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(54) Processing solution and method for processing a silver halide color photographic light-sensitive material.

(57) A solution suitable for processing a silver halide color photographic light-sensitive material which comprises not less than 0.1 mol/ℓ of a thiocyanate and not less than 0.2 mol/ℓ of a thiosulfate, wherein not more than 50 mol% of the cations in the solution are ammonium ions.

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FIELD OF THE INVENTION

The present invention relates to a processing solution and method for processing a silver halide color photographic light-sensitive material. More specifically, this invention relates to a high preservable processing solution and a method for processing a silver halide color photographic light-sensitive material, which are less pollutive to the environment.

BACKGROUND OF THE INVENTION

In silver halide photographic light-sensitive materials, color images are formed generally by a series of photographic processes after image-wise exposure, which basically comprise a color developing process and desilvering process.

In the color developing process, dye images are formed in image patterns and reduced silver is generated at the same time, when an oxidation product of a color developing agent couples with a color coupler which coexists therein. The reduced silver formed therein is oxidized by a bleaching agent in the succeeding desilvering process and then converted into a soluble silver complex by the action of a fixing agent, subsequently dissolved and removed by washing.

In automatic processors which carry out such developing process, there has been extensively introduced a wash-free processing technology for the purpose of decreasing environmental pollution. Now, almost all mini-laboratories have come to use such wash-free automatic processors.

Since the introduction of the wash-free processor to the mini-laboratory market, however, there have come to be found problems such as frequent scratching of color films, and jamming of films in extreme cases, in the wash-free automatic processor for color negative film. As a result of study, there are found in processors for color negative films which have undergone such troubles (1) that large quantities of caked matter stick to racks outside liquid of a fixing bath and stabilizing bath, gears, and a rack connecting the fixing bath to the stabilizing bath, which are responsible for such scratching and jamming, and (2) that such large quantities of hard matter stick so firmly to the above portions that they can be hardly removed.

In automatic processor for color paper, there have been also found scratching, though less frequent than in machines for color negative film, and local fixing failure, stain, sticking of foreign matter much frequently than scratching. As a result of study, there are clarified (3) that such a caked matter is small in quantity and can be readily removed, and (4) that the caked matter is present on the surface or bottom of a processing bath and can be hardly dissolved.

Further, in automatic processors of hanger type, there are found generation of stains and sticking of foreign matter, which are attributable to deposits or floats.

In recent years, development with a less replenishing quantity is strongly demanded under the increasing necessity of pollution control and cost reduction. Under such circumstances, solution of the above problems has come to be much more important.

That is, with the spread of wash-free mini-laboratory, the freedom of selecting installation locations and persons in charge becomes larger; on the contrary, odors of chemicals, especially ammonia odor, come to attract a large attention in respect to working environments and environmental pollution. Under the circumstances, development of a less pollutive processing technology is strongly demanded.

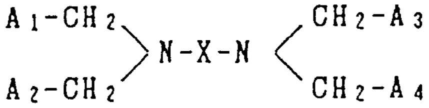
SUMMARY OF THE INVENTION

An object of the present invention is to provide a method of processing silver halide color photographic light-sensitive materials prevented from causing cakes, desotits and floats of components of processing solution as well as free from scratching and adhering foreign matters. Another object of the present invention is to provide a processing solution and method for processing silver halide color photographic light-sensitive materials improved in pollution preventive measures.

The processing solution for silver halide color photographic light-sensitive materials of the invention has a fixing ability for silver halide light-sensitive material and contains at least 0.1 mol/ℓ of a thiocyanate and at least 0.2 mol/ℓ of a thiosulfate, and ammonium ions contained therein are not more than 50 mol% of the total cations, preferably not more than 20 mol% of the total cations.

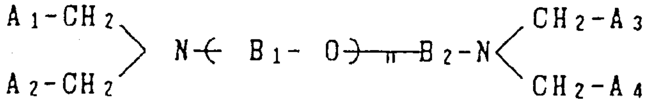
This processing solution having a fixing ability is used as a fixing solution or bleachfixer. When used as a bleachfixing solution, a bleaching agent is further added to the solution. As a bleaching agent, organic acid ferric salts represented by the following formula A or B are preferably used.

Formula A



wherein A_1 to A_4 each represent $-CH_2OH$, $-COOM$ or $PO_3M_1M_2$, and may be the same with or different from one another; M, M_1 and M_2 independently represent a hydrogen atom, alkali metal or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms.

Formula B



wherein A_1 to A_4 are the same as those defined for Formula A; n represents an integer of 1 to 8; B_1 and B_2 each represent substituted or unsubstituted alkylene group having 2 to 5 carbon atoms, which may be the same with or different from each other.

The method of processing silver halide color photographic materials according to the invention comprises the steps of color developing of a light-sensitive material followed by processing with a processing solution having a fixing ability, and then stabilizing it. As such a processing solution having a fixing ability, there is used a solution which contains as a fixing agent at least 0.1 mol/ℓ of thiocyanate and at least 0.2 mol/ℓ of thiosulfate and whose ammonium ion content is less than 50 mol% of the amount of total cations.

One preferable embodiment of the invention is to process a light-sensitive material, after color development, with a bleaching solution and then to process it with a processing solution having a fixing ability of the invention, i.e. fixing solution, and subsequently to process it with a stabilizer solution. Another preferable embodiment of the invention is to process a light-sensitive material, after color development, with a processing solution having a fixing ability and containing a bleaching agent according to the invention, i.e. bleach-fixing solution, and then to process it with a stabilizer solution.

The bleaching agent used in the above bleach-fixing solution contains preferably a ferric salt of organic acid represented by the above Formula A or B, and the amount of ammonium ions in the bleach-fixing solution is preferably less than 50 mol% and especially less than mol% of the total cation content.

DETAILED DESCRIPTION OF THE INVENTION

Sticking, deposition and flotation of processing solution components are attributable to thiosulfates, and ammonium ions also have an adverse effect on this problem. On the contrary, decrease of ammonium ion concentration in a fixing-capable solution deteriorates its fixing capability to a large extent. However, a combined use of specific amounts of thiocyanates and thiosulfates makes it possible to prevent sticking, deposition and flotation of processing solution components without lowering the fixing capability at a low ammonium ion content less than 50 mol% of the total cations, or even under a condition where ammonium ions are not present substantially. As a result, scratching and sticking of foreign matters are prevented, in addition to the attainment of a low pollutive processing method.

The following are suitable processes in the processing method using a processing solution having a fixing ability of the invention.

(1) Color developing → Bleach-fixing → Stabilizing
(2) Color developing → Bleaching → Fixing → Stabilizing
(3) Color developing → Bleaching → Bleach-fixing → Stabilizing
(4) Color developing → Bleach-fixing → Fixing → Stabilizing
(5) Color developing → Bleach-fixing → Bleach-fixing → Stabilizing

Among the foregoing, processes (1) and (2) are preferred, and process (2) is particularly preferred. That is, the solution having a fixing ability used in the invention can vary its usable modes according to processes, as seen in the above instances such as a single bleach-fixing solution and various combinations of bleaching solution and fixing solution, bleaching solution and bleach-fixing solution, bleach-fixing solution and fixing solution, and bleach-fixing solution and bleach-fixing solution.

In the above usable modes, the solution having a fixing ability of the invention is used as a fixing solution or bleach-fixing solution. When it is used as a bleach-fixing solution, the following organic acid ferric salts are added thereto. In these solutions, the content of thiocyanates is at least 0.1 mol/l, preferably 0.2 mol/ℓ to 3.2 mol/ℓ and especially 0.5 mol/ℓ to 2.0 mol/ℓ. The content of thiosulfates is at least 0.2 mol/ℓ, preferably 0.3 mol/ℓ to 2.8 mol/ℓ and especially 0.5 mol/ℓ to 1.8 mol/ℓ. It is preferable for negative film processing that the contents of thiocyanate and thiosulface are 0.3 mol/ℓ or more and 0.5 mol/ℓ or more respectively. In general, a low ammonium ion concentration has adverse effect on fixing, but the combined use of thiocyanates and thiosulfates provides a good fixing capability even at a low ammonium ion concentration.

The replenishment of the fixing solution or bleach-fixing solution is preferably in the range of 10 to 600 mℓ per m^2 of light-sensitive material.

The processing time in the fixing solution or bleach-fixing solution is preferably less than 120 seconds and especially in the range of 5 to 100 seconds.

The present invention exhibits a good desilvering capability particularly in a rapid processing. The term "processing time in the fixing solution or bleach-fixing solution" means a time from when the head of a light-sensitive material starts dipping into a fixing solution or bleach-fixing solution till the head comes out of the fixing solution or bleach-fixing solution.

In the invention, the ammonium ion content in the fixing solution or bleach-fixing solution is less than 50 mol%, preferably less than 20 mol% of the total cation content.

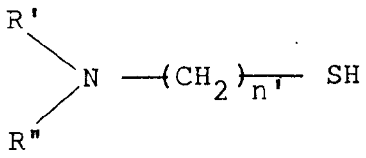
Suitable thiosulfates are sodium thiosulfate, ammonium thiosulfate and potassium thiosulfate; suitable thiocyanates include ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate.

The fixing solution or bleach-fixing solution may contain, singly or in combination, pH buffers comprising weak acids or salts such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate or ammonium hydroxide. Other usable compounds are alkali halides and ammonium halides such as potassium bromide, sodium bromide, sodium chloride, ammonium bromide; and alkylamines, polyethylene oxides. When ammonium salts are used, the amount of ammonium is required to be within the limit of the invention.

There may be added, to the fixing solution or bleach-fixing solution, compounds described in Japanese Patent O.P.I. Publication No. 295258/1989 and represented by the following Formula FA as well as exemplified compounds thereof. This addition allows, as additional effect, the fixing solution or bleach-fixing solution to process light-sensitive materials in small quantities over a long period of time, keeping the formation of sludge at a very low level.

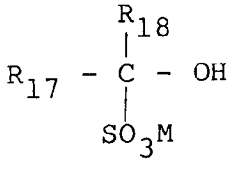
The compounds represented by Formula FA can be synthesized by such conventional methods as described in U.S. Patent Nos. 3,335,161 and 3,260,718. These compounds may be used singly or in combination. The addition thereof in an amount of 0.1 to 200 g per liter of processing solution gives favorable results.

Formula FA

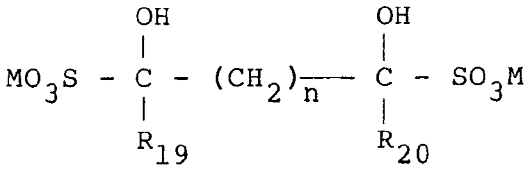


wherein R′ and R″ individually represent a hydrogen atom or an alkyl, aryl, aralkyl or nitrogen-containing heterocyclic group; and n′ represents 2 or 3.

The fixing solution or bleach-fixing solution may use sulfites or sulfite-releasing compounds, such as potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. Further, there are also contained compounds described in Japanese Patent Application No. 48931/1988 and represented by following formulas.



$$R_{17}-\overset{\displaystyle R_{18}}{\underset{\displaystyle SO_3M}{C}}-OH$$



$$MO_3S-\overset{\displaystyle OH}{\underset{\displaystyle R_{19}}{C}}-(CH_2)_n-\overset{\displaystyle OH}{\underset{\displaystyle R_{20}}{C}}-SO_3M$$

wherein R_{17} represents a hydrogen atom or alkyl group having 1 to 5 carbon atoms; R_{18} represents an alkyl group having 1 to 5 carbon atoms, which may have a substituent; M represents an alkali metal; R_{19} and R_{20} individually represent a hydrogen atom or alkyl group having 1 to 5 carbon atoms which may have a substituent; and n represents an integer of 0 to 4.

These sulfites and sulfite-releasing compounds are used in sulfite ion concentrations of at least 0.05 mol per liter of fixing solution or bleach-fixing solution, generally in a range of 0.08 mol/ℓ to 0.65 mol/ℓ, preferably in a range of 0.10 mol/ℓ to 0.50 mol/ℓ and especially in a range of 0.12 mol/ℓ to 0.40 mol/ℓ.

Further, silver may be recovered from the fixing solution or bleach-fixing solution according to known methods. Useful methods include the electrolyzing method (described in French Patent No. 2,299,667), precipitation method (described in Japanese Patent O.P.I. Publication No. 73037/1977, German Patent No. 2,331,220), ion exchange method (described in Japanese Patent O.P.I. Publication No. 17114/1976, German Patent No. 2,548,237) and metal displacement method (described in British Patent No. 1,353,805). In recovering silver, it is particularly preferable that the silver be recovered from processing baths by an inline method using electrolysis or anionic ion exchange resins in order to enhance effects of the invention and to facilitate rapid processing. But the silver is also preferably recovered from overflowed waste solutions in order to enhance effects of the invention and to facilitate rapid processing.

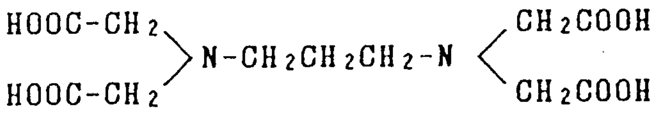
The bleaching solution used in combination with the bleach-fixing solution or fixing solution of the invention contains organic acid ferric complex salts represented by the above Formula A or B.

Next, the compound shown by Formula A is described in detail.

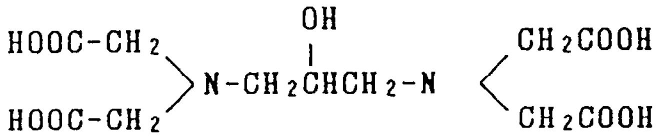
In Formula A, A_1 to A_4 are may be the same with or different from one another and independently represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$; M, M_1 and M_2 independently represent a hydrogen atom, alkali metal such as sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group such as propylene, butylene, pentamethylene, and the substituent is a hydroxyl group or alkyl group having 1 to 3 carbon atoms.

Preferable examples of the compound represented by Formula A are as follow:

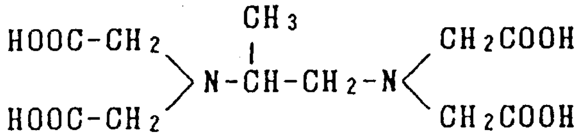
(A − 1)



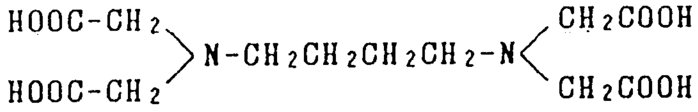
(A − 2)



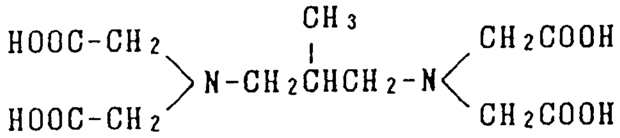
(A − 3)



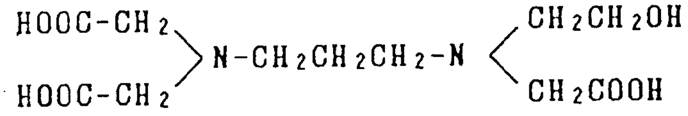
(A − 4)



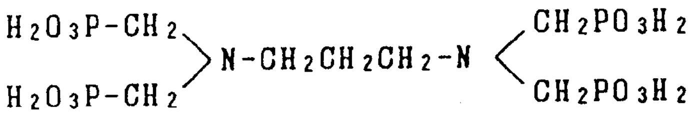
(A − 5)



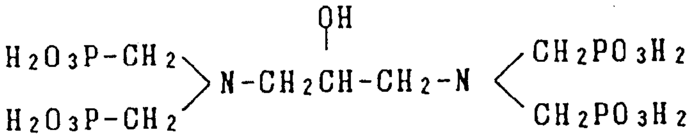
(A − 6)



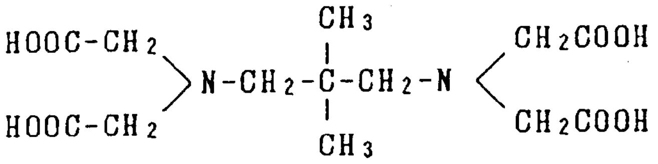
(A − 7)



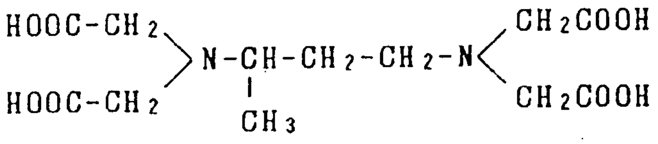
(A − 8)



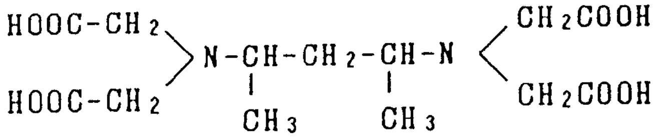
(A − 9)



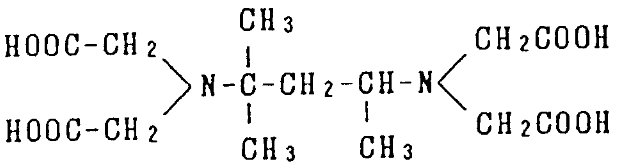
(A − 10)



(A − 11)



(A − 12)



As ferric complex salts of compounds (A-1) to (A-12), sodium salts, potassium salts or ammonium salts thereof may be arbitrarily used. Ammonium salts and potassium salts are preferably used in view of the effect of the invention and their solubilities.

