 70°C, a pAg of 7.8 and a pH of 7.0, the seed emulsion in an amount equivalent to 0.34 mol was added with vigorous stirring.

Formation of inner high-iodine phase (core phase)

While maintaining a 1:1 flow rate ratio, solutions H-1 and S-1 were added at increasing flow rates (the final flow rate was 3.6 times the initial flow rate) over a period of 86 minutes.

Formation of outer low-iodine phase (shell phase)

Subsequently, solutions H-2 and S-2 were added at increasing flow rates (the final flow rate was 5.2 times the initial flow rate) and a pAg of 10.1 and a pH of 6.0 over a period of 60 minutes while keeping a flow rate ratio of 1:1.

During grain formation, pAg and pH were regulated by the use of an aqueous solution of potassium bromide and a 56% aqueous solution of acetic acid. After grain formation, the mixture was washed by the conventional flocculation method, redispersed in gelatin, and then adjusted to a pH of 5.8 and a pAg of 8.06 at 40°C.

The resulting emulsion was a monodispersed emulsion comprising octahedral silver iodobromide grains having an average grain size of 0.8 µm, a distribution width of 12.4% an average silver iodide content of 8.5 mol%.

G-1

Ossein gelatin	100.0 g
10% by weight methanol solution of Compound I	25.0 ml
28% aqueous ammonia	440.0 ml
56% aqueous solution of acetic acid	660.0 ml

Water was added to make a total quantity of 5000.0 ml.

H-1

Ossein gelatin	82.4 g
Potassium bromide	151.6 g
Potassium iodide	90.6 g

Water was added to make a total quantity of 1030.5 ml.

S-1

Silver nitrate	309.2 g
28% aqueous ammonia	Equivalent amount

Water was added to make a total quantity of 1030.5 ml.

H-2

Ossein gelatin	302.1 g
Potassium bromide	770.0 g
Potassium iodide	33.2 g

Water was added to make a total quantity of 3776.8 ml.

S-2

Silver nitrate	1133.0 g
28% aqueous ammonia	Equivalent amount

Water was added to make a total quantity of 3776.8 ml.

Compound-1

$$HO(CH_2CH_2O)m(CH(CH_3)CH_2O)k(CH_2CH_2O)nH$$

(average molecular weight = about 1300)

Emulsions having different average grain sizes and silver iodide contents were prepared in the same manner as above except that seed crystal average grain size, temperature, pAg, pH, flow rate, addition time and halide composition were changed.

All these emulsions were core/shell type monodispersed emulsions having a distribution width of not more than 20%. Each emulsion was subjected to optimum chemical sensitization with sodium thiosulfate, chloroauric acid and ammonium thiocyanate, and sensitizing dyes, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole were added.

The color film sample thus prepared was subjected to exposure through an optical wedge by a conventional method and then processed in the following procedures:

Processing procedure	Temperature	Time
Color development	38 ± 0.3°C	3 minutes 15 seconds
Bleaching	38 ± 2.0°C	45 seconds
Fixation	38 ± 2.0°C	1 minute 30 seconds
Stabilization*	38 ± 5.0°C	30 seconds for the first tank, 30 seconds for the second tank
Drying	60 ± 5.0°C	1 minute

*: The first and second stabilizing tanks are of the counter current type, and the replenisher was supplied to the second tank. The processing solutions used in the respective processes are as follows:

Color developer (tablet processing agent for 1 liter)

Potassium carbonate	30 g
Sodium hydrogen carbonate	3.5 g
Sodium 1-hydroxyethane-1,1-diphosphonate	2.5 g
Sodium diethylenetriaminepentaacetate	2.0 g
4-amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate CD-4	4.8 g
Sodium sulfite	3.5 g
Hydroxylamine sulfate	2.8 g
Sodium bromide	1.3 g
Potassium iodide	0.8 mg

Bleacher (tablet processing agent for 1 liter)

Potassium ferric 1,3-propaneaminetetraacetate	180 g
Sodium ferric 1,3-ethylenediaminetetraacetate	40 g
Sodium ethylenediaminetetraacetate	5 g
Potassium bromide	150 g
Sodium nitrate	35 g
Maleic acid	28 g

Fixer (tablet processing agent for 1 liter)

The previously prepared tablet fixing agent was dissolved to yield a processing solution, which was stored at 38°C for 10 days before use.

