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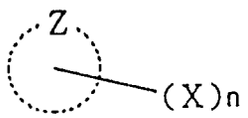
(54) **Method for processing a silver halide color photographic light-sensitive material.**

(57) 1. A method for processing a silver halide color photographic light-sensitive material is disclosed. The method comprises the steps of exposing the material, developing the exposed material, processing the developed material with a processing solution having a fixing ability, and stabilizing the processed material with a stabilizer, wherein the concentration of ammonium ions in said processing solution is not more than 50 mol% of the total cations, and said stabilizer contains in an amount of 0.05 to 20g per litre at least one compound selected from those represented by the following Formula (F):

Formula (F)



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FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic light-sensitive material, particularly to a method for processing a silver halide color photographic light-sensitive material less in base-side scum, precipitation of sulfides, pollution load, stains after processing and improved in solution preservability.

BACKGROUND OF THE INVENTION

After being exposed imagewise, a silver halide color photographic light-sensitive material is generally color developed and then subjected to processing having a fixing ability such as bleaching and fixing, or bleach-fixing, followed by processes such as stabilizing and washing. And, in the washing process that follows the processing with a processing solution having a fixing ability, it is known that thiosulfates and other water-soluble silver complex salts formed on reaction with silver halide as well as sulfites and metabisulfites used as preservatives are brought therein by adhering to a light-sensitive material and, thereby, exert harmful influences on image preservability when the amount of washing water is small.

To avoid such problems, these salts are washed out from a light-sensitive material with a large amount of running water in actual operations. However, because of exhaustion of water resources, rises in water and sewage rates and utilites costs, in addition to reasons for pollution control, there is demanded in recent years a processing method less in water consumption and improved in antipollution measure.

As a preventive measure against these problems, there has so far been proposed a method of allowing water to flow countercurrently in a multistage washing tank by German Pat. No. 2,920,222 and S.R. Goldwasser, "Water Flow Rate In Immersion-Washing of Mortion-picture Film" SMPTE, Vol. 64, pp. 248-253 (May, 1955).

There is also known a processing method in which a pre-washing bath is provided directly after the fixing bath to reduce the amount of pollutive components brought into the washing bath together with a light-sensitive material and thereby to reduce the amount of washing water eventually.

However, these techniques still require use of water. Therefore, with the constant decrease in water resources and the rise in washing cost, use of washing water has become a big problem.

On the other hand, there is also known a processing method, in which a light-sensitive material is subjected to stabilizing immediately after the photographic process without being washed. As an example thereof, a silver-stabilizing process by use of thiocyanates is disclosed in U.S. Pat. No. 3,335,004. But, this method has a disadvantage that stains may occur on the surface of a light-sensitive material after drying because of a large amount of inorganic salts contained in the stabilizing bath.

It is also found that this method is accompanied by another disadvantage of deteriorating dye images when a light-sensitive material is stored over a long period.

Meanwhile, in processing a photographic color light-sensitive material represented by the photographic light-sensitive material containing silver iodobromide as the silver halide, a stabilizing bath containing formalin is generally used in the final process which follows a washing process.

Formalin contained in the above stabilizing bath functions to prevent changes in physical properties of a color photographic light-sensitive material, particularly, it is effective in preventing scratches on the surface of a light-sensitive material and gradation changes attributable to hardening of a light-sensitive material which proceeds gradually in proportion to aging. In addition, formalin has a function to prevent dye images from being deteriorated by unreacted couplers remaining in a light-sensitive material.

However, formalin added in a stabilizing bath for the purpose of stabilizing a color image has a defect that it forms an adduct on reaction with sulfite ions brought from the preceding bath (containing a processing solution having a fixing ability) and the adduct adheres to a light-sensitive material. As a result, not only its primary function of image stabilization is lowered, but also precipitation of sulfides is accelerated. Although U.S. Pat. No. 4,786,583 proposes use of alkanolamines as a countermeasure against the problem, the use of alkanolamines tends to cause yellow stains in unexposed portions and is not necessarily satisfactory in preventing sulfides from precipitating.

Further, formalin has a problem in the safety for the human body. In the United States, CIIT disclosed that rats had developed nasal cancers in an environment containing 15 ppm of formalin, and both NIOS and ACGIH issued a warning that it might be a carcinogenic substance. Use of formalin is strictly regulated in Europe, too. And in Germany, the formalin concentration in dwellings has been regulated to be less than 0.1 ppm since ten years ago.

In Japan, use of formalin is regulated, because of its stimulation against the mucous membrane, by the law concerning deleterious and poisonous substances, the regulation of organic solvents by special

chemical rule, regulations on household goods, fibers and plywoods, and a regulation on underwears and baby clothings newly enforced in 1975 by the Welfare Ministry. Under such circumstances, technical development of a processing method using less formalin has been demanded.