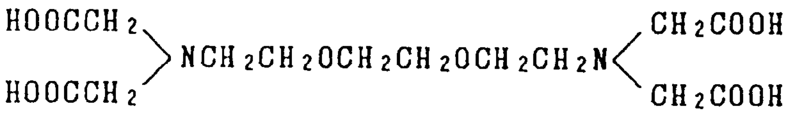
Among these exemplified compounds, (A-1), (A-3), (A-4), (A-5) and (A-9) are preferred, and (A-1) is especially preferred.

Next, the compound shown by Formula B is described in detail.

In Formula B, A_1 to A_4 are the same as those defined in Formula A; n represents an integer from 1 to 8; and B_1 and B_2 may be the same or different and independently represent a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms such as ethylene, propylene, butylene and pentamethylene group, and the substituent is a hydroxyl group or lower alkyl group having 1 to 3 carbon atoms such as methyl, ethyl and propyl group.

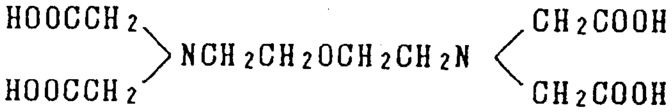
Preferable examples of the compound represented by Formula B are as follow:

(B − 1)



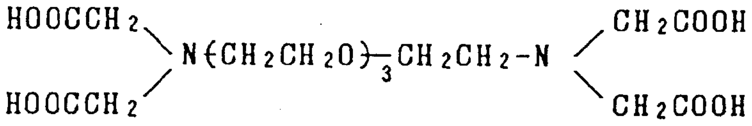
$$(HOOCCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2COOH)_2$$

(B − 2)



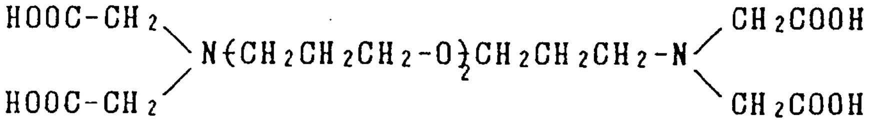
$$(HOOCCH_2)_2NCH_2CH_2OCH_2CH_2N(CH_2COOH)_2$$

(B − 3)



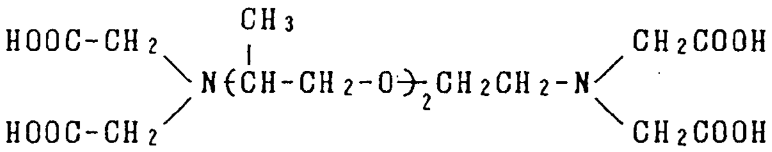
$$(HOOCCH_2)_2N(CH_2CH_2O)_3CH_2CH_2\text{-}N(CH_2COOH)_2$$

(B − 4)



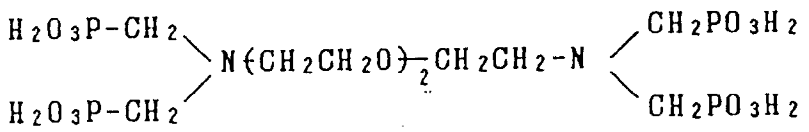
$$(HOOC\text{-}CH_2)_2N(CH_2CH_2CH_2\text{-}O)_2CH_2CH_2CH_2\text{-}N(CH_2COOH)_2$$

(B − 5)

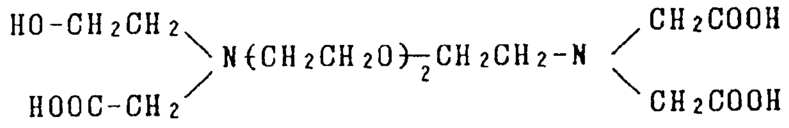


$$(HOOC\text{-}CH_2)_2N(CH(CH_3)\text{-}CH_2\text{-}O)_2CH_2CH_2\text{-}N(CH_2COOH)_2$$

(B - 6)



(B - 7)



As ferric complex salts of compounds (B-1) to (B-7), sodium salts, potassium salts or ammonium salts thereof may be arbitrarily used.

Among the above exemplified compounds, (B-1), (B-2) and (B-7) are preferred, and (B-1) is especially preferred.

The ferric complex salt of organic acid represented by Formula A or B is used in an amount of 0.1 mol or more per liter of the bleaching solution, preferably 0.2 mol or more, and especially in a range of 0.2 to 1.5 mol per liter.

The bleaching agent usable jointly with the compound of Formula A or B in the bleach fixing solution or the bleaching solution is, for example, a ferric complex salt of the following compound such as ammonium, sodium, potassium or triethanolamine salt.

(A′-1)	Ethylenediaminetetracetic acid
(A′-2)	Trans-1,2-cyclohexanediaminetetracetic acid
(A′-3)	Dihydroxyethylglycinic acid
(A′-4)	Ethylenediaminetetrakismethylene phosphonic acid
(A′-5)	Nitrilotrismethylene phosphonic acid
(A′-6)	Diethylenetriamine pentakismethylene phosphonic acid
(A′-7)	Diethylenetriamine pentacetic acid
(A′-8)	Ethylenediamine diorthohydroxyphenyl acetic acid
(A′-9)	Hydroxyethylethylenediamine triacetic acid
(A′-10)	Ethylenediamine dipropionic acid
(A′-11)	Ethylenediamine diacetic acid
(A′-12)	Hydroxyethylimino diacetic acid
(A′-13)	Nitrilotriacetic acid
(A′-14)	Nitrilotripropionic acid
(A′-15)	Triethylenetetramine hexacetic acid
(A′-16)	Ethylenediamine tetrapropionic acid

These organic acid ferric complex salts may be added in the form of complex salt, or ferric ion complexes may be formed in a solution using ferric salts such as ferric sulfate, ferric chloride, ferric acetate, ammonium ferric sulfate, ferric phosphate and aminopolycarboxylic acids or salt thereof. When added in the form of complex salt, these complex salts may be used singly or in combination. In case these complex salts are formed in a solution using ferric salts and aminopolycarboxylic acids, such ferric salts may be used singly or in combination of two or more kinds. Further, the aminocarboxylic acid may be used in an excess over an amount necessary to form a ferric complex salt in both cases.

In the bleaching solution containing the above ferric complex salt, there may be contained ions of metals other than iron such as cobalt, copper, nickel or zinc.

The ammonium ion content in the fixing solution or bleach-fixing solution used in the invention is preferably less than 50 mol% of the total cations, especially less than 20 mol% of the total cations. That is, the desilverizing ability is substantially improved by reducing the content of ammonium ions in the bleaching solution and using concurrently an organic acid ferric complex salt represented by Formula A or B such as 1,3-diaminopropane tetracetate as a bleaching agent.

In the bleaching solution may be used the inidazole compounds or compounds of Formulas I to IX described in the specification of Japanese Patent O.P.I. Publication No. 295258/1989 for the purpose of enhancing a rapid-bleaching capability.

Besides the above bleaching accelerator, there may be also used the compounds exemplified on pp. 51-115 of the specification of Japanese Patent O.P.I. Publication No. 123459/1987, the compounds exemplified on pp. 22-25 of the specification of Japanese Patent O.P.I. Publication No. 17445/1988 as well as the compounds described in Japanese Patent O.P.I. Publication Nos. 95630/1978 and 28426/1978.

These bleaching accelerators may be used singly or in combination. The addition amount thereof is generally in a range of about 0.01 to 100 g per liter of bleaching solution, preferably 0.05 to 50 g per liter and especially 0.05 to 15 g per liter.

The bleaching accelerators may be added as they are, but these are generally dissolved beforehand in water, alkalis or organic acids and then added; if necessary, organic solvents such as methanol, ethanol and acetone may be used to dissolve them.

The pH of the bleaching solution is normally 5.5 or less, preferably 2.5 to 5.5. Here, the pH of the bleaching solution means the pH of a solution in a processing bath where a silver halide light-sensitive material is being processed, and is clearly distinguished form the pH of a replenishing solution.

The bleaching solution is used in a temperature range of preferably 20°C to 50°C, especially 25°C to 45°C.

The processing time with the bleaching solution is normally less than 50 seconds for color paper, and preferably more than 3 seconds and less than 40 seconds. For color negative film, processing of less than 90 seconds is preferred, and that of more than 10 seconds and less than 60 seconds is particularly preferred. The term "processing time with the bleaching solution" used here means a time from when the head of a light-sensitive material starts to dip into a bleaching solution till the head comes out of the bleaching solution.

Halides such as ammonium bromide, potassium bromide and sodium bromide may be generally added to the bleaching solution, but non-ammonium cationic salts are preferred because of the need to be free of ammonium. Further, fluorescent brightening agents, defoamers and surfactants can be also contained.

Replenishment of the bleaching solution for color paper is made in an amount of less than 100 mℓ per square meter of light-sensitive material, preferably more than 10 mℓ and less than 50 mℓ per square meter; and that for color negative film is normally less than 200 mℓ per square meter of light-sensitive material, preferably more than 30 mℓ and less than 180 mℓ per square meter. The effect of the present invention becomes larger with the decrease in replenishing quantities.

In embodying the invention, the activity of the bleaching solution or bleach-fixing solution may be enhanced, if desired, by blowing oxygen or air into a processing bath and a replenishing solution tank, or by adding thereto suitable oxidizing agents such as hydrogen peroxide, bromates and persulfates.

In the processing according to the invention, it is preferable that the bleaching solution or bleach-fixing solution, or the fixing solution or bleach-fixing solution be subjected to forced stirring in order to impart a rapid processability. The forced stirring means to stir the solution forcedly with a stirring means mounted thereon, unlike the usual diffusive shifting of the solution. As means for forced stirring, there may be used the means described in Japanese Patent O.P.I. Publications No. 222259/1989 and No. 206343/1989.

In the present invention, a favorable effect is obtained on bleach fogging, in addition to the primary effect of the invention, by setting a crossover time of 10 seconds or less , preferably 7 seconds or less, for each of the crossovers between tanks such as that from the color developer tank to the bleaching tank. Another preferable embodiment of the invention is to reduce the amount of a processing solution brought in together with a light-sensitive material by attaching a duckhill valve and the like thereto.

In the invention, the processing with the processing solution having a fixing ability is followed by a stabilizing process with a stabilizing solution.

It is preferable that such a stabilizing solution contain a chelating agent having a chelate stability constant of 8 or more with respect to iron ions. The term "chelate stability constant" used here means the constant which is publicly known by L.G. Sillen and A.E. Martell, "Stability Constants of Metal-ion Complexes", The Chemical Society, London (1964), S. Chaberek and A.E. Martell, "Organic Sequestering Agents", Willey (1959).

As chelating agents having a chelate stability constant of 8 or more, there are used organic carboxylic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxy compounds. In the above description, iron ions mean ferric ions (Fe^{3+}).

Examples of the chelating agent having a chelate stability constant of 8 or more are shown below, but useful compounds are not limited to them; namely, ethylenediaminediorthohydroxyphenylacetic acid, diaminopropanetetracetic acid, nitrilotriacetic acid, hydroxyethylenediamine triacetic acid, dihydroethyl glycine, ethylenediaminediacetic acid, ethylenediamine-dipropionic acid, iminodiacetic acid, diethylenetriamine-pentacetic acid, hydroxyethylimonodiacetic acid, diaminoipropanol tetracetic acid, transcyclohexanediamine-tetracetic acid, glycoletherdiaminetetracetic acid, ethylenediaminetetramethylenephosphonic acid, nitrilotrimethylenephsphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-diphosphonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate. Among them, diethylenetriaminepentacetic acid, nitrilotriacetic acid, nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid are preferred, and 1-hydroxyethylidene-1,1-diphosphonic acid is particularly preferred.

It is preferable for enhancing effects of the invention that these chelating agents each are used in an amount of 0.01 to 50 g, preferably 0.05 to 20 g per liter of stabilizing solution.

Further, compounds which are favorably added to the stabilizing solution are ammonium compounds. Examples of such ammonium compounds are ammonium hydroxide, ammonium bromide, ammonium carbonate, ammonium chloride, ammonium hypophsphite, ammonium phosphate, ammonium phosphite, ammonium fluoride, acid ammonium fluoride, ammonium fluoroborate, ammonium arsenate, ammonium hydrogencarbonate, ammonium hydrogen fluoride, ammonium hydrogensulfate, ammonium sulfate, ammonium iodide, ammonium nitrate, ammonium pentaborate, ammonium acetate, ammonium adipate, ammonium laurintricarboxylate, ammonium benzoate, ammonium carbamate, ammonium citrate, ammonium diethyldithiocarbamate, ammonium formate, ammonium hydrogenmalate, ammonium hydrogenoxalate, ammonium phthalate, ammonium hydrogentartrate, ammonium thiosulfate, ammonium sulfite, ammonium ethylenediamine tetracetate, ammonium ferric ethylenediaminetetracetate, ammonium lactate, ammonium malate, ammonium maleate, ammonium oxalate, ammonium phthalate, ammonium picrate, ammonium pyrrolizinedithiocarbamate, ammonium salicylate, ammonium succinate, ammonium sulfanilate, ammonium tartarate, ammonium thioglycolate and ammonium 2,4,6-trinitrophenol. These may be used singly or in combination. The addition amount of these ammonium compounds is in the range of 0.001 to 1.0 mol, preferably 0.002 to 2.0 mols per liter of stabilizing solution. Use of these ammonium compounds is effective not only for enhancing effects of the invention but also for improving stability of images formed on the processed light-sensitive material.

Further, the stabilizing solution contains preferably sulfites. Such sulfites may be any of organic and inorganic ones which are capable of releasing sulfite ions; but, preferred examples are inorganic salts such as sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. These sulfites are added to the stabilizing solution, for their capability of preventing stains, in an amount at least 1 X 10^{-3} mol/ℓ, preferably in an amount of 5 X 10^{-3} to 10^{-1} mol/ℓ. These may be directly added to the stabilizing solution, but the addition to a replenishing solution is preferred. These sulfite compounds are effective not only for enhancing effects of the invention but also for inhibiting stain formed on the processed light-sensitive material.

In order to effectively prevent formation of floats, the stabilizing solution may contain N-methylol compounds,hexamethylenetetramine or triazine-type compounds.