Stabilizer (pasty processing agent for 1 liter)

m-hydroxybenzaldehyde	2 g
Hexamethylenetetramine	1.5 g
Polyethylene glycol (molecular weight 1540)	2 g
p-octylphenol adduct with 10 mol ethylene oxide	2 g
Diethylene glycol	5 g

After three rounds of running processing, the transmitted red color density in the maximum density portion (determined using an photoelectric densitometer) and the amount of residual silver in the unexposed portion in the processed sample were measured. Also, 1 liter of the fixer tank solution was placed in a beaker with an opening area ratio of 50 cm^2/liter and stored at 38°C to obtain the number of days required for sulfation.

Table 5 gives data on the ratio of ammonium cations in the fixer, caking condition, transmitted red color density in the maximum density portion, the amount of residual silver in the exposed portion, days until sulfation and tablet strength.

Table 5

No.	Thiosulfate* (mol)	Thiocyanate* (mol)	Ratio of ammonium cations (mol%) in the fixer	Transmitted red color density in the maximum density portion	Amount of residual silver (mg/dm^2) in the unexposed portion	Days until sulfation	Tablet strength	Remark
4-1	1.2	-	5	2.25	0.6	26	A	Inventive
4-2	1.3	-	5	2.25	0.5	26	A	Inventive
4-3	1.4	-	5	2.25	0.5	28	A	Inventive
4-4	1.2	0.9	5	2.25	0.3	30	A	Inventive
4-5	1.2	1.0	5	2.25	0.2	31	A	Inventive
4-6	1.2	1.1	5	2.25	0.0	33	A	Inventive
4-7	1.2	1.3	5	2.25	0.0	33	A	Inventive
4-8	1.2	1.2	5	2.25	0.0	32	A	Inventive
4-9	1.2	1.2	0	2.25	0.0	33	A	Inventive
4-10	1.2	1.2	10	2.25	0.0	32	A	Inventive
4-11	1.2	1.2	20	2.23	0.2	30	B	Inventive
4-12	1.2	1.2	30	2.21	0.5	25	B-C	Inventive
4-13	1.2	1.2	40	2.21	0.5	25	C	Inventive
4-14	1.2	1.2	50	2.18	0.6	24	C	Inventive
4-15	1.2	1.2	60	2.00	1.6	20	D	Comparative
4-16	1.2	1.2	70	1.98	1.8	18	E	Comparative

* Potassium salt, ammonium salt.

From Table 5, it is seen that sample Nos. 4-1 through 4-14, all of which were prepared in accordance with the present invention and wherein the ammonium cation ratio (mol%) in the fixer was not more than 50 mol%, are better than comparative samples with respect to all items, with still better results obtained from sample Nos. 4-1 through 4-11, wherein the ratio was not more than 20 mol%. Sample Nos. 4-4 through 4-8, incorporating a thiocyanate (potassium salt, ammonium salt) also gave excellent results.

Example 5

To fixing agent sample solution No. 4-14 (ammonium cation ratio 50 mol%) prepared in Example 4, each of the compound represented by formula FA and a compound in the compound group FB was added at 5 g/l as shown in Table 6 to yield sample Nos. 5-1 through 5-8.

Exposed color negative films were processed with the above samples in the fixing process to yield processed color negative films, and the amount of residual silver in the unexposed portion was determined. The results are shown in Table 6.

Table 6

Sample No.	Fixation accelerator (5g/l)	Amount of residual silver in the unexposed portion (mg/dm^2)
5-1	Not added	0.6
5-2	FA-12	0.3
5-3	FA-38	0.2
5-4	FA-21	0.3
5-5	FA-32	0.2
5-6	FB-1	0.3
5-7	FB-2	0.2
5-8	(FB-1)/(FA-21)=1/1	0.2

From Table 6, it is seen that the effect of the present invention is enhanced by using the compound represented by formula FA and a compound in the compound group FB in combination.