Recently, a method for processing a color negative film called process C-41B and C-41RA has come to be known widely, which were developed by Eastman Kodak Co. for the purposes of rapid processing and labor saving. This process is a rapid processing using substantially no water and comprises the steps of (color developing)-(bleaching)-(fixing)-(stabilizing)- (drying). And there has been widely known the use of hexatetramine compounds and hexahydrotriazine compounds, which are employed in the stabilizing bath of this stabilizing process and further as substitutes for formalin as described, for example, in Japanese Pat. O.P.I. Pub. Nos. 244036/1988, 27742/1987, and 151538/1986. However, these hexatetramine compounds and hexahydrotriazine compounds, though effective in preventing color fading, have proved to be liable to cause base-side scum that a stabilizer containing these compounds adheres to a light-sensitive material, particularly the backside of a photographic film, and produces patches on the surface of the film, when the light-sensitive material is processed in such a stabilizer directly after a fixing process or a bleach-fixing process without a substantial use of washing water. It is also found that when such a stabilizer is used over a long time, particularly in the case of processing small batches of light-sensitive materials over a long time, sulfur or sulfides precipitate in the stabilizer to cause processing stains though no formalin is contained therein.

Especially, when the replenishing amount of the stabilizer is small, this problem becomes critical.

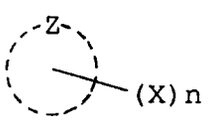
SUMMARY OF THE INVENTION

Accordingly, the object of the present invention is to provide a method for processing a silver halide color photographic light-sensitive material, in which base-side scum, precipitation of surfur or sulfides in a stabilizer, and stains on the film caused by the pracipitation are prevented and the pollution load is minimized by excluding formaldehyde to be added in a stabilizer for the above effects.

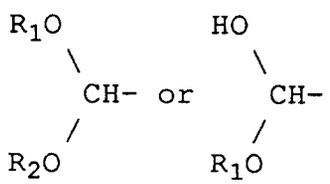
The present inventors have made a close study to achieve the above object and accomplished the present invention.

The method for processing a silver halide color photographic light-sensitive material according to the invention is a method for processing a silver halide color light-sensitive material by steps of processing said light-sensitive material with a processing solution having a fixing ability and then processing it with a stabilizer, wherein the concentration of ammonium ions in the processing solution having a fixing ability is not more than 50 mol% of the total cations contained therein and the stabilizer contains at least one compound selected from those represented by the following Formula (F):

Formula (F)



In the formula, Z represents a group of atoms necessary to form a substituted or unsubstituted carbocycle or a substituted or unsubstituted heterocycle; X represents an aldehyde group,



(R_1 and R_2 each represent a lower alkyl group); and n represents an integer of 1 to 4.

The present invention is accomplished based on the present inventors' findings that stabilization of dye images and control of stains can be achieved even in the absence of formaldehyde by incorporating the compound represented by Formula (F) in a stabilizer, and that the disadvantages resulting from use of these compounds, such as base-side scum, precipitation of sulfur or sulfides in a stabilizer, stains,

scratches and adhesion of foreign matters, depend upon the amount of ammonium cations contained in the preceding bath, namely the processing solution having a fixing ability, though the mechanism is not clear yet.

DETAILED DESCRIPTION OF THE INVENTION

The following are processes appropriate for the processing method using the processing solution 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 → fixing → bleach-fixing → stabilizing
(6) Color developing → bleaching → bleach-fixing → fixing → stabilizing

Among the above processes, processes (1), (2) and (3) are preferred. That is, the expression "a processing solution having a fixing ability" used in the invention indicates various processing solutions and combinations thereof, such as a bleach-fixer, a bleacher and a fixer, a bleacher and a bleach-fixer, a bleach-fixer and a fixer, and a fixer and a bleach-fixer which are each exemplified above.

As fixing agents for the fixer or the bleach-fixer, thiocyanates and thiosulfates are preferably employed. The content of thiocyanates is usually not less than 0.1 mol/l; in processing a color negative film, it is preferably not less than 0.3 mol/l, more preferably not less than 0.5 mol/l. The content of thiosulfates is usually not less than 0.2 mol/l; in processing a color negative film, it is preferably not less than 0.5 mol/l. Decreasing the content of ammonium ions exerts harmful effects on the fixing ability at times; but, in the invention, the fixing ability can be kept good by the combined use of thiocyanates and thiosulfates even when the content of ammonium ions is reduced.

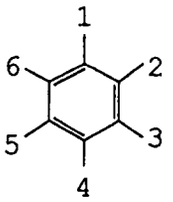
In the invention, the content of ammonium ions in the fixer or the bleach-fixer is not more than 50 mol %, preferably not more than 20 mol % of the total cations. The invention is characterized in that such a low ammonium ion content produces better results in preventing precipitation of sulfur or sulfides and processing stains. Further, using an ammonia-less state in the invention brings out the following advantages. That is, it is a natural demand to eliminate ammonium ions, the source of the offensive smell; but, to decrease simply the content of ammonium ions often exerts a harmful influence on the fixing ability. However, the fixing ability can be kept on a high level even in an ammonia-less state by the combined use of thiocyanates and thiosulfates as fixing agents.