The stabilizing solution contains preferably metal salts in combination with the above chelating agent. 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 can be fed in the form of inorganic salts such as halides, hydroxides, sulfates, carbonates, phosphates or acetates, or as water-soluble chelated agents. The addition amount thereof is 1 X 10^{-4} to 10^{-1} mol, preferably 4 X 10^{-4} to 2 X 10^{-2} mol per liter of stabilizing solution.

There may be added to the stabilizing solution organic acids such as citric acid, acetic acid, succinic acid, oxalic acid, benzoic acid; pH regulators such as phosphates, borates, hydrochlorides, sulfates; and fungicides. These compounds may be used, in any combination, in an amount within the limits necessary to maintain the pH of the stabilizing solution at a proper value and causing no deposits and no adverse effect on the stability of color images during storage.

Preferred fungicides for the stabilizing solution are hydroxybenzoates, phenol compounds, thiazole compounds, pyridine compounds, guanidine compounds, carbamate compounds, morpholine compounds, quaternary phosphonium compounds, quaternary ammonium compounds, urea compounds, isoxazole compounds, propanolamine compounds, sulfamide compounds, aminoic acid compounds, active-halogen-releasing compounds and benzotriazole compounds.

Among the above fungicides, the preferred are phenol compounds, thiazole compounds, pyridine compounds, guanidine compounds, quaternary ammonium compounds, active-halogen-releasing compounds and benzotriazole compounds; and phenol compounds, thiazole compounds, active-halogen-releasing compounds and benzotriazole compounds are particularly preferred in view of preservability of the solution.

The addition amount of these fungicides to the stabilizing solution is 0.001 to 50 g per liter of stabilizing solution, preferably 0.005 to 10 g per liter.

The stabilizing solution may contain surfactants. Suitable examples of the surfactant include the compounds represented by Formula I or II described in Japanese Patent O.P.I. Publication No. 250449/1987 as well as water-soluble organic siloxane compounds.

In the processing according to the invention, silver may be recovered from the stabilizing solution also by the methods described above, or by subjecting the stabilizing solution to a treatment of ion exchange, electrodialysis or reverse osmosis (see Japanese Patent O.P.I. Publication No. 28949/1986. It is preferable that water used in the stabilizing solution be deionized beforehand, because this helps enhance a mildewproof capability, stability of the stabilizing solution and image preservability. While there may be used any of deionizing measures which can reduce the Ca and Mg ion content of treated water to less than 5 ppm, treatments with ion exchange resins or reverse osmosis membranes are preferably used singly or in combination from the viewpoint of reducing washer liquid. Ion exchange resins and reverse osmosis membranes are described in detail in KOKAIGIHOU No. 87-1984.

It is preferable that the salt concentration of the stabilizing solution be less than 1,000 ppm and especially less than 800 ppm.

In order to enhance the effect of the invention, it is preferable that soluble iron ions be present in the stabilizing solution.

The soluble iron ions are contained in the stabilizing solution at a concentration of at least 5×10^{-3} mol/ℓ preferably in a range of 8×10^{-3} to 150×10^{-3} mol/ℓ, and especially in a range of 12×10^{-3} to 100×10^{-3} mol/ℓ. These soluble iron ions may be added to the stabilizing bath by being added to a replenising stabilizing solution, or they may be added to a light-sensitive material in order to make them dissolve in the stabilizing bath, or to the preceding processing bath so that they are attached to a light-sensitive material and brought into the stabilizing bath.

Further, the stabilizing solution may use the fluorescent brightening agents (E-1 to E-45) shown on pages 28-32 of the specification of Japanese Patent Application No. 146957/1990.

In the present invention, pH of the stabilizing solution is preferably 5.5 to 10.0. pH regulators used in the stabilizing solution may be any of conventional alkali agents and acid agents.

In the stabilizing process, processing temperature is normally 15°C to 70°C, preferably 20°C to 55°C; processing time is normally less than 120 sec, preferably 3 to 90 sec and especially 6 to 50 sec.

The replenished amount of the stabilizing solution is preferably 0.1 to 50 times, and especially 0.5 to 30 times the amount of solution brought from the preceding bath or bleach-fixing bath per unit area of a light-sensitive material, in view of rapid processing capability and image preservability.

It is preferable that the stabilizing unit have a plural tank structure. The number of tanks is generally from 2 to 6, and preferably from 2 to 3. The particularly preferred is to used two tanks connected in the counter current mode in which the solution is fed to the succeeding bath and overflows from the preceding bath.

No washing is required after stabilization, but a short-time rinsing or surface cleaning with a small amount of water may be made if necessary.

While aminophenol compounds and p-phenylenediamine compounds are available as color developing agents used in color developing process, p-phenylenediamine compounds which possess water-soluble groups are preferred in the invention.

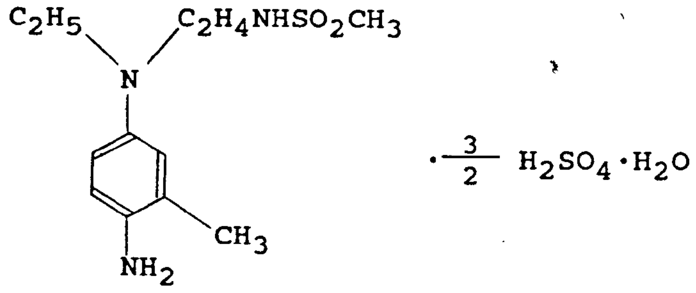
At least one of such water-soluble groups is present on an amino group or benzene ring. Preferable examples of the water-soluble group are:

$-(CH_2)_n-CH_2OH$,
$-(CH_2)_m-NHSO_2-(CH_2)_n-CH_3$,
$-(CH_2)_m-O-(CH_2)_n-CH_3$,
$-(CH_2CH_2O)_nC_mH_{2m+1}$

wherein m and n each represent an integer larger than zero, $-COOH$, and $-SO_3H$.

Typical examples of the preferred color developing agent are as follows:

(A - 1)



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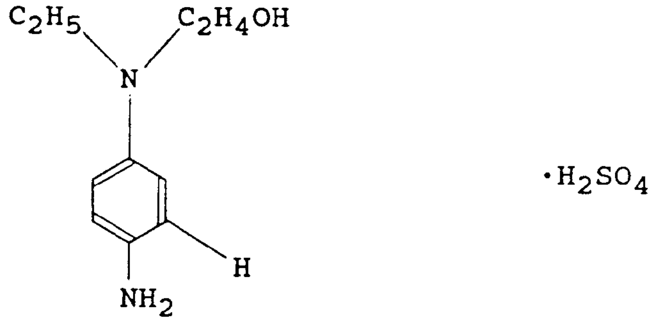

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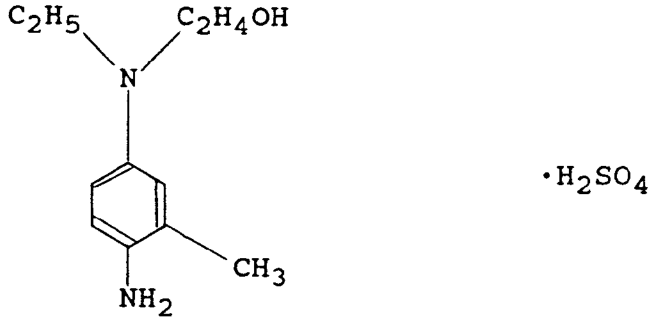

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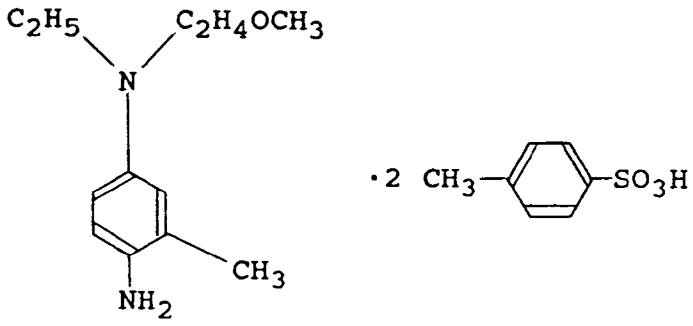

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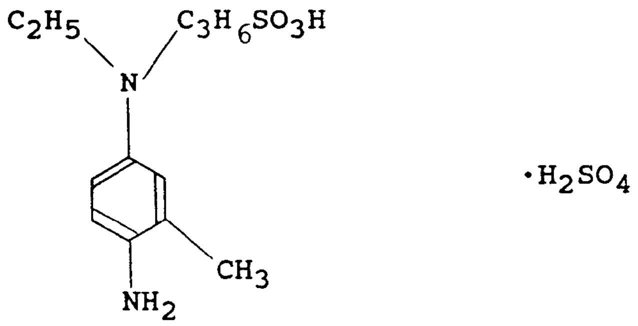
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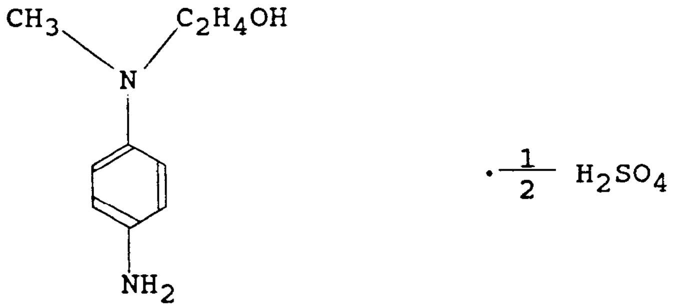
N
CH3
NH2
·H2SO4

(A - 6)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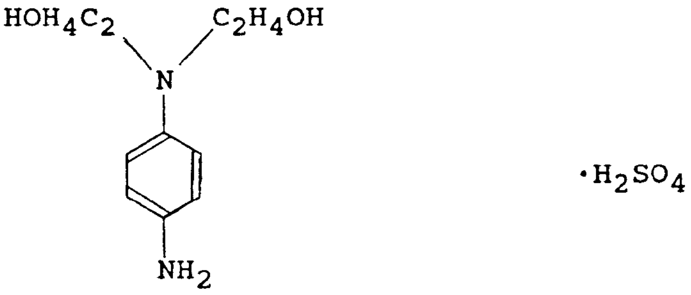
C2H4OH
N
NH2
· 1/2 H2SO4

(A - 7)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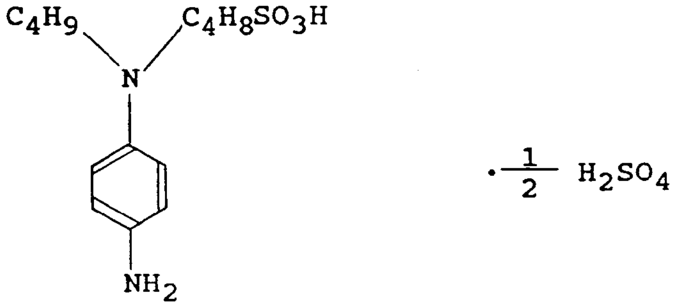
C2H4OH
N
NH2
·H2SO4

(A - 8)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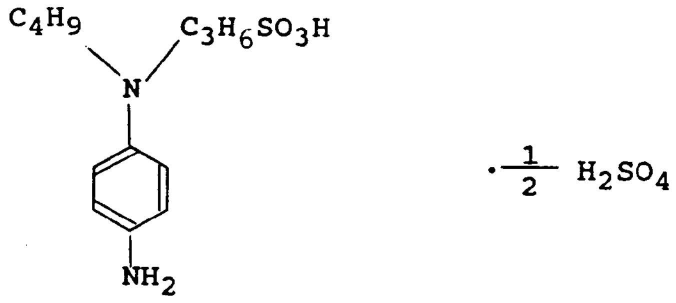
N
NH2
· 1/2 H2SO4

(A - 9)



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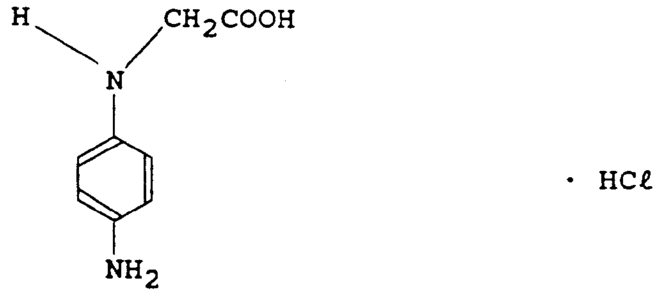

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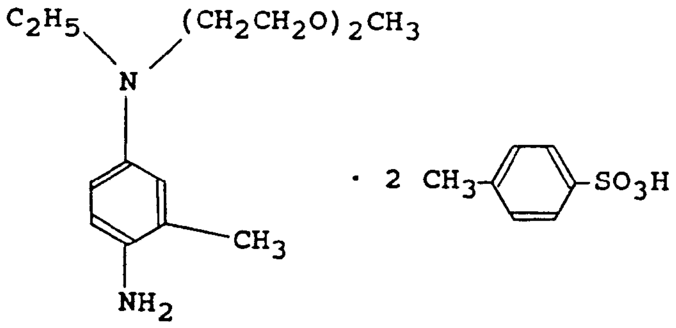

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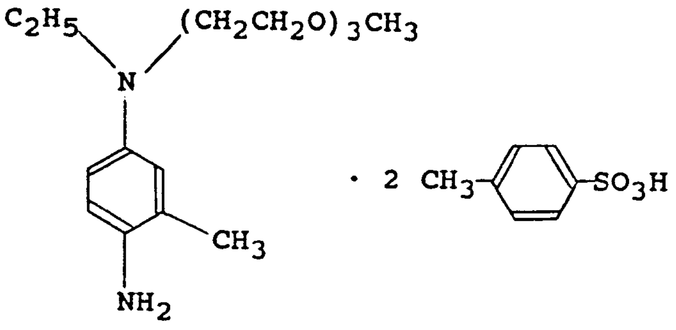

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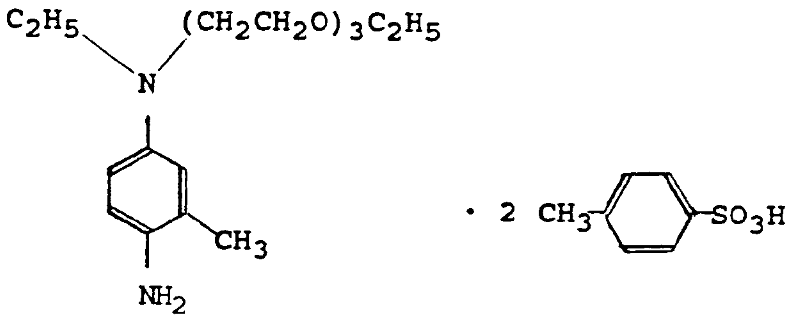
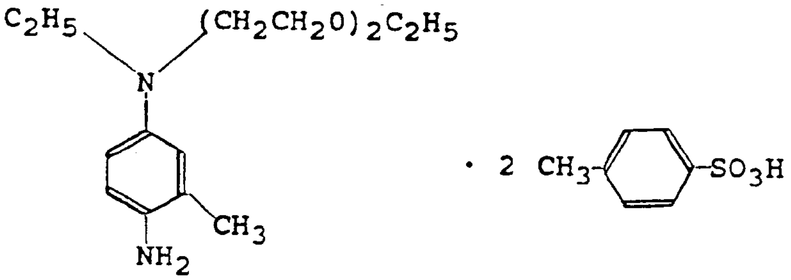


(A - 14)



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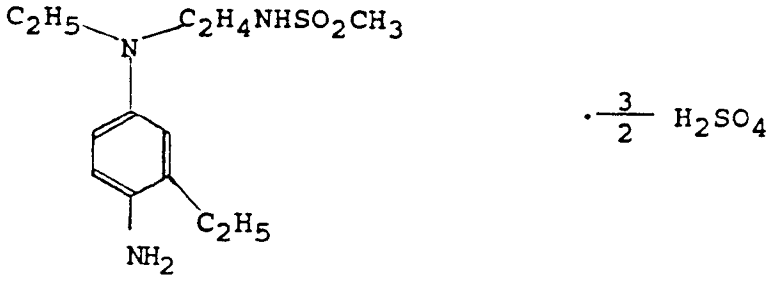
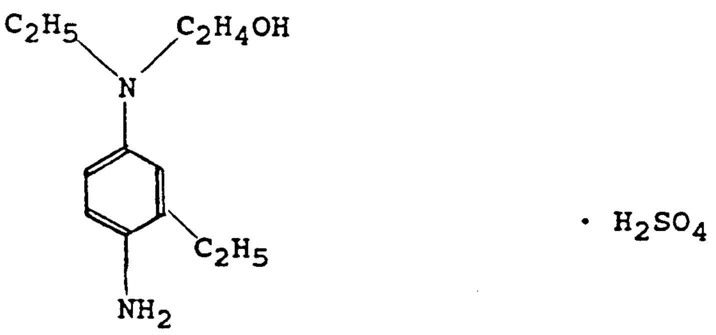


(A - 16)



[Exemplified color developing agents]

Among the above color developing agents, preferred compounds are (A-1), (A-2), (A-3), (A-4), (A-6), (A-7),(A-15); particularly (A-1) and (A-3).