The present invention provides a solid processing agent for silver halide photographic light-sensitive material capable of fixation which has improved storage stability, improved solubility and increased wear resistance and which is free of color image density reduction after development.

This is more suitable to the social and working environments and reduces transport and storage costs as a result of saving packing materials, particularly plastic bottles, prevention of dust formation, weight reduction and so on.

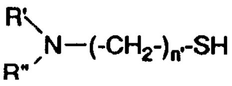
Claims

1. A solid processing agent for silver halide photographic light-sensitive material capable of fixation containing at least one kind of thiosulfate,
   wherein a content of ammonium cations to a total cation content is not more than 50 mol%.

2. The solid processing agent of claim 1, wherein the content is not more than 20 mol%.

3. The solid precessing agent of claim 1 further comprising a compound represented by formula FA, thiourea or thiocyanocatechol,

   Formula FA



$$\begin{matrix} R' \\ \quad \end{matrix}\!\!\!\!> N-(-CH_2-)_{n'}-SH \quad (R', R'' \text{ on } N)$$

   wherein R' and R" independently represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a nitrogen-containing heterocyclic group; n' is an integer 2 or 3.

4. The solid processing agent of claim 3, wherein the compound represented by formula FA, thiourea or thiocyanocatechol is used in an amount of 0.1g to 300g per liter of a processing solution.

5. The solid processing agent of claim 4, wherein the amount is 0.5g to 150g.

6. The solid processing agent of claim 1 for silver halide photographic light-sensitive material comprising a silver halide grain in which a silver chloride content to total silver halide is not less than 90 mol%.

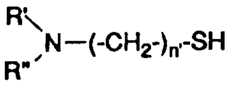
7. The solid processing agent of claim 6, wherein the silver chloride content is not less than 99 mol%.

8. The solid processing agent of claim 1, having a apparent density of 0.4 to 0.9 g/cm^3 in a granule form.

9. The solid processing agent of claim 8, wherein the apparent density is 1.1 to 2.1 g/cm^3 in a tablet form.

10. A solid processing agent in a tablet form having a apparent density of 0.4 to 2.1 g/cm^3, for silver halide photographic light-sensitive material in which a content of silver chloride to total silver halide is not less than 99 mol%;
wherein said solid processing agent being capable of fixation when dissolved in predetermined amount of water for making a processing solution, contains at least one thiosulfate;
and a compound represented by formula FA, thiourea or thiocyanocatechol,

Formula FA



$$\begin{matrix} R' \\ & N-(-CH_2-)_{n'}-SH \\ R'' \end{matrix}$$

wherein R' and R" independently represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a nitrogencontaining heterocyclic group; n' is an integer 2 or 3; in an amount of 0.1g to 300g per liter of the processing solution;
wherein a content of ammonium cation to a total cation in the solution is not more than 20 mol%.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 31 1116

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y A	US-A-4 029 510 (DANIEL EARLE SPEERS) * claims 1,2; example 10 *	1 6,7 2,8-10	G03C5/38
X Y A	US-A-2 759 823 (DONALD J. KRIDEL ET AL.) * the whole document *	1,2 6,7 8-10	
X Y A	US-A-2 592 366 (EDWIN S. WIITALA , DONALD J. KRIDEL) * the whole document *	1,2 6,7 8-10	
P,Y	EP-A-0 466 510 (KONICA CORPORATION) * page 17, line 27 - line 31; claim 1 *	6,7	
A	EP-A-0 080 905 (KONISHIROKU PHOTO INDUSTRY CO., LTD.) * page 28; claim 1 *	6,7	
A	EP-A-0 329 086 (KONICA CORPORATION) * page 35, line 25 - page 38, line 37 *	3-5	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	EP-A-0 329 088 (KONICA CORPORATION) * page 16, line 12 - line 27 *	3-5	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04 MARCH 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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