The compound represented by Formula (F) for use in the invention is described hereunder. In Formula (F), Z represents a group of atoms necessary to form a substituted or unsubstituted carbocycle or a substituted or unsubstituted heterocycle, and the carbocycle and the heterocycle may be a monocycle or a condensed ring. Preferably, Z is an aromatic carbocycle having a substituent or a heterocycle having a substituent. The substituent of Z is preferably an aldehyde group, a hydroxyl group, an alkyl group (e.g., methyl, ethyl, methoxyethyl, benzyl, carboxymethyl, sulfopropyl),an aralkyl group, an alkoxyl group(e.g., methoxy,ethxy,methoxyethoxy) a halogen atom, a nitro group, a sulfo group, a carboxyl group, an amino group (e.g., N,N-dimethylamino, N-ethylamino, N-phenylamino), a hydroxyalkyl group, an aryl group (e.g., phenyl, p-methoxyphenyl), a cyano group, an aryloxy group (e.g., phenoxy, p-carboxyphenyl), an acyloxy group, an acylamino group, sulfonamido group, a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl), a carbomoyl group (e.g., carbamoyl, N-methylcarbamoyl, N,N-tetramethylenecarbamoyl) or a sulfonyl group (e.g., methanesulfonyl, ethanesulfonyl, benzenesulfonyl, p-toluenesulfonyl).

The carbocycle represented by Z is preferably a benzene ring, and the heterocycle represented by Z is preferably a five- or six-membered heterocycle. Examples of the five-membered one include thiophene, pyrrole, furan, thiazole, imidazole, pyrazole, succinimide, triazole and tetrazole; examples of the six-membered one include pyridine, pyrimidine, triazine and thiadiazine. Examples of the condensed ring include naphthalene, benzofuran, indole, thionaphthalene, benzimidazole, benzotriazole and quinoline.

In a preferable mode of the compound represented by Formula (F), the substituent of Z is an aldehyde group, a hydroxyl group, an alkyl group, an aralkyl group, an alkoxy group, a halogen atom, a nitro group, a sulfo group, a carboxyl group, an amino group, a hydroxyalkyl group, an aryl group, a cyano group, an aryloxy group, an acyloxy group, an acylamino group, a sulfonamido group, a sulfamoyl group, a carbamoyl group or a sulfonyl group.

Preferred ones among the compounds represented by Formula (F) are exemplified below.



As shown in the table below, exemplified compounds (F-1) to (F-52) are obtained by introducing a substituent to one or more of positions 1 to 6 of the above formula.

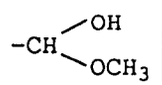
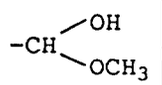
Table 1

No	1	2	3	4	5	6
(F-1)	-CHO	H	H	H	H	H
(F-2)	-CHO	H	H	-OH	H	H
(F-3)	-CHO	H	-OH	H	H	H
(F-4)	-CHO	-OH	H	H	H	H
(F-5)	-CHO	-OH	H	-OH	H	H
(F-6)	-CHO	H	-OH	H	-OH	H
(F-7)	-CHO	-OH	-OH	H	H	H
(F-8)	-CHO	H	-CHO	H	-OH	H
(F-9)	-CHO	H	-CHO	H	H	-OH
(F-10)	-CHO	-OH	-CHO	H	H	H
(F-11)	-CHO	H	-CHO	H	-CHO	H
(F-12)	-CHO	-OH	-CHO	H	-CHO	H
(F-13)	$-CH(OCH_3)_2$	H	-OH	H	H	H
(F-14)	$-CH(OCH_3)_2$	H	H	-OH	H	H
(F-15)	$-CH(OCH_3)_2$	H	-OH	H	-OH	H
(F-16)	-CHO	H	$-NO_2$	H	H	H

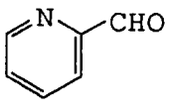
Table 2

No	1	2	3	4	5	6
(F-17)	-CHO	H	H	$-NO_2$	H	H
(F-18)	-CHO	$-NO_2$	H	H	H	H
(F-19)	-CHO	H	$-NO_2$	H	$-NO_2$	H
(F-20)	-CHO	H	H	$-OCH_3$	H	H
(F-21)	-CHO	H	$-OCH_3$	H	-0H	H
(F-22)	-CHO	H	-OH	$-OCH_3$	H	H
(F-23)	-CHO	H	$-OCH_3$	-OH	H	H
(F-24)	-CHO	H	-OH	$-OCH_3$	-OH	H
(F-25)	-CHO	H	Cl	H	H	H
(F-26)	-CHO	H	H	C1	H	H
(F-27)	-CHO	H	Cl	H	Cl	H
(F-28)	-CHO	H	-COOH	-COOH	H	H
(F-29)	-CHO	H	Br	H	H	H
(F-30)	-CHO	H	H	Br	H	H
(F-31)	-CHO	H	-OH	$-SSO_3H$	H	H
(F-32)	-CHO	H	H	$-NH_2$	H	H