In general, these color developing agents are used in the form of salts such as hydrochlorides, sulfates or p-toluenesulfonates.

The addition amount of the color developing agent is more than 0.5 X 10 $^{-2}$ mol per liter of color developer, preferably in a range of 1.0 X 10 $^{-2}$ to 1.0 X 10 $^{-1}$ per liter, and especially 1.5 X 10 $^{-2}$ to 7.0 X 10 $^{-2}$ per liter.

In the color developer used color developing process, there may be contained conventional alkali agents such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sidium carbonate, potassium carbonate, sodium sulfate, sodium metaborate and borax. Other usable additives are benzyl alcohol; alkali halides such as potassium bromide and potassium chloride; development control agents such as citrazinic acid; preservatives such as hydroxylamine, hydroxylamine derivatives such as diethylhydroxylamine,and hydrazine derivatives such as hydrazinodiacetic acid,and sulfites.

Moreover, there may be optionally used defoamers surfactants or organic solvent such as methanol, dimethylformamide and dimethylsulfoxide.

The pH of the color developer is normally more than 7, preferably 9 to 13.

According to a specific requirement, the color developer may use anti-oxidants such as tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, aromatic secondary alcohols, hydroxamic acid, pentose, hexose, pyrogallol-1,3-dimethyl ether.

In the color developer, various chelating agents may be contained as a sequestering agent. Examples of the chelating agent include aminopolycarboxylic acids such as ethylenediaminetetracetic acid and diethylenetriaminepentacetic acid; organic phosphonic acids such as 1-hydroxyethylidene-1.1-diphosphonic acid; amonopolyphosphonic acids such as aminotri(methylene phosphonic acid) and ethylenediaminetetraphophoric acid; oxycarboxylic acids such as citric acid and gluconic acid; phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarbonic acid; and polyphosphoric acids such as tripolyphosphoric acid and hexametaphosphoric acid.

In a continuous processing of color negative film, the color developer is replenished in an amount of less than 1,500 mℓ, preferably in a range of 250 mℓ to 900 mℓ and especially 300 mℓ to 700 mℓ per square meter of light-sensitive material. For a continuous processing of color paper, an amount of 20 mℓ to 300 mℓ is preferred, and an amount of 30 mℓ to 160 mℓ is particularly preferred.

Silver halide grains contained in the light-sensitive material may be any of silver chloride, silver chlorobromide, silver iodobromide and silver chloroiodobromide. In case the light-sensitive material is a color photographic paper, silver chloride-rich silver halide grains containing at least 80 mol% of silver chloride is favorably used. In this case, the silver chloride content is generally more than 90 mol%, preferably more than 95 mol%, and especially more than 99 mol%. Such a silver chloride-rich silver halide emulsion may contain, as a silver halide component, silver bromide and/or silver iodide in addition to silver chloride. In this case, the amount of silver bromide is generally less than 20 mol%, preferably less than 10 mol%, and especially less than 3 mol%. When silver iodide is present, its amount is generally less than 1 mol%, preferably less than 0.5 mol% and especially zero. Such silver chloride-rich silver halide grains containing more than 80 mol% of silver chloride is preferably used at least in one silver halide emulsion layer, especially in all silver halide emulsion layers.

In case the light-sensitive material is a color photographic negative film, there is favorably used silver iodobromide of which silver iodide content is more than 2 mol%, preferably more than 5 mol%. Said silver halide composition is preferably used at least in one silver halide emulsion layer, especially in all silver halide emulsion layers.

The crystal form of the above silver halide grains may be of regular crystal or twin crystal, and the ratio of [100] faces to [111] surfaces may be any value. Further, the crystal structure thereof may be uniform from outer portion to inner portion of the grain, or may be a layer structure, core/shell type, different from outer portion to inner portion of the grain. These silver halides may be ones in which latent images are mainly formed on the surface of grains, or ones in which latent images are mainly formed inside of grains. Moreover, there may also be used tabular silver halide grains, see Japanese Patent O.P.I. Publication Nos. 113934/1983 and 170070/1984 as well as silver halide grains described in Japanese Patent O.P.I. Publication Nos. 26837/1989, 26838/1989 and 77047/1989.

The above silver halide grains can be prepared by any of the acid method, neutral method and ammoniacal method, or by combination thereof. For example, silver halide grains are prepared by steps of making seed grains by the acid method, and then growing the seed grain to a prescribed size by the ammoniacal method which allows them to grow faster. In growing silver halide grains, it is preferable that pH and pAg in the reaction vessel be controlled, and that silver ions and halogen ions be simultaneously added in amounts corresponding to the growth rate of silver halide grains as described, for example, in Japanese Patent O.P.I. Publication No. 48521/1979.

Silver halide emulsion layers of the light-sensitive material to be processed according to the invention contains color couplers. These color couplers react with an oxidation product of color developing agent to form non-diffusible dyes. The color couplers are advantageously united, in the non-diffusible state, in a light-sensitive layer or closely adjoining thereto.

Thus, a red-sensitive layer can contain non-diffusible color couplers, for example, phenol or α-naphthol type couplers which forms cyan-color images; a green-sensitive layer can contain at least one non-diffusible color coupler, for example, a 5-pyrazolone type coupler and pyrazolotriazole usually which form magenta-color images; and a blue-sensitive layer can contain at least one non-diffusible color coupler, for example, a color coupler generally having an open chain ketomethylene group which forms yellow-color images. These color couplers may be a six-, four- or two-equivalent coupler.

In the invention, two-equivalent couplers are particularly preferred.

Suitable couplers are disclosed, for example, in the following publications: W. Pelz, "Farbkuppler (Color Coupler)" on p.111 of Mitteilungln ausden Forshungslaboratorien der Agfa (Research Papers of Agfa), vol. III, Leverkusen/Munchen (1961); K. Venkataraman, The Chemistry of Synthetic Dyes", vol. 4, pp. 341-387, Academic Press and The Theory of the Photographic Process", 4th ed., pp. 353-362; and Research Disclosure No. 17643, sec. VII.

In view of the effect of the invention, it is preferred to use magenta couplers represented by Formula M-1 given on page 26 of the specification of Japanese Patent O.P.I. Publication No. 106655/1988 examples thereof are Nos. 1 to 77 on pages 29-34 of the same specification; cyan couplers represented by Formula C-I or C-II given on 34 page of the same specification, examples thereof are (C′-1) to (C′-82) and (C″-1) to (C″-36) on pages 37-42 of the specification; and high-sensitive yellow couplers described on 20 page of the same specification,examples thereof are (Y′-) to (Y′-39) on pages 21-26 of the specification.

Use of a nitrogen-containing heterocyclic mercapto compound in a light-sensitive material is a preferred mode for the invention, because it not only brings out the effect of the invention, but also minimizes adverse effect on photographic properties when the bleacher solution or bleach-fixing solution is mixed in the developer solution.

Examples of the nitrogen-containing heterocyclic mercapto compound include exemplified compounds (I′-1) to (I′-87) on pages 42-45 of the specification of Japanese Patent O.P.I. Publication No. 106655/1988.

While silver halide emulsions may be prepared according to conventional methods, for example, single-jet inflow or double-jet inflow of raw materials at a constant speed or accelerated speed, preparation by the double-jet inflow method under a controlled pAg value is particularly preferred see Research Disclosure No. 17643, sec. I and II.

These emulsions may be chemically sensitized. Addition of a sulfur-containing compound such as allylisothiocyanate, allylthiourea or thiosulfate is particularly preferred. Reducing agents can also be used as a chemical sensitizer; examples thereof include silver compounds such as those described in Belgian Patent Nos. 493,464 and 568,687; polyamines such as diethylenetriamine described in Belgian Patent Nos. 547,323; and aminomethylsulfine derivatives. Precious metals such as gold, platinum, palladium, iridium, ruthenium and rhodium as well as compounds thereof are also useful sensitizers. This chemical sensitization is described by R. Kosiovsky in Z. Wiss. Photo., vol. 46, pp.65-72 (1951) (see the above Research Disclosure No. 17643, sec. III, too).

These emulsions may be optically sensitized according to conventional methods using, for example, polymethine dyes such as neutrocyanine, basic or acid carboxycyanine, rhodacyanine and hemicyanine; styryl dyes; and oxonol and analogues thereof. Refer to F.M. Harmer, "Cyanine Dyes and Related Compounds" (1964), "Ullmanns Enzyklopadie der technischen Chemie" 4th ed., vol. 18, p. 431, and the above Research Disclosure No. 17643, sec. IV.

The emulsions may use usual antifoggants and stabilizers. Azaindenes are suitable stabilizers; tetra- and penta-azaindene are preferred, and those substituted by a hydroxy or amino group are particularly preferred. These compounds appear, for example, in Birr's paper on Z. Wiss. Photo., vol. 47 (1952), pp. 2-58, and the above Research Disclosure No. 17643, sec. IV.

These components of a light-sensitive material can be incorporated by conventional methods; usable methods can be seen, for example, in U.S. Patent Nos. 2,322,027, 2,533,514, 3,689,271, 3,764,336 and 3,765,897.

Some components such as couplers and UV absorbents can be incorporated in the form of charged latex as disclosed in German Offenlegungsschrift No. 2,541,274 and European Patent Application 14,921. Further, some components can be fixed as a polymer in a light-sensitive material as described in German Offenlegungsschrift No. 2,044,992, U.S. Patent Nos. 3,370,952 and 4,080,211.

Light-sensitive materials to be processed according to the invention may use conventional supports. Color papers, for example, can use reflective supports such as paper supports which may be covered with polyolefin such as polyethylene or polypropylene (Refer to the above Research Disclosure No. 17643 sec. V and VI.

Further, light-sensitive materials of incorporated coupler type, can be used in any of color paper, color negative film, color positive film, color reversal film for slide, color reversal film for movie, color reversal film for TV and reversal color paper.

EXAMPLES

Multilayered silver halide color photographic light-sensitive material (1) was prepared by forming the layers having the following compositions on a titanium-containing polyethylene side of a paper support laminated with titanium-containing polyethylene on one side and with polyethylene on the other side. Coating solutions were prepared in the following manner.

Coating solution for 1st layer

There were dissolved 26.7 g of yellow coupler (Y-1), 10.0 g of dye-image stabilizer (ST-1), 6.67 g of dye-image stabilizer (ST-2) and 0.67 g of additive (HQ-1)in 6.67 g of high boiling solvent (DNP) and 60 mℓ of ethyl acetate. The solution was then dispersed in 220 mℓ of a 10% aqueous solution of gelatin containing 7 mℓ of 20% surfactant (SU-1) with a supersonic homogenizer to prepare a yellow coupler dispersion. The dispersion obtained was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared by the following procedure, so that 1st coating solution was prepared.

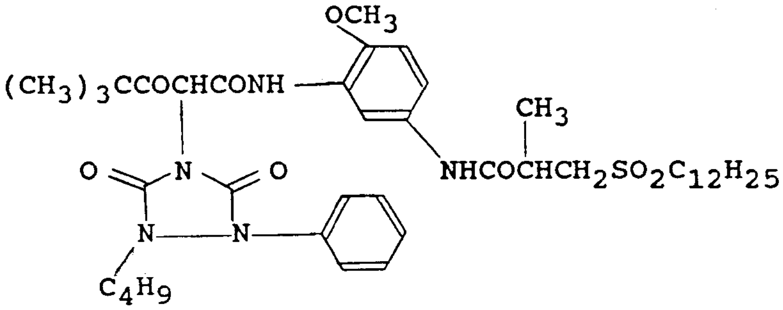
Coating solutions for 2nd to 7th layers were prepared in manners similar to that with coating solution for 1st layer.

As hardeners, (H-1) was added in 2nd and 4th layers, and (H-2) in 7th layer. As a coating aid, surfactant (SU-2) and (SU-3) were added to adjust surface tension.

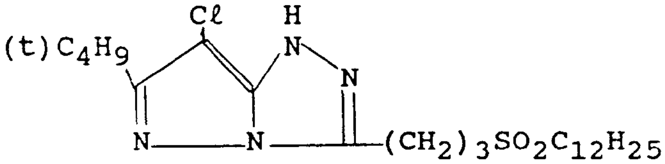
Layer	Composition	Addition amount (g/m^2)
Layer 7 (Protective layer)	Gelatin	1.0
Layer 6 (Ultraviolet absorbing layer)	Gelatin UV absorbent (UV-1) UV absorbent (UV-2) UV absorbent (UV-3) Antistaining agent (HQ-1) DNP PVP Anti-irradiation dye (AI-2)	0.4 0.10 0.04 0.16 0.01 0.2 0.03 0.02
Layer 5 (Red-sensitive layer)	Gelatin Red-sensitive silver chlorobromide emulsion (EmC) Cyan coupler (C-1) Cyan coupler (C-2) Dye image stabilizer (ST-1) Antistaining agent (HQ-1) HBS-1 DOP	1.30 0.21 0.17 0.25 0.20 0.01 0.20 0.20
Layer 4 (UV absorbing layer0	Gelatin UV absorbent (UV-1) UV absorbent (UV-2) UV absorbent (UV-3) Antistaining agent (HQ-1) DNP	0.94 0.28 0.09 0.38 0.03 0.40

Layer	Composition	Addition amount (g/m^2)
Layer 3 (Green-sensitive layer)	Gelatin	1.40
	Green-sensitive silver chlorobromide emulsion (EmB)	0.17
	Magenta coupler (M-1)	0.35
	Dye image stabilizer (ST-3)	0.15
	Dye image stabilizer (ST-4)	0.15
	Dye image stabilizer (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 chloro bromide emulsion EmA in terms of 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	

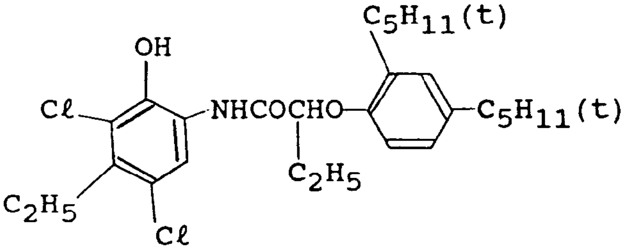
Y - 1



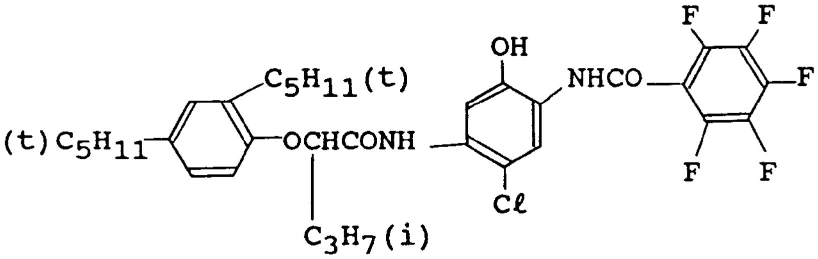
M - 1



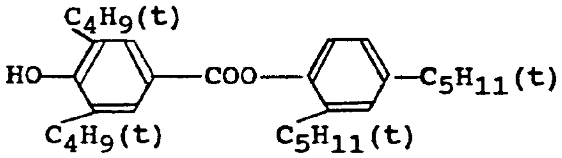
C - 1



C - 2



ST - 1



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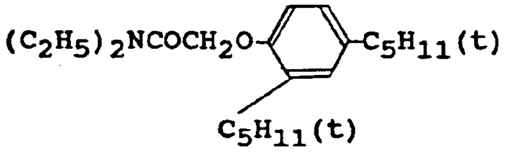
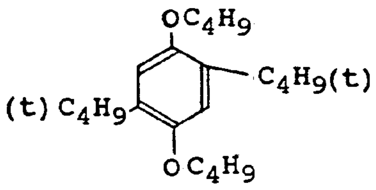
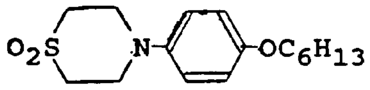


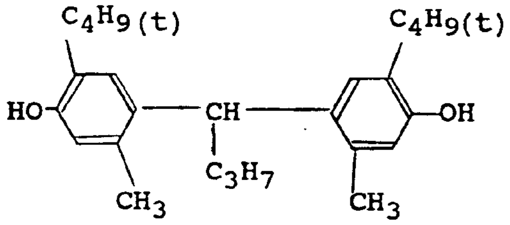
ST - 3



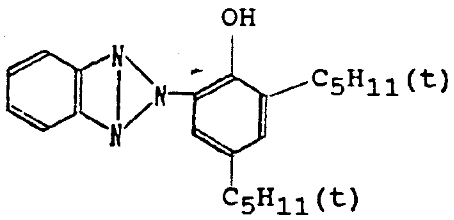
ST - 4



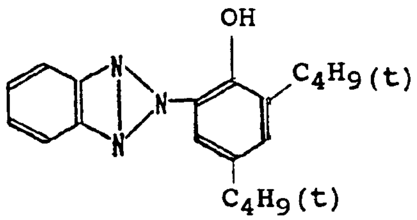
ST - 5



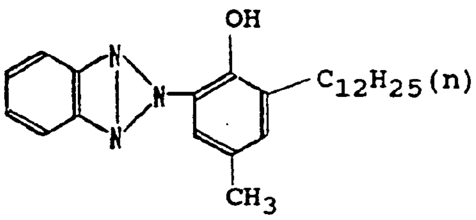
UV - 1



UV - 2

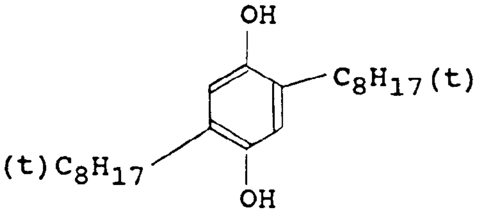


UV - 3

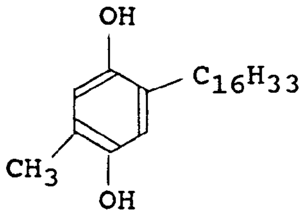


DOP	Dioctyl phthalate	DNP	Dinoyl phthalate
DIDP	Diisodecyl phthalate	PVP	Polyvinylpyrrolidone

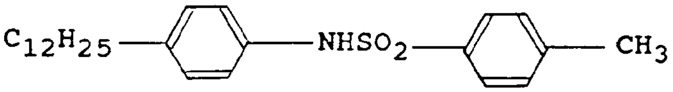
HQ - 1



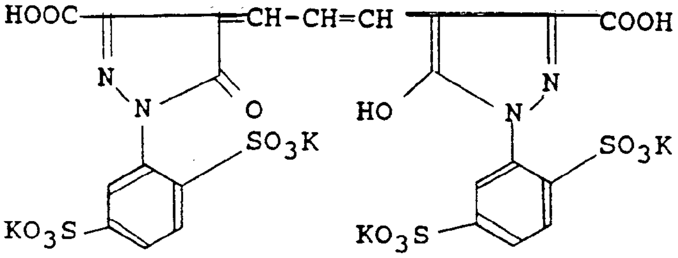
HQ - 2



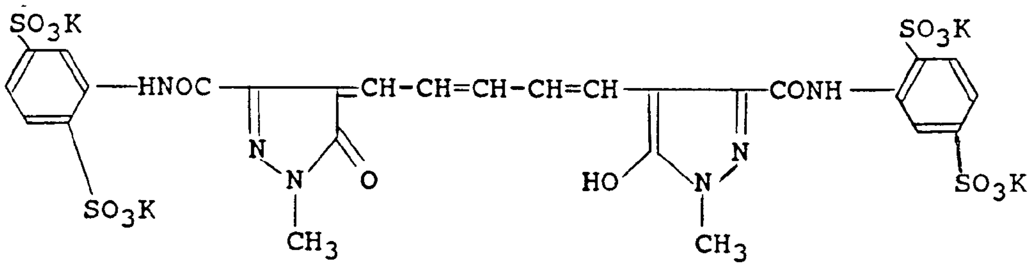
HBS - 1



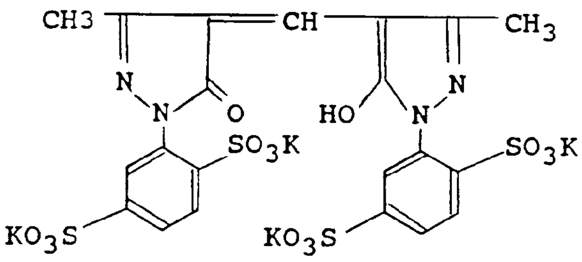
AI - 1



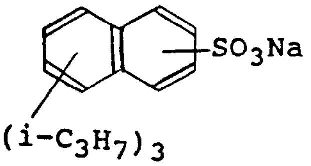
AI - 2



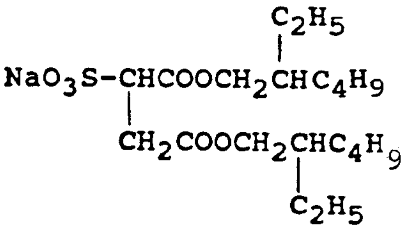
AI - 3



SU - 1

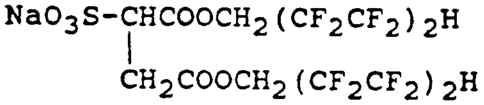


SU - 2



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

SU - 3

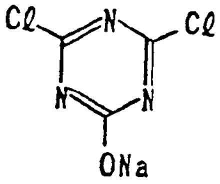


$$NaO_3S-\underset{CH_2COOCH_2(CF_2CF_2)_2H}{CH}COOCH_2(CF_2CF_2)_2H$$

H - 1

$C(CH_2SO_2CH=CH_2)_4$

H - 2



Preparation of blue-sensitive silver halide emulsion

The following solution A and solution B were added over a period of 30 minutes to 1,000 mℓ of a 2% aqueous solution of gelatin kept at 40°C, while maintaining pAg at 6.5 and pH at 3.0. Then, the following solution C and solution D were simultaneously added thereto over a period of 180 minutes, while maintaining pAg at 7.3 and pH 5.5.

During the addition, pAg was controlled according to the method described in Japanese Patent O.P.I. Publication No. 45437/1984, control of pH was made with an aqueous solution of sulfuric acid or that of sodium hydroxide.

(Solution A)

Sodium hydroxide	3.42 g
Potassium bromide	0.03 g
Water added to make	200 mℓ

(Solution B)

Silver nitrate	10 g
Water added to make	200 mℓ

(Solution C)

Sodium hydroxide	102.7 g
Potassium bromide	1.0 g
Water added to make	600 mℓ

(Solution D)

Silver nitrate	300 g
Water added to make	600 mℓ

After addition, the emulsion obtained was subjected to desalination with a 5% solution of Demol N (product of Kao Atlas) and a 20% aqueous solution of magnesium sulfate, and then mixed with an aqueous solution of gelatin.

Monodispersed cubic emulsion EMP-1 thus prepared had an average grain size of 0.85μm, variation coefficient (σ/r) of 0.07, and silver chloride content of 99.5 mol%. In the above, σ is a standard deviation of the grain size distribution and r is an average grain size of the emulsion.

Blue-sensitive silver halide emulsion Em-B was prepared by subjecting the above emulsion EMP-1 to chemical sensitization for 90 minutes at 50°C using the following compounds.

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

There was prepared monodispersed cubic emulsion EMP-2 having an average grain size of 0.43 μm, variation coefficient (σ/r) of 0.08, and silver chloride content of 99.5 mol% in the same manner as with EMP-1, except that the addition time of solution A & solution B and that of solution C & solution D were changed.

Green-sensitive silver halide emulsion Em-G was prepared by subjecting emulsion EMP-2 to chemical sensitization for 120 minutes at 55°C using the following compounds.

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

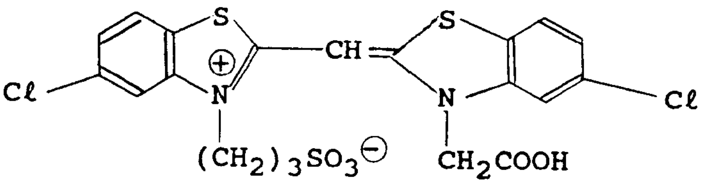
Preparation of red-sensitive silver halide emulsion

There was prepared monodispersed cubic emulsion EMP-3 having an average grain size of 0.50 μm, variation coefficient (σ/r) of 0.08, and silver chloride content of 99.5 mol% by in the same manner as with EMP-1, except that the addition time of solution A & solution B and that of solution C & solution D were changed.

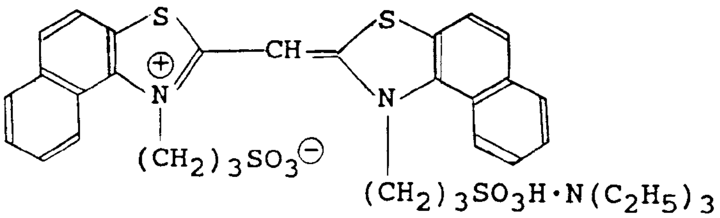
Red-sensitive silver halide emulsion Em-R was prepared by subjecting emulsion EMP-3 to chemical sensitization for 90 minutes at 60°C using the following compounds.

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	1×10^{-4} mol/mol AgX

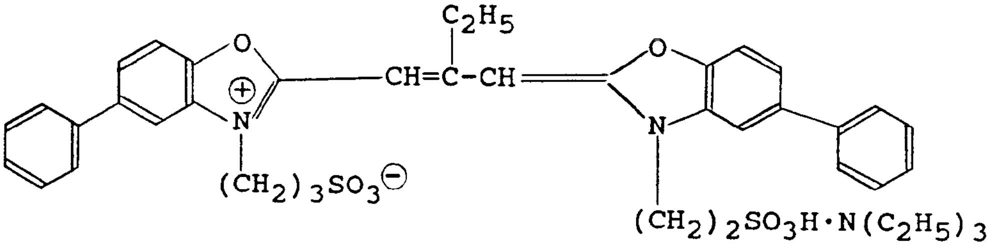
BS - 1



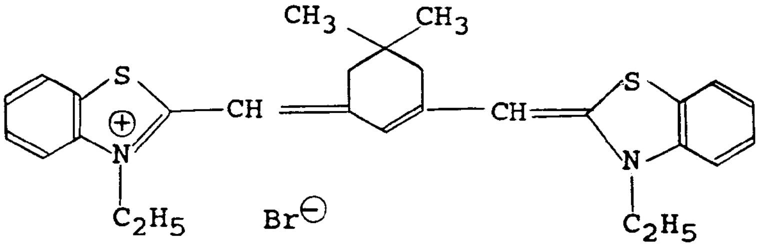
BS - 2



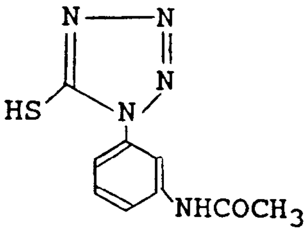
GS - 1



RS - 1



STAB - 1



The samples prepared as above were subjected to wedge exposure by a usual method and then to running treatment according to the following processes.

Process	Temperature (°C)	Time (sec)	Volume replenished (mℓ/m^2)
(1) Color developing	38	20	61
(2) Bleach-fixing	38	40	90
(3) Stabilizing*	30	1st tank 20 2nd tank 20	101
(4) Drying	60 to 80	30	-

* Two-tank counter current mode was used, the replenishing solution was added to the 2nd tank.

(Color developer tank solution)

Diethylene glycol	15 g
Potassium bromide	0.01 g
Potassium chloride	2.3 g
Potassium sulfite (50% solution)	0.5 mℓ
Color developing agent 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidethyl)-aniline sulfate	6 g
Diethylhydroxylamine (85%)	5 g
Triethanolamine	10 g
Potassium carbonate	30 g
Ethylenediamine tetractic acid	2 g
Fluorescent brightener (PK-Conc., product of Nisso)	2 g

Water was added to make 1 liter, and pH was adjusted to 10.15 with potassium hydroxide or sulfuric acid.

(Color developer replenishing solution)

Diethylene glycol	17 g
Potassium chloride	3 g
Potassium sulfite (50% solution)	1.0 mℓ
Color developing agent 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidethyl)-aniline sulfate	8.8 g
Diethylhydroxylamine (85%)	7 g
Triethanolamine	10 g
Potassium carbonate	30 g
Ethylenediaminetetracetic acid	2 g
Fluorescent brightener (PK-Conc., product of Nisso)	2.5 g

Water was added to make 1 liter, and pH was adjusted to 11.0 with potassium hydroxide or sulfuric acid.

(Bleach-fixing tank solution and replenishing solution)

Ferric ethylenediaminetetracetate complex salt	0.3 mol
Ethylenediaminetetracetic acid	2 g
Thiosulfate and thiocyanate (shown in Table 1)	
Sulfite	22.5 g

pH was adjusted to 6.0 with aqueous ammonia, aqueous caustic potash or glacial acetic acid. As thiosulfates and thiocyanates, ammonium salt and potassium salt were used and the concentration of ammonium ions in the total cations was adjusted as shown in Table 1 by changing kinds of the salts. Subsequently, water was added to make the total volume 1 liter.

(Stabilizer tank solution and stabilizer replenishing solution)

Orthophenylphenol	0.15 g
$ZnSO_4 7H_2O$	0.2 g
Ammonium sulfite (40% solution)	5.0 mℓ
1-hydroxyethylidene-1,1-diphosphonic acid (60% solution)	2.5 g
Ethylenediaminetetracetic acid	2.0 g
Fluorescent brightener (Tinopal SFP, product of Ciba Geigy)	2.0 g

pH was adjusted to 7.8 with aqueous ammonia or sulfuric acid, and water was added to make the tolal volume 1 liter.

The processing was conducted by steps of filling an automatic developing machine with tank solutions of color developer, bleach-fixing and stabilizer, and then processing the above color paper sample while feeding the above replenishing solutions of color developer, bleach-fixing and stabilizer at prescribed replenishing rates through volume measuring pumps.

The processing was run till the replenished volume came to twice the volume of the tank solution.

After running of the processing, the amount of residual silver in the exposed portion of the processed sample was measured by the fluorescent X-ray method. The processed samples were visually evaluated for scratch and sticking of foreign matters. The processing solutions were visually evaluated if there were any deposits or floats. Sticking of caked matters to the developing machine was evaluated by visual observation of racks outside liquid of a fixing bath and stabilizing bath, gears, and a rack connecting the fixing bath to the stabilizing bath.