Table 3

No	1	2	3	4	5	6
(F-33)	-CHO	H	H	$-N(CH_3)_2$	H	H
(F-34)	-CHO	H	H	$-N(C_2H_5)_2$	H	H
(F-35)	-CHO	H	H	$-CONH_2$	H	H
(F-36)	-CHO	H	H	$-SO_2NH_2$	H	H
(F-37)	-CHO	H	H	SO_3H	H	H
(F-38)	-CHO	H	H	-CN	H	H
(F-39)	-CHO	H	H	$-COOCH_3$	H	H
(F-40)	-CHO	H	H	-COOH	H	H
(F-41)	-CHO	H	$-SO_3H$	H	H	H
(F-42)	-CHO	H	-COOH	H	H	H
(F-43)	-CHO	H	-CN	H	H	H
(F-44)	-CHO	H	$-COOHCH_3$	H	H	H
(F-45)	-CHO	H	$-CONH_2$	H	H	H
(F-46)		H	-OH	H	H	H
(F-47)		H	H	-OH	H	H
(F-48)	-CHO	H	-OH	$-CH_3$	H	H
(F-49)	-CHO	$-SO_3Na$	H	H	H	H
(F-50)	-CHO	H	$-OCH_2CH_2CH_2SO_3Na$	H	H	H
(F-51)	-CHO	H	$-CH_2SO_3Na$	H	H	H
(F-52)	-CHO	-OH	-OH	-CHO	H	H

(F-53)



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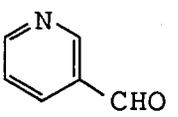

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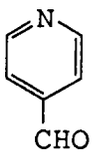

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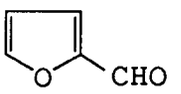

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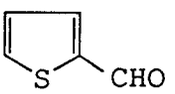

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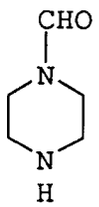

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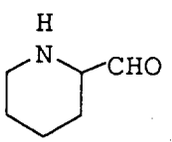

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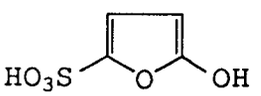

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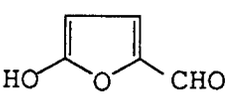

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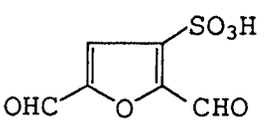

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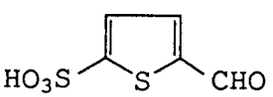

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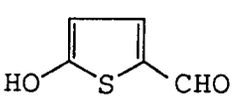

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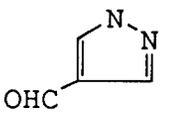

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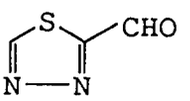

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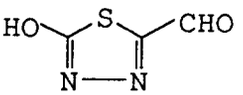

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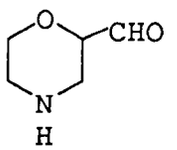

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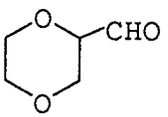

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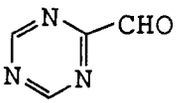

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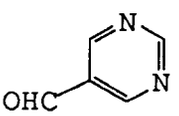
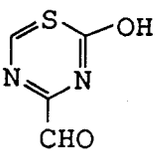


(F-72)



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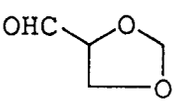

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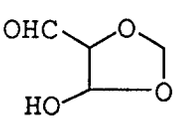

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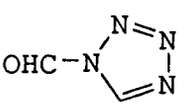

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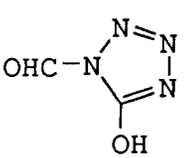

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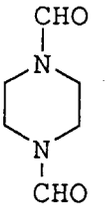


Besides the above exemplified compounds, suitable examples include compounds (76) to (90) shown on pages 13-14 of Japanese Pat. Appl. No. 89686/1991.

Among the above examples of the compound represented by Formula (F), preferred ones are those denoted by (F-2), (F-3), (F-4), (F-6), (F-23), (F-24), (F-52) and (F-62), and (F-3) is particularly preferred.

The compounds represented by Formula (F) are also be commercially available.

The compounds represented by Formula (F) is contained in a stabilizer for processing a silver halide color photographic light-sensitive material. It may also be contained, besides in a stabilizer, in a processing solution used in the bath preceding the processing bath having a bleaching ability, a processing solution having a bleaching ability, and a processing solution having a fixing ability.

The addition amount of the compound respresented by Formula (F) is preferably 0.05 to 20 g, more preferably 0.1 to 15 g and most preferably 0.5 to 10 g per liter of stabilizer.

The compound represented by Formula (F) has a feature of providing a good image preservability, particularly under low moisture conditions, when compared with conventional formaldehyde substitutes.

In the invention, it is preferable that the stabilizer contain a chelating agent having a chelate stability constant not less than 8 against ferric ions. "Chelate stability constant" means the constant generally known by L.G. Sillen and A.E. Martell, "Stability Constants of Metal-ion Complexes", The Chemical Society, London (1964) and S. Chaberek and A.E. Martell, "Organic Sequestering Agents", Willey (1959).

The chelating agent having a chelate stability constant not less than 8 against iron ions includes organic carboxylic acid chelating agents, organic phophoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxy compounds. The above iron ions mean ferricions. (Fe^{3+})

Typical examples of the chelating agent having a chelate stability constant not less than 8 against ferric ions include the following compounds, but not limited to them. That is, suitable ones are ethylenediamine-diorthohydroxyphenylacetic acid, diaminopropanetetracetic acid, nitrilotriacetic acid, hydroxyethylenediaminetriacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentacetic acid, hydroxyethyliminodiacetic acid, diaminopropanoltetracetic acid, transcyclohexanediaminetetracetic acid, glycoletherdiaminetetracetic acid, ethylenediaminetetrakismethylenephosphonic acid, nitrilotrimethylenephosphonic 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-disulfonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate. Among these, preferred ones are dietylenetriaminepentacetic acid, nitrilotriacetic acid, nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphoni acid, and 1-hydroxyethylidene-1,1-diphosphonic acid is particularly preferred.

The above chelating agents are used in an amount of preferably 0.01 to 50 g per liter of stabilizer, an addition amount of 0.05 to 20 g/l produces particularly preferable results.

Preferably, the stabilizer contains an ammonium compound as an additive. Though such an ammonium compound may be selected from various inorganic ammonium salts, preferable ones are ammonium hydoxide, ammonium bromide, ammonium carbonate, ammonium chloride and ammonium phosphate. These compounds are used, singly or in combination of two or more types, in an amount of preferably 0.001 to 1.0 mol and more preferably 0.002 to 0.2 mol per liter of a stabilizer.

It is preferable that the stabilizer further contains a sulfite. Such a sulfite may be any of organic and inorganic sulfites as long as it releases a sulfite ion, but an inoreganic salt is preferred. Suitable examples thereof include sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and sodium hydrosulfite. These sulfites are added in the stabilizer in an amount of preferably not less than 1×10^{-3} mol/l; an addition amount of 5×10^{-3} to 10^{-1} mol/l is more preferable and more effective in stain prevention. While these may be added directly to the stabilizer, addition to a stabilizing replenisher is

preferred.

It is preferable that a metal salt be contained in the stabilizer in combination with the above chelating agent. Such a metal salt includes a salt of Ba, Ca, Co, Ce, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al or Sr, and can be fed in the form of an inorganic salt of a halide, hydroxide, sulfate, carbonate, phosphate or acetate, or a water-soluble chelating agent. Such a compound is employed in an amount of preferably 1×10^{-4} to 1×10^{-1}, more preferably 4×10^{-4} to 2×10^{-2} mol per liter of stabilizer.

An organic acid (e.g., citric acid, acetic acid, succinic acid, oxalic acid or benzoic acid) and a pH regulator (e.g., phosphates, borates, hydrochlorides or sulfates) may be added to the stabilizer. These compounds may be used in any combination within the limits of amount necessary to maintain the pH of the stabilizer and not to exert a harmful influence upon storage stability of color photographic images and formation of precipitates.

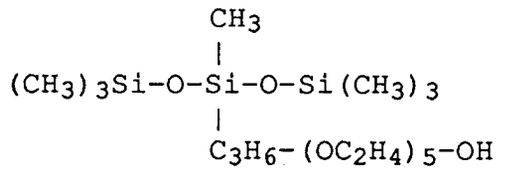
In addition, a conventional fungicide, such as 5-chloro-2-methylisothiazoline -3-one or benzisothiazoline, may be jointly used in an amount not harmful to the effect of the invention.

Preferably, the stabilizer further contains a surfactant. Suitable surfactants are those represented by Formula (II) described on page 6 of Japanese Pat. O.P.I. Pub. No. 149438/1992, particularly preferred examples thereof are the following water-soluble organic siloxane compounds. Further, the compounds represented by Formula (I) or (II) described in Japanese Pat. O.P.I. Pub. No. 250449/1987 may also be used.

The surfactant content of the stabilizer is 0.01 to 20 g/litre, and preferably 0.05 to 10 g/litre.