The results are shown in Table 1.

Table 1

Experiment No.	Thiocyanate content (mol/ℓ)	Thiosulfate content (mol/ℓ)	Ammonia ratio to total cations	Residual silver amount in exposed portion (mg/cm^2)	Rating of sticking	Rating of deposits and floats	Scratch and sticking of foreign matters after processing	Remarks
1-1	0.05	-	20 mol%	3.2	A	B	B	Comparative
1-2	0.10	-	20 mol%	1.3	A	B	B	Comparative
1-3	0.20	-	20 mol%	1.1	A	B	B	Comparative
1-4	0.50	-	20 mol%	0.9	A	B	B	Comparative
1-5	-	0.10	20 mol%	3.6	B	C	C	Comparative
1-6	-	0.20	20 mol%	2.8	B	C	C	Comparative
1-7	-	0.30	20 mol%	2.1	C	D	D	Comparative
1-8	-	0.50	20 mol%	1.3	E	D	D	Comparative
1-9	0.05	0.10	20 mol%	2.1	B	C	C	Comparative
1-10	0.05	0.50	20 mol%	0.6	D	C	C - D	Comparative
1-11	0.10	0.10	20 mol%	0.9	A	B	B	Comparative
1-12	0.10	0.20	20 mol%	0.2	B	C	B	Inventive
1-13	0.20	0.30	20 mol%	0.1	B	C	B	Inventive
1-14	0.50	0.10	20 mol%	0.4	B	C	C	Comparative
1-15	0.50	0.20	20 mol%	0.0	A	B	B	Inventive
1-16	0.20	0.30	0	0.2	A	B	B	Inventive
1-17	0.20	0.30	30 mol%	0.1	B	C	B	Inventive
1-18	0.20	0.30	50 mol%	0.0	B	C	B	Inventive
1-19	0.20	0.30	60 mol%	0.0	C	C - D	C	Comparative
1-20	0.20	0.30	80 mol%	0.0	C	D	D	Comparative
1-21	0.50	0.50	20 mol%	0.0	A	B	B	Inventive
1-22	0.50	0.50	80 mol%	0.0	C - D	C - D	D	Comparative

Rating of sticking

A: No cakes on surface, no surface deterioration
B: Cakes slightly sticking to surface, but removal by rubbing
C: Cakes sticking to surface, removal by vigorous rubbing
D: Cakes sticking to surface, slightly deteriorating surface
E: Cakes firmly sticking to surface, substantially deteriorating surface

Rating of deposits and floats

A: None
B: Slightly present
C: Fairly present

Scratch and sticking of foreign matters ater processing

A: None
B: No scratch, slight foreign matter
C: Scratch and foreign matters are both present

As apparent from Table 1, bleach-fixing solutions containing 0.1 mol/ℓ or more of thiocyanates and 0.2 mol/ℓ or more of thiosulfates have high desilvering abilities, even when their ammonia contents are less than 50 mol% of the total cations.

Further, an ammonia content over 50 mol% tends to cause sticking, deposits and floats of processing solutions' components as well as scratches and foreign matter sticking to light-sensitive materials, even when concentrations of thiocyanates and thiosulfates are within the limits of the invention.

Much the same results were obtained even when the combination of cation species was changed to a combination of ammonium ions and sodium ions or that of ammonium ions, potassium ions and sodium ions.

Example 2

Samples prepared in Example 1 were exposed through an optical wedge by a regular method and then subjected to running treatment according to the following procedure.

Process	Temperature (°C)	Time (sec)	Volume replenished (mℓ/m^2)
(1) Color developing	38	20	61
(2) Bleach-fixing	38	20	20
(3) Fixing	38	20	20
(4) Stabilizing*	30	1st tank 20 2nd tank 20	101
(5) Drying	60 to 80	30	-

* Two-tank counter current mode was used, the replenishing solution was added to the 2nd tank.

There were used the same color developer tank solution, color developer replenishing solution and stabilizer tank solution and stabilizer replenishing solution as those used in Example 1.

(Bleacher tank solution)

Ferric 1,3-diaminopropane tetracetate complex salt	0.3 mol
Ethylenediamine tetracetic acid	2 g
Bromide	1.81 mol
Glacial acetic acid	50 mℓ

In the formula, species of cations of the ferric complex salt and bromide were decided so that the ammonium content was adjusted to 20 mol% to the total cations.

pH was adjusted to 4.5 with aqueous ammonia, aqueous caustic potash or glacial acetic acid, and then water was added to make the total volume 1 liter.

(Bleacher replenishing solution)

Ferric 1,3-diaminopropanetetracetate complex salt	0.36 mol
Ethylenediamine tetracetic acid	2 g
Bromide	178 g
Glacial acetic acid	50 mℓ

Species of cations of the ferric complex salt and bromide were decided so that the ammonium content was adjusted to 20 mol% to the total cations.

pH was adjusted to 4.0 with aqueous ammonia, aqueous caustic potash or glacial acetic acid.

(Fixer tank solution and fixer replenising solution)

Thiosulfate (see Table 2)	
Thiocyanate (see Table 2)	
Metabisulfite	3 g
Ethylenediaminetetracetic acid	0.8 g

Water was added to 1 liter, pH was adjusted to 6.5 with acetic acid, aqueous ammonia and aqueous caustic potash. In the formula, species of cations, ammonium and potassium, of the thiosulfate, thiocyanate and metabisulfite were decided so that the ammonium content was adjusted to the values shown in Table 2.

The processing was run till the replenished volume came to twice the volume of the tank solution.

As apparent from Table 2, the results were much the same as those in Example 1 even when fixer solutions were used as a solution having a fixing ability.

Similar results were obtained for different combinations of cation species, namely, a combination of ammonium ions and sodium ions and that of ammonium ions, potassium ions and sodium ions.

Table 2

Experiment No.	Thiocyanate content (mol/l)	Thiosulfate content (mol/l)	Ammonia ratio to total cations	Residual silver amount in exposed portion (mg/cm^2)	Rating of sticking	Rating of deposits and floats	Scratch and sticking of foreign matters after processing	Remarks
2-1	0.05	-	20 mol%	2.9	A	B	B	Comparative
2-2	0.10	-	20 mol%	1.2	A	B	B	Comparative
2-3	0.20	-	20 mol%	1.0	A	B	B	Comparative
2-4	0.50	-	20 mol%	0.8	A	B	B	Comparative
2-5	-	0.10	20 mol%	3.2	B	C	C	Comparative
2-6	-	0.20	20 mol%	2.2	B	C	C	Comparative
2-7	-	0.30	20 mol%	1.9	C	D	D	Comparative
2-8	-	0.50	20 mol%	1.2	E	D	D	Comparative
2-9	0.05	0.10	20 mol%	1.8	B	C	C	Comparative
2-10	0.05	0.50	20 mol%	0.5	D	C - D	C - D	Comparative
2-11	0.10	0.10	20 mol%	0.8	A	B	B	Comparative
2-12	0.10	0.20	20 mol%	0.2	B	C	B	Inventive
2-13	0.20	0.30	20 mol%	0.1	B	C	B	Inventive
2-14	0.50	0.10	20 mol%	0.4	B	C	C	Comparative
2-15	0.50	0.20	20 mol%	0.0	A	B	B	Inventive
2-16	0.20	0.30	0	0.1	A	B	B	Inventive
2-17	0.20	0.30	30 mol%	0.1	B	C	B	Inventive
2-18	0.20	0.30	50 mol%	0.0	B	C	B	Inventive
2-19	0.20	0.30	60 mol%	0.0	C	C - D	C	Comparative
2-20	0.20	0.30	80 mol%	0.0	C	D	D	Comparative
2-21	0.50	0.50	20 mol%	0.0	A	B	B	Inventive
2-22	0.50	0.50	80 mol%	0.0	C - D	C - D	D	Comparative

Example 3

Multilayered color photographic light-sensitive samples were prepared by forming the layers of the following compositions on a triacetylcellulose film support. The amounts of colloidal silvers and silver halide emulsions are mentioned in terms of silver.

	Addition amount (g/m^2)
1st layer: antihalation layer	
Black colloidal silver	0.2
UV absorbent (UV-1)	0.23
High boiling solvent (Oil-1)	0.18
Gelatin	1.4
2nd layer: 1st intermediate layer	
Gelatin	1.3
3rd layer: low-speed red-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.4μmm, AgI content: 2.0 mol%)	1.0
Sensitizing dye (SD-1)	1.8×10^{-5} mol/mol Ag
Sensitizing dye (SD-2)	2.8×10^{-4} mol/mol Ag
Sensitizing dye (SD-3)	3.0×10^{-4} mol/mol Ag
Cyan coupler (C-1)	0.70
Colored cyan coupler (CC-1)	0.066
DIR compound (D-1)	0.03

DIR compound (D-3)	0.01
High boiling solvent (Oil-1)	0.64
Gelatin	1.2
4th layer: medium-speed red-sensitive layer	0.8
Silver iodobromide emulsion (average grain size: 0.7 μm, AgI content: 8.0 mol%)	
Sensitizing dye (SD-1)	2.1 X 10^{-5} mol/mol Ag
Sensitizing dye (SD-2)	1.9 X 10^{-4} mol/mol Ag
Sensitizing dye (SD-3)	1.9 X 10^{-4} mol/mol Ag
Cyan coupler (C-1)	0.28
Colored cyan coupler (CC-1)	0.027
DIR compound (D-1)	0.01
High boiling solvent (Oil-1)	0.26
Gelatin	0.6
5th layer: high-speed red-sensitive layer	1.70
Silver iodobromide emulsion (average grain size: 0.8 μm, AgI content: 8.0 mol%)	
Sensitizing dye (SD-1)	1.9 X 10^{-5} mol/mol Ag
Sensitizing dye (SD-2)	1.7 X 10^{-4} mol/mol Ag
Sensitizing dye (SD-3)	1.7 X 10^{-4} mol/mol Ag
Cyan coupler (C-1)	0.05
Cyan coupler (C-2)	0.10
Colored cyan coupler (CC-1)	0.02

DIR compound (D-1)	0.025
High boiling solvent (Oil-1)	0.17
Gelatin	1.2

6th layer: 2nd intermediate layer

Gelatin	0.8

7th layer: low-speed green-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.4 μm, AgI content: 2.0 mol%)	1.1
Sensitizing dye (SD-4)	6.8 X 10^{-5} mol/mol Ag
Sensitizing dye (SD-5)	6.2 X 10^{-4} mol/mol Ag
Magenta coupler (M-1)	0.54
Magenta coupler (M-2)	0.19
Colored magenta coupler (CM-1)	0.06
DIR compound (D-2)	0.017
DIR compound (D-3)	0.01
High boiling solvent (Oil-2)	0.81
Gelatin	1.8

8th layer: medium-speed green-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.7 μm, AgI content: 8.0 mol%)	0.7
Sensitizing dye (SD-6)	1.9 X 10^{-4} mol/mol Ag
Sensitizing dye (SD-7)	1.2 X 10^{-4} mol/mol Ag
Sensitizing dye (SD-8)	1.5 X 10^{-5} mol/mol Ag

Magenta coupler (M-1)		0.07
Magenta coupler (M-2)		0.03
Colored magenta coupler (CM-1)		0.04
DIR compound (D-2)		0.018
High boiling solvent (Oil-2)		0.30
Gelatin		0.8
9th layer: high-speed green-sensitive emulsion layer		
Silver iodobromide emulsion (average grain size: 1.0 μm, AgI content: 8.0 mol%)		1.7
Sensitizing dye (SD-6)	1.2×10^{-4} mol/mol Ag	
Sensitizing dye (SD-7)	1.0×10^{-4} mol/mol Ag	
Sensitizing dye (SD-8)	3.4×10^{-6} mol/mol Ag	
Magenta coupler (M-1)		0.09
Magenta coupler (M-3)		0.04
Colored magenta coupler (CM-1)		0.04
High boiling solvent (Oil-2)		0.31
Gelatin		1.2
10th layer: yellow filter layer		
Yellow colloidal silver		0.05
Antistain agent (SC-1)		0.1
High boiling solvent (Oil-2)		0.13
Gelatin		0.7
Formalin scavenger (HS-1)		0.09
Formalin scavenger (HS-2)		0.07

11th layer: low-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.4 µm, AgI content: 2.0 mol%)	
Silver iodobromide emulsion (average grain size: 0.7 µm, AgI content: 8.0 mol%)	0.5
Sensitizing dye (SD-9)	5.2×10^{-4} mol/mol Ag
Sensitizing dye (SD-10)	1.9×10^{-5} mol/mol Ag
Yellow coupler (Y-1)	0.65
Yellow coupler (Y-2)	0.24
DIR compound (D-1)	0.03
High boiling solvent (Oil-2)	0.18
Gelatin	1.3
Formalin scavenger (HS-1)	0.08

12th layer: high-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 1.0 µm, AgI content: 8.0 mol%)	1.0
Sensitizing dye (SD-9)	1.8×10^{-4} mol/mol Ag
Sensitizing dye (SD-10)	7.9×10^{-5} mol/mol Ag
Yellow coupler (Y-1)	0.15
Yellow coupler (Y-2)	0.05
High boiling solvent (Oil-2)	0.074
Gelatin	1.30

Formalin scavenger (HS-1)	0.05
Formalin scavenger (HS-2)	0.12

13th layer: 1st protective layer

Fine grain silver iodobromide emulsion (average grain size: 0.08 μm, AgI content: 1 mol%)	0.4
UV absorbent (UV-1)	0.07
UV absorbent (UV-1)	0.10
High boiling solvent (Oil-1)	0.07
High boiling solvent (Oil-3)	0.07
Formalin scavenger (HS-1)	0.13
Formalin scavenger (HS-2)	0.37
Gelatin	1.3

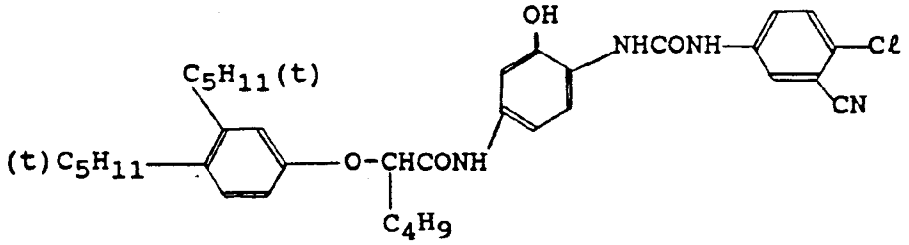
14th layer: 2nd protective layer

Alkali-soluble matting agent (average grain size: 2 μm)	0.13
Polymethylmethacrylate (average particle size: 3 μm)	0.02
Slipping agent (WAX-1)	0.04
Gelatin	0.6

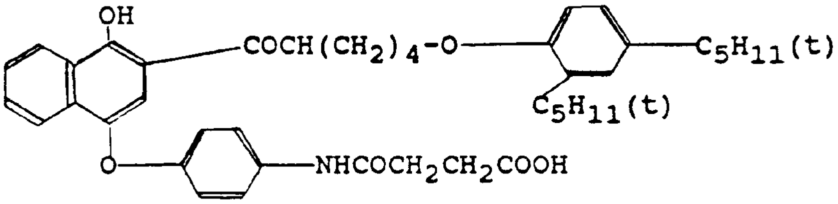
In addition to the above compounds, there were added coating aid Su-1, dispersing aid Su-2, viscosity adjusting agent, hardeners H-1 and H-2, stabilizer ST-1 and antifoggants AF-1 (Mw: 10,000) and AF-2 (Mw: 1,100,000).

The emulsions used in the above samples were prepared in the same manner as in Example 1 and then optimumly subjected to gold-sulfur sensitization. Their average grain sizes are shown by sizes of cubes converted from actual shapes.