(Water-soluble organic siloxane compounds)

(1)



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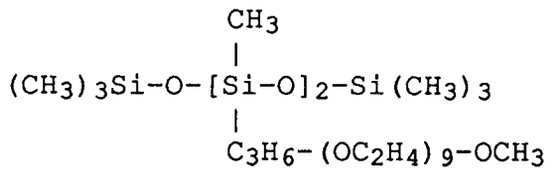

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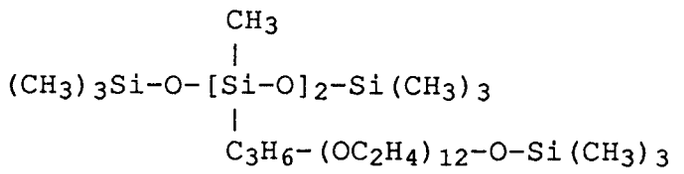

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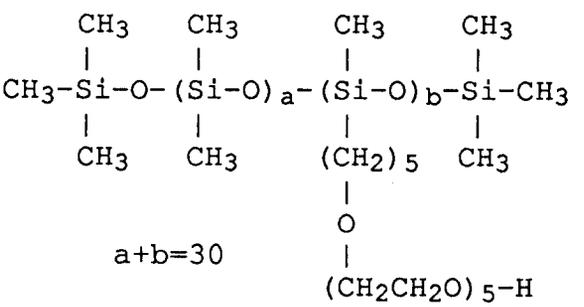
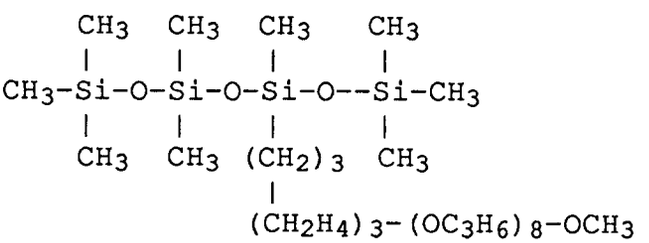


(15)



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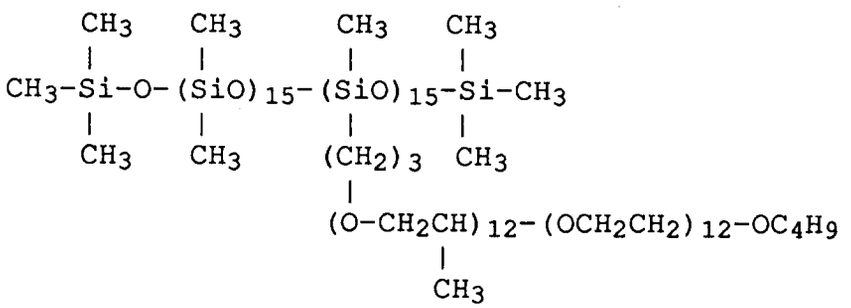

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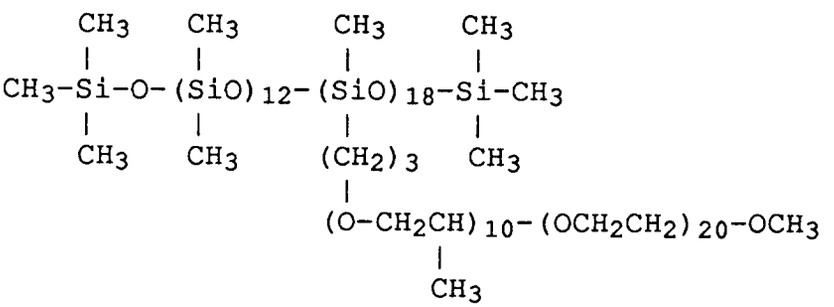


Other typical exemplified compounds are those denoted by (II-2), (II-4) to (II-6), (II-8) to (II-12) and (II-14) on pages 67-70 of Japanese Pat. O.P.I. Pub. No. 149438/1992.

When these water-soluble organic siloxane compounds having a polyoxyalkylene group are used in an amount of 0.01 to 20 g per liter of stabilizer, favorable results can be obtained.

An amount less than 0.01 g per liter causes surface stains on a light-sensitive material; an amount more than 20 g per liter allows the organic siloxane compound to deposit on a light-sensitive material and thereby accelerates staining.

In the processing according to the invention, silver may be recovered from the stabilizer. Further, it is preferable in embodying the invention that the stabilizer be subjected to ion exchange treatment, electrodialysis (see Japanese Pat. O.P.I. Pub. No. 28949/1986) or reverse osmosis (see Japanese Pat. O.P.I. Pub. Nos. 241053/1985, 254151/1987, 132440/1990). Moreover, it is also preferable to use a deionized water in the stabilizer preparation, in order to enhance the stabilizer's antimold property and stability as well as the preservability of dye images. The means for the deionization is not particularly limited as long as it can reduce the Ca and Mg ion content of a deionized water to 5 ppm or less; but, a preferable example is to treat water using an ion-exchange resin and a reverse osmosis membrane singly or in combination. Usable ion-exchange resins and reverse osmosis membranes can be seen in Journal of Technical Disclosure No. 87/1984.

The salt concentration of the stabilizer is preferably not bore than 1,000 ppm, especially not more than 800 ppm.

In order to bring out the effect of the invention fully, it is preferable that a soluble iron salt be present in the stabilizer. Such a soluble iron salt is contained in the stabilizer at a concentration desirably not less than 5×10^{-3}mol/l, more desirably 8×10^{-3} to 150×10^{-3} mol/l and most desirably 12×10^{-3} to 100×10^{-3} mol/l.