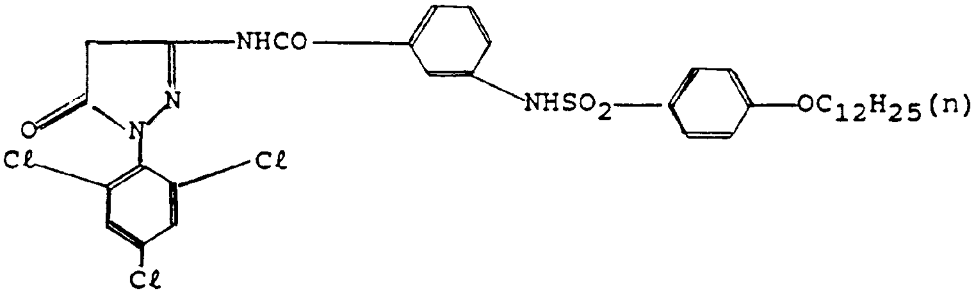
C - 1


OH
NHCONH
Cℓ
CN
$C_5H_{11}(t)$
$(t)C_5H_{11}$
O-CHCONH
C_4H_9

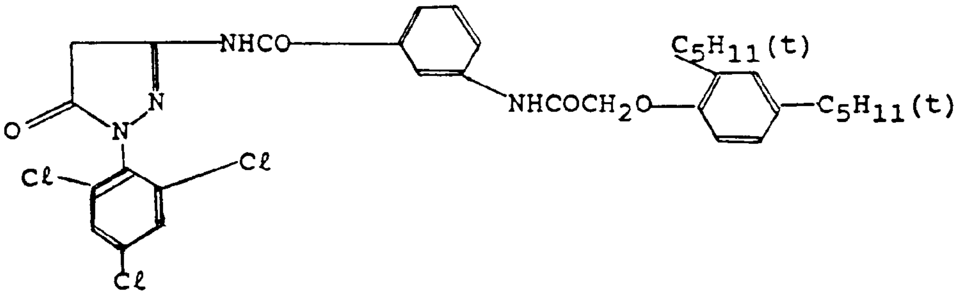
C - 2


OH
$COCH(CH_2)_4$-O
$C_5H_{11}(t)$
$C_5H_{11}(t)$
O
$NHCOCH_2CH_2COOH$

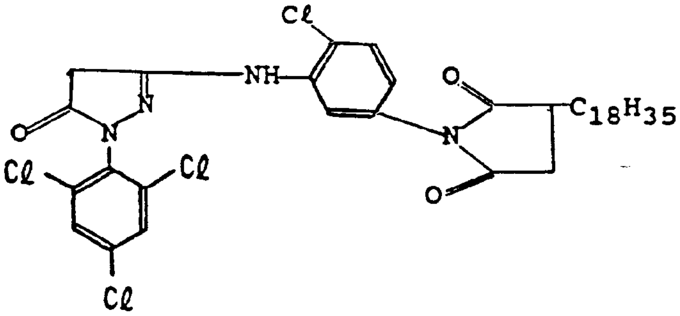
M - 1


NHCO
$NHSO_2$
$OC_{12}H_{25}(n)$
O
N
N
Cℓ
Cℓ
Cℓ

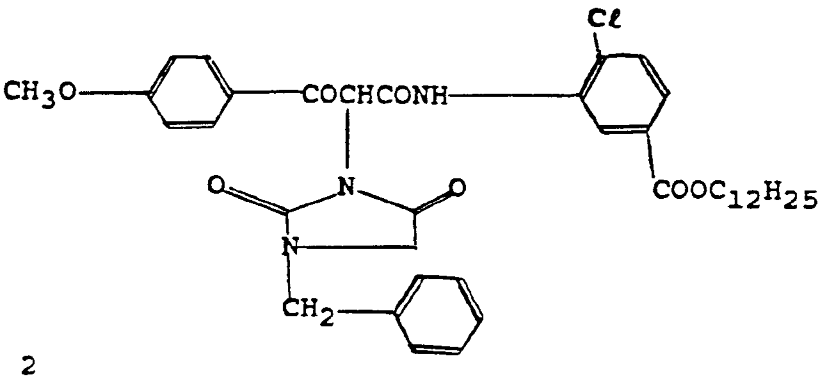
M - 2


NHCO
$C_5H_{11}(t)$
$NHCOCH_2O$
$C_5H_{11}(t)$
O
N
N
Cℓ
Cℓ
Cℓ

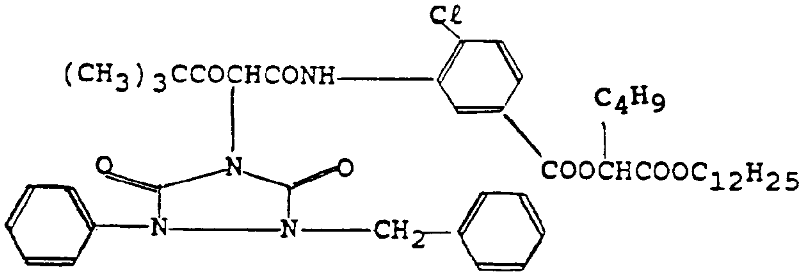
M - 3


Cℓ
NH
O
$C_{18}H_{35}$
O
N
N
N
O
Cℓ
Cℓ
Cℓ

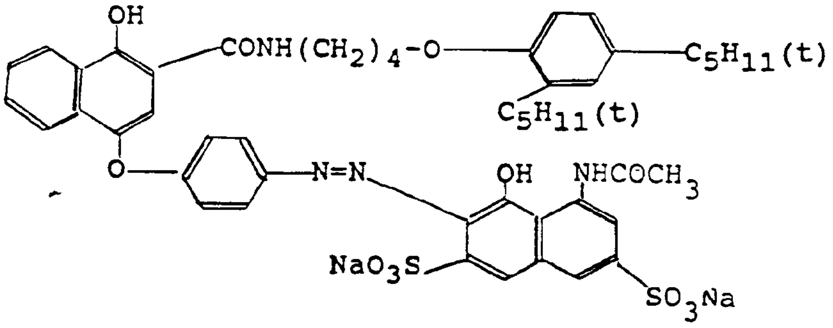
Y - 1


Cℓ
CH3O
COCHCONH
COOC12H25
O
N
O
N
CH2

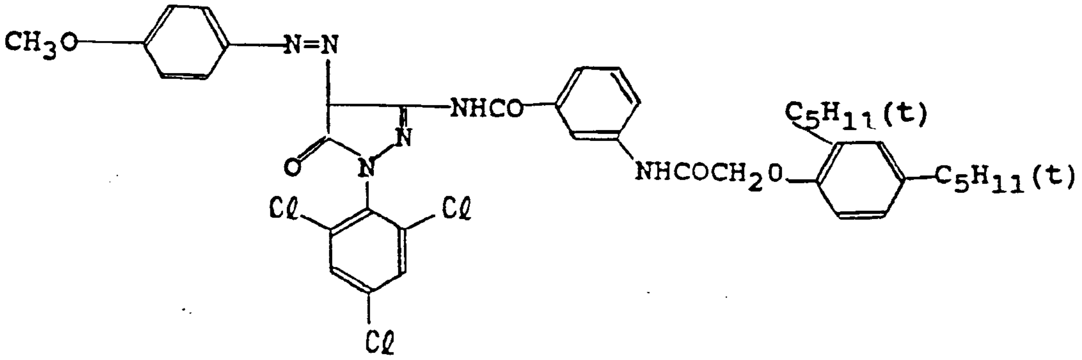
Y - 2


Cℓ
(CH3)3CCOCHCONH
C4H9
COOCHCOOC12H25
O
N
O
N
N
CH2

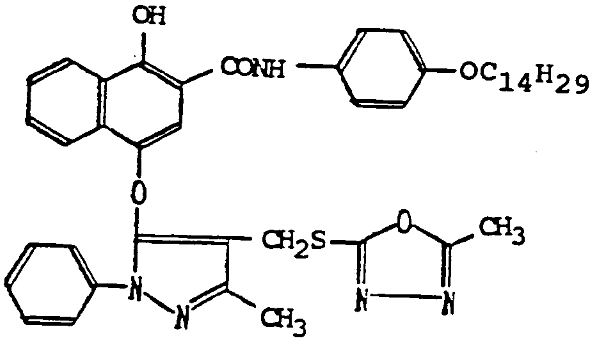
CC - 1


OH
CONH(CH2)4-O
C5H11(t)
C5H11(t)
O
N=N
OH
NHCOCH3
NaO3S
SO3Na

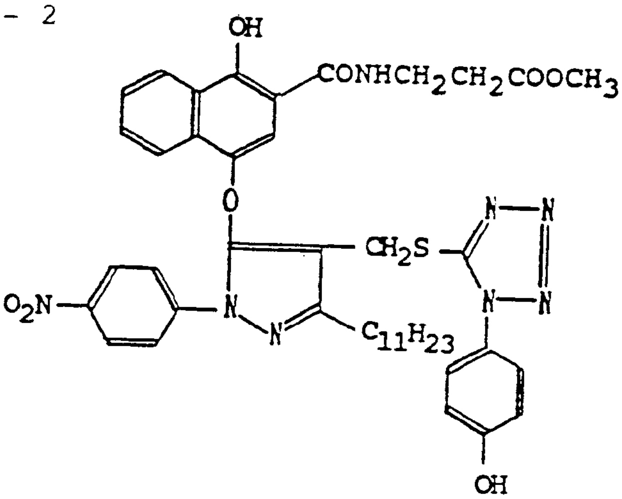
CM - 1


CH3O
N=N
NHCO
C5H11(t)
N
O
N
NHCOCH2O
C5H11(t)
Cℓ
Cℓ
Cℓ

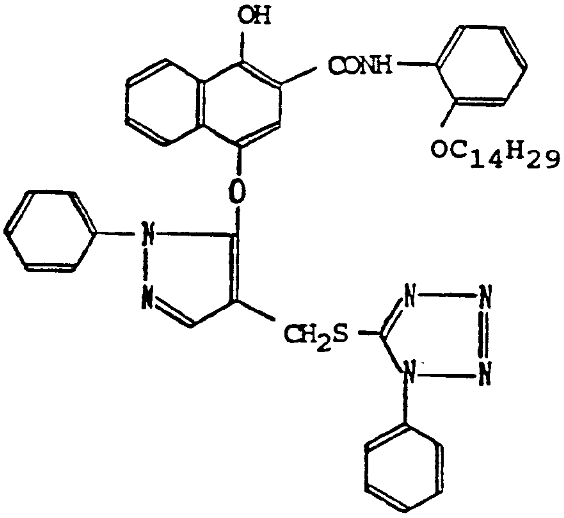
D - 1


OH
CONH
OC14H29
O
CH2S
O
CH3
N
N
N
N
CH3

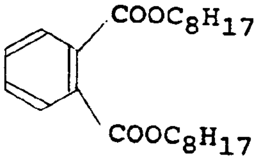
D - 2


OH
CONHCH2CH2COOCH3
O
CH2S
N
N
N
N
O2N
N
N
C11H23
OH

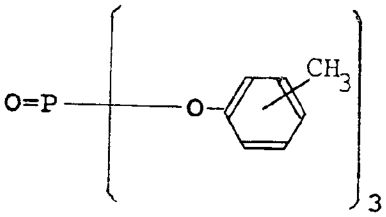
D - 3


OH
CONH
OC14H29
O
N
N
CH2S
N
N
N
N

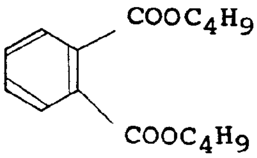
Oil - 1



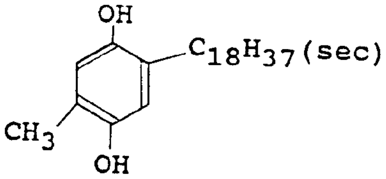
Oil - 2



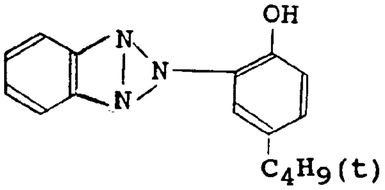
Oil - 3



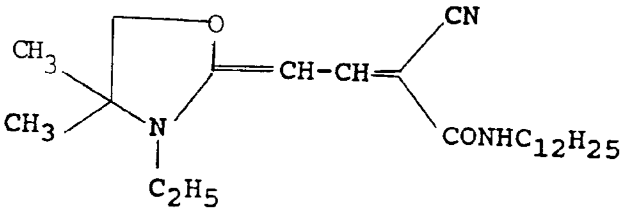
SC - 1



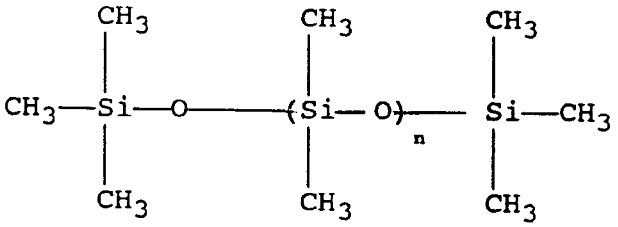
UV - 1



UV - 2



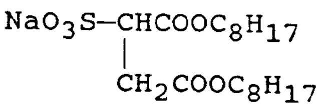
WAX - 1



$$CH_3-Si(CH_3)_2-O-(Si(CH_3)_2-O)_n-Si(CH_3)_2-CH_3$$

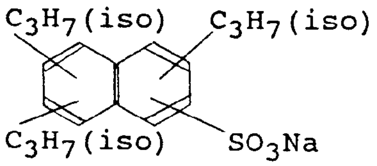
Weight-average molecular weight Mw=3,000