In the invention, the pH of the stabilizer is desirably not less than 6.0, more desirably not less than 7.0 and most desirably 7.5 to 9.0. The pH regulator used in the stabilizer may be any of generally known alkaline agents and acid agents.

The processing temperature of the stabilization is desirably 15 to 70 °C, more desirably 20 to 55 °C. The processing time is desirably not more than 120 sec, more desirably 3 to 90 sec and most desirably 6 to 50 sec.

The replenishing amount of the stabilizer is desirably not more than 670 ml, more desirably 100 to 500 ml and most desirably 160 to 460 ml per square meter of light-sensitive material, in view of rapid processability and dye-image preservability. A replenishing amount of more than 670 ml/m^2 does not bring

out the effect of the invention satisfactorily. And the effect of the invention can be revealed more clearly as the replenishing amount decreases.

In the invention, "the replenishing amount" means an amount substantially replenished; therefore, in the reactivation of the stabilizer, the amount of a reactivator fed corresponds to the replenishing amount.

It is advantageous that the stabilizer tank is made up of a plurality of tanks, desirably 2 to 6 tanks. In a particularly preferable embodiment of the invention, stabilization is carried out in a countercurrent mode (the replenisher is fed to the rear tank and the overflow is poured into the preceding tank) using 2 or 3 tanks, especially 2 tanks.

Though no washing process is required after the stabilization, a short-time rinsing or surface washing with a small amount of water may be performed when necessary.

Color developing agents used in color development are aminophenol compounds and p-phenylenediamine compounds. Of these, p-phenylenediamine compounds having a water-solubilizing group are preferred in the invention.

At least one water-solubilizing group is required to be present on the amino group or the benzene ring of the p-phenylene diamine compound. Preferable examples of such a water-solubilizing group include
$-(CH_2)n-CH_2OH$,
$-(CH_2)m-NHSO_2-(CH_2)n-CH_3$,
$-(CH_2)m-O-(CH_2)n-CH_3$,
$-(CH_2CH_2O)nCmH_{2m+1}$ (m and n each represent an integer of 0 or more.), -COOH group and $-SO_3H$ group .

The addition amount of these color developing agents is desirably not less than 0.5×10^{-2} mol, more desirably 1.0×10^{-2} to 1.0×10^{-1} mol and most desirably 1.5×10^{-2} to 7.0×10^{-2} mol per liter of color developer.

The above color developing agents are usually used in the form of salts such as hydrochlorides, sulfates and p-toluenesulfonate.

The color developer used in the color developing process may contain an alkaline agent usually employed in a developer, such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate,potassium carbonate, sodium sulfate, sodium metaborate or borax. There may also be contained various additives such as benzyl alcohol, alkali halides, potassium bromide, potassium chloride, development control agents such as citrazinic acid, preservatives such as hydroxylamine, hydroxylamine derivatives (e.g., diethylhydroxylamine), hydrazine derivatives (e.g., hydrazinodiacetic acid) and sulfites.

Further, various defoamers and surfactants, and organic solvents such as methanol, dimethylformamide, dimethylsulfoxide may also be contained according to a specific requirement.

The pH of the color developer is usually not less than 7, preferably about 9 to 13.

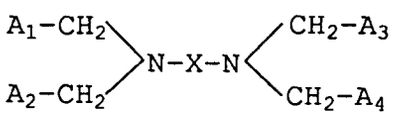
When necessary, the color developer may contain an antioxidant such as tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetotone, aromatic secondary alcohols, hydroxamic acid, pentose, hexose or pyrogallol-1,3-dumethyl ether.

The color developer may use various chelating agents as sequestrants. Examples thereof include aminopolycarboxylic acids such as ethylenediaminetetracetic acid, diethylenetriaminepentacetic acid, organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, aminopolyphosphonic acids such as aminotrimethylenephosphinic acid, ethylenediamineteytraphosphoric acid, oxycarboxylic acids such as citric acid, gluconic acid, phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid, and polyphosphoric acids such as tripolyphosphoric acid,and hexametaphosphoric acid.

In a continuous processing, the replenishing amount of the color developer for color negative films is desirably not more than 15.0 ml, more desirably 2.5 to 9.0 ml and most desirably 3.0 to 7.0 ml per square meter of light-sensitive material.

In the invention, the bleaching agent used in a bleacher is preferably a ferric salt of the organic acid represented by the following Formula (A).

Formula (A)

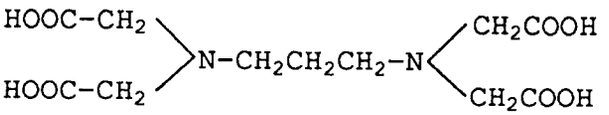


In Formula (A), A_1 to A_4 may be the same or different and each represent $-CH_2OH$, -COOM or $-OP_3M_1M_2$, where M, M_1 and M_2 each represent a hydrogen atom, an alkali metal atom (e.g., sodium,

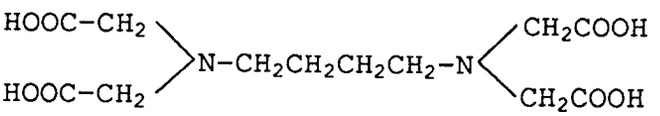
potassium) or an ammonium group; X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms (e.g., propylene, butylene, pentamethylene); the substituent is a hydroxyl group or an alkyl group having 1 to 3 carbon atoms.