Su - 1

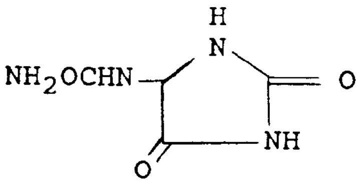


$$NaO_3S-CH(CH_2COOC_8H_{17})COOC_8H_{17}$$

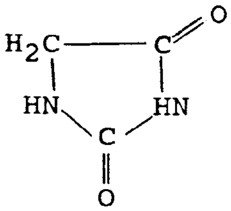
Su - 2



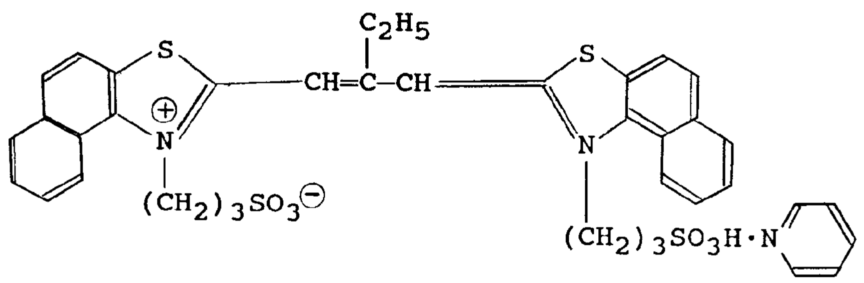
HS - 1



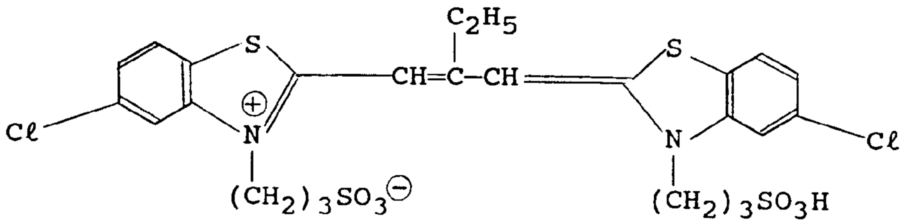
HS - 2



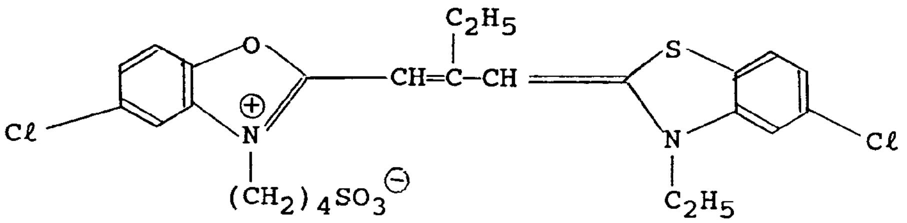
SD - 1



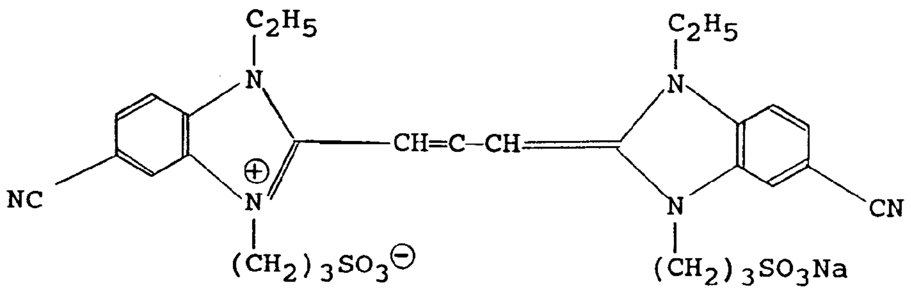
SD - 2



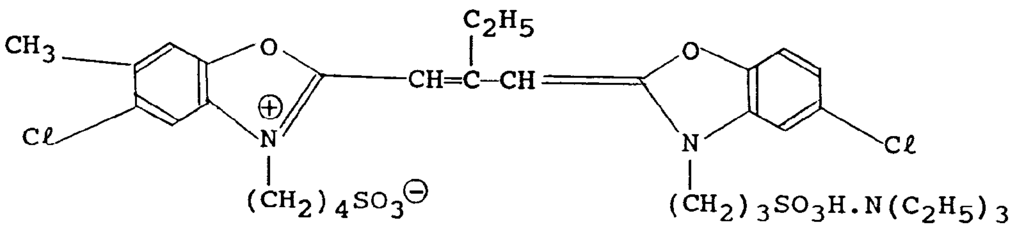
SD - 3



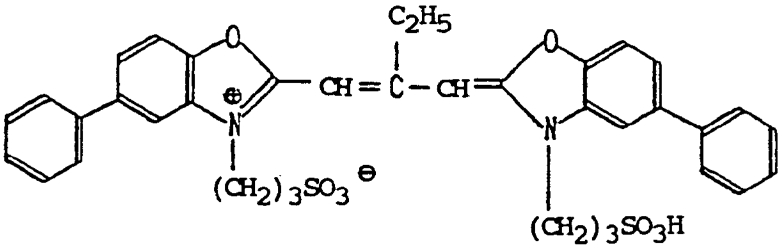
SD - 4



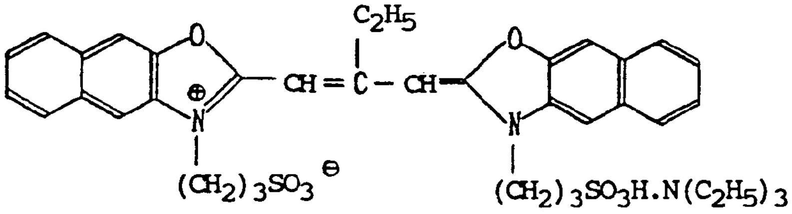
SD - 5



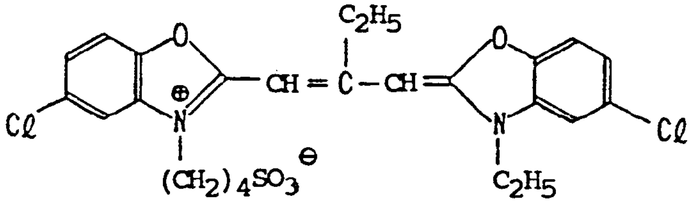
SD - 6



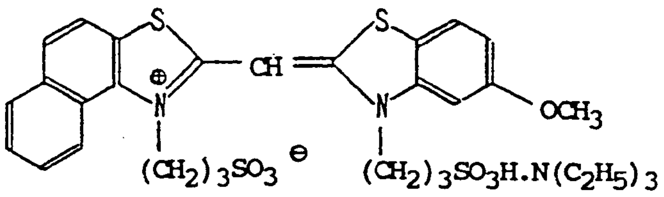
SD - 7



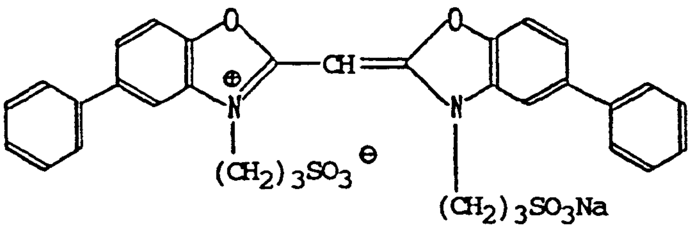
SD - 8



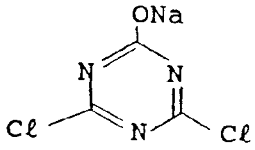
SD - 9



SD - 10



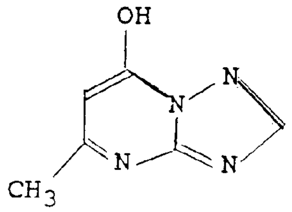
H - 1



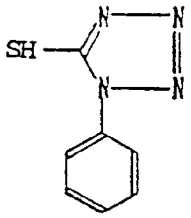
H - 2

$(CH_2=CHSO_2CH_2)_2O$

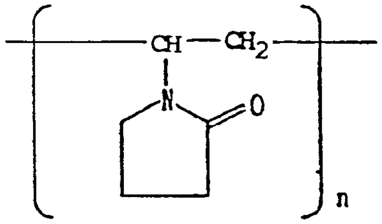
ST - 1



AF - 1



AF - 2



n: Degree of polymerization

The samples prepared as above were subjected to wedge exposure with white light through an optical wedge and then processed under the following conditions.

Process	Time	Temp. (°C)	Replenishing* amount
Color developing	3 min 15 sec	38	536 mℓ
Bleaching	45 sec	38	134 mℓ
Fixing	1 min 30 sec	38	536 mℓ
Stabilizing**	1 min 30 sec	38	536 mℓ
Drying	1 min	40 - 70	

* The amount is per m^2 of light-sensitive material.

** Three-tank conter current mode was used, the replenishing solution was fed to the final tank.

Compositions of the processing solutions were as follows.

(Color developer solution)

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	4.5 g
Diethylenetriamine pentacetic acid	3.0 g
Potassium hydroxide	1.2 g

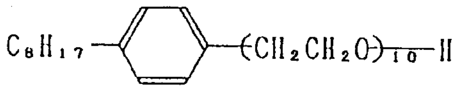
Water was added to make 1 liter, and pH was adjusted to 10.06 with potassium hydroxide or 20% sulfuric acid.

(Color developer replenishing solution)

Potassium carbonate	35 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	5.8 g
Potassium hydroxide	2 g
Diethylenetriamine pentacetic acid	3.0 g

Water was added to make 1 liter, and pH was adjusted to 10.12 with potassium hydroxide or 20% sulfuric acid.

(Stabilizer tank solution and replenishing solution)

	0.5 g
Formaldehyde (37% solution)	3.0 mℓ

Water was added to make 1 liter, and pH was adjusted to 7.5 to 8.5 with sodium hydroxide or sulfuric acid.

The bleacher tank solution, fixer tank solution and respective replenishing solutions were prepared as shown in Table 3 according to the formulations used in Example 2.

The processing was carried out till the replenishment amounted to twice the volume of the tank solution. Evaluation items and methods thereof were the same as in Example 1. The results obtained are shown in Table 3.

As apparent from Table 3, the effect of the invention was well exhibited for an ammonium content of less than 50 mol% of the total cation.

Much the same results were obtained for different cationic combinations of ammonium ions and sodium ions, and ammonium ions, potassium ions and sodium ions.

Example 4

Samples prepared in Example 1 were subjected to wedge exposure in a regular manner and then to running treatment according to the following procedure.

Process	Temperature (°C)	Time (sec)	Volume replenished (mℓ/m²)
(1) Color developing	38	20	61
(2) Bleach-fixing	38	20	20
(3) Fixing	38	20	20
(4) Stabilizing	30	1st tank 20 2nd tank 20	101
(5) Drying	60 to 80	30	-

There were used the same color developer tank solution, color developer replenishing solution and stabilizer tank solution and stabilizer replenishing solution as those in Example 1.

The fixer tank solution and fixer replenishing solution were prepared in the same manner as with experiment No. 2-13 of Example 2.

The bleaching tank solution and bleaching replenishing solution were prepared by adjusting respective pHs to 4.5 and 4.0 with aqueous caustic potash, aqueous ammonia or glacial acetic acid. As the ferric complex salt and bromide, ammonium salts and potassium salts were used in the solution. Cation species of the ferric complex salt and bromide in the solutions, were decided so that the ammonium ion ratio to the total cations in the solution is adjusted to the value shown in Table 4. In the preparation, organic acid ferric complex salts shown in Table 4 were used as bleaching agents.

The processing was carried out the volume of the replenishing solution came to twice the volume of the tank solution. Evaluation items and evaluation methods were the same as in Example 1. The results are shown in Table 4.

As apparent from Table 4, the effect of the invention was clearly demonstrated by the use of bleaching solutions containing ferric 1,3-diaminopropane tetracetate (PDTA.Fe) as a bleaching agent and having an ammonium content of less than 50 mol%.

Much the same results were obtained as long as the concentration of ammomium ions was the same, even when combination of cation was changed from that of ammonium ions and sodium ions to that of ammonium ions, potassium ions and sodium ions.

An experiment using exemplified compound (B-1).Fe instead of PDTAEFe also gave similar results.

Table 3

Experiment No.	Thiocyanate content (mol/ℓ)	Thiosulfate content (mol/ℓ)	Ammonia ratio to total cations	Residual silver amount in exposed portion (mg/cm^2)	Rating of sticking	Rating of deposits and floats	Scratch and sticking of foreign matters after processing	Remarks
3-1	1.6	1.4	80 mol%	0.0	E	D	D	Comparative
3-2	1.6	1.4	60 mol%	0.0	D	D	D	Comparative
3-3	1.6	1.4	50 mol%	0.2	B	C	C	Inventive
3-4	1.6	1.4	30 mol%	0.3	A	B	B	Inventive
3-5	1.6	1.4	20 mol%	0.3	A	B	B	Inventive
3-6	1.6	1.4	0	0.4	A	B	B	Inventive
3-7	2.0	1.8	20 mol%	0.0	A	B	B	Inventive
3-8	3.2	2.8	20 mol%	0.1	B	B - C	B - C	Inventive
3-9	3.3*	3.0*	20 mol%	0.1	B	C	C	Inventive

Complate dissolution of the chemicals become to hard when the contents of thiocyanate and thiosulfate are exceeded 3.3 mol/ℓ and 3.0 mol/ℓ respectively.

Table 4

Experiment No.	Bleaching agent	Ammonia ratio to total cations	Fixing solution	Residual silver amount in exposed portion (mg/cm^2)	Rating of sticking	Rating of deposits and floats	Scratch and sticking of foreign matters after processing	Remarks
4-1	EDTA-Fe	20 mol%	2-13	0.9	B	C	B	Inventive
4-2	PDTA-Fe	80 mol%	2-13	0.0	B	C	B	Inventive
4-3	PDTA-Fe	60 mol%	2-13	0.0	B	B	B	Inventive
4-4	PDTA-Fe	50 mol%	2-13	0.1	A	B	B	Inventive
4-5	PDTA-Fe	20 mol%	2-13	0.1	A	B	B	Inventive
4-6	PDTA-Fe	0	2-13	0.2	A	B	B	Inventive

Notes: EDTAE-Fe: Frric ethylenediamine tetracetate complex salt
PDTAE-Fe: Frric 1,3-diaminopropane tetracetate complex salt

Claims

1. A solution suitable for processing a silver halide color photographic light-sensitive material which comprises not less than 0.1 mol/ℓ of a thiocyanate and not less than 0.2 mol/ℓ of a thiosulfate, wherein not more than 50 mol% of the cations in the solution are ammonium ions.

2. A solution according to claim 1 which comprises from 0.2 mol/ℓ to 2.8 mol/ℓ of the thiocyanate.

3. A solution according to claim 2 which comprises from 0.5 mol/ℓ to 1.8 mol/ℓ of the thiocyanate.

4. A solution according to any one of the preceding claims which comprises from 0.3 mol/ℓ to 2.8 mol/ℓ of the thiosulfate.

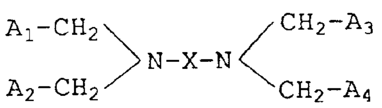
5. A solution according to claim 4 which comprises from 0.5 mol/ℓ to 1.8 mol/ℓ of the thiosulfate.

6. A solution according to one of the preceding claims wherein not more than 20 mol% of the cations in the solution are ammonium ions.

7. A solution according to claim 1 or 3 which comprises from 0.5 mol/ℓ to 2.0 mol/ℓ of the thiocyanate and from 0.5 mol/ℓ to 1.8 mol/ℓ of the thiosulfate, wherein not more than 20 mol% of the cations in the solution are ammonium ions.

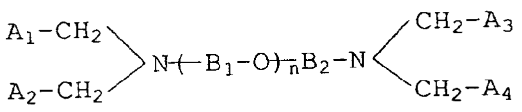
8. A method for processing a silver halide color photographic light-sensitive material which comprises:
   a) developing the light-sensitive material with a color developer;
   b) treating the developed light-sensitive material with a solution as defined in any one of the preceding claims; and
   c) stabilizing the treated light-sensitive material with a stabilizing solution.

9. A method according to claim 8 which further comprises bleaching the developed light-sensitive material, before the treating step b), with a bleaching solution which comprises a ferric complex salt of an organic acid of formula A or B, wherein not more than 50 mol% of the cations in the solution are ammonium ions:



(A)

wherein A_1, A_2, A_3 and A_4 are independently a $-CH_2OH$ group, a $-COOM$ group or a $-PO_3M_1M_2$ group, in which M, M_1 and M_2 are independently a hydrogen atom, an alkali metal atom or an ammonium group; and X is a substituted or unsubstituted alkylene group having from 3 to 6 carbon atoms;



(B)

wherein A_1, A_2, A_3 and A_4 are as defined above; n is an integer of from 1 to 8; and B_1 and B_2 are independently a substituted or unsubstituted alkylene group having from 2 to 5 carbon atoms.

10. A method according to claim 9 wherein the bleaching solution comprises the compound of formula A or B in an amount of not less than 0.1 mol/ℓ.

11. A method according to claim 10 wherein the bleaching solution comprises the compound of formula A or B in an amount of from 0.2 mol/ℓ to 1.5 mol/ℓ.

12. A method according to any one of claims 9 to 11 wherein not more than 20 mol% of the cations in the bleaching solution are ammonium ions.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 6358

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	GB-A-774 194 (K.I.JACOBSON) * examples 1,2 * ---	1-7	G03C7/42
X	US-A-4 029 510 (D.E.SPEERS) * example 2 *	1-7	
A	* column 2, line 47 - line 51 * * column 5, line 57 - column 6, line 5 * ---	8	
X	FR-A-1 553 350 (FUJI SHASHIN FILM KK) * example 3 * ---	1-7	
A	EP-A-0 329 088 (KONICA CORPORATION) * abstract * * page 7, line 49 - line 51 *	9-12	
A	* page 19, line 13 - line 25 * ---	8	
A	DATABASE WPI ,No.76-50628X[27] Derwent Publications Ltd.,London,GB &JP-A-51056228(MITSUBISHI PAPER MILL)18-05-1987 *Abstract* -----	9-12	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 OCTOBER 1991	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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