Preferable examples of the compound represented by Formula (A) are shown below:

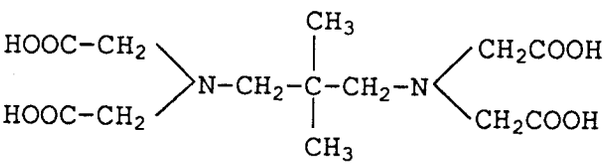
(A-1)



(A-4)



(A-9)



Other preferable examples are those exemplified on pages 89-90 of Japanese Pat. O.P.I. Pub. No. 149438/1992 bearing denotations of (A-2), (A-3), (A-5) to (A-8), (A-10) to (A-12).

As ferric salts of these compounds (A-1) to (A-12), sodium salts, potassium salts or ammonium salts of their ferric complex salts may be arbitrarily used. From the viewpoint of the effect of the invention and solubilities thereof, ammonium salts of their ferric complex salts are preferably used. Of the above compounds, (A-1) is particularly preferred in the invention.

In another favorable embodiment of the invention, the concentration of ammonium salts is desirably not more than 50 mol%, more desirably not more than 20 mol% and most desirably not more than 10 mol%, since these oxidizing agents have considerably high oxidizing powers and oxidation fogs are liable to occur at a high ammonium salt concentration.

The addition amount of the organic acid ferric complex salt is desirably 0.1 to 2.0 mol, more desirably 0.15 to 1.5 mol per liter of bleacher.

When a ferric complex salt of the organic acid represented by Formula (A) is used in combination with ferric complex salts of other organic acids such as ethylenediaminetetracetic acid, it is advantageous that a ferric complex salt of the compound represented by Formula (A) amounts to 70 mol% or more in order to bring out the effect of the invention fully. This value is desirably 80 mol% or more, more desirably 90 mol% or more, and most desirably 95 mol% or more.

Such organic acid ferric complex salts may be used in the form of complex salts, or these may be formed in the bleacher by adding thereto ferric sulfate, ferric chloride, ferric acetate, ammonium ferric sulfate or ferric phosphate and an aminopolycarboxylic acid or its salt. When used in the form of complex salts, these complex salts may be used singly or in combination of two or more types. When complex salts are formed in the bleacher by use of ferric salts and aminopolycarboxylic acids, both the ferric salts and the aminopolycarboxylic acids may be used singly or in combination of two or more types. In each case, the aminopolycarboxylic acid may be used in excess over the amount necessary to form a ferric complex salt.

The rapidity of the processing capability of the bleacher can be raised by adding at least one compound selected from imidazole, its derivatives described in Japanese Pat. O.P.I. Pub. No. 295258/1989, the compounds represented by one of Formulas (I) to (IX) described in the same patent application and the

exemplified compounds thereof.

Besides these bleaching accelerators, there may also be used for the same purpose the compounds exemplified on pages 51-115 of Japanese Pat. O.P.I. Pub. No. 187370/1986, the compounds exemplified on pages 22-25 of Japanese Pat. O.P.I. Pub. No. 17445/1988, and the compounds described in Japanese Pat. O.P.I. Pub. Nos. 95630/1978, and 28426/1978.

These bleaching accelerators may be used singly or in combination. The addition amount is desirably in a range of about 0.01 to 100 g, more desirably 0.05 to 50 g, and most desirably 0.05 to 15 g per liter of bleacher.

The bleaching accelerators may be directly added as they are, but, these are generally dissolved firstly in water, an aqueous alkali or an organic acid and then added. If necessary, these may be dissolved in an organic solvent such as methanol, ethanol or acetone.

The bleacher is used at a temperature of usually 20 to 50° C, preferably 25 to 45° C.

The pH of the bleacher is preferably not more than 6.0 and especially in a range of 1.0 to 5.5. "The pH of the bleacher" is the pH of a bleaching bath where a silver halide light-sensitive material is being processed and clearly distinguished from the pH of the so-called replenisher.

Usually, halides such as ammonium bromide, potassium bromide and sodium bromide are added in the bleacher. Further, there may also be contained various optical whitening agents, defoamers and surfactants.

The replenishing amount of the bleacher is desirably not less than 500 ml, more desirably 20 to 400 ml and most desirably 40 to 350 ml per square meter of light-sensitive material. The effect of the invention comes to be revealed more clearly as the replenishing amount decreases.

For the purpose of raising activity of the bleacher, air or oxygen may be blown into the bleaching bath or the storage tank for replenisher, or a suitable oxidizing agent such as hydrogen peroxide, a bromate or a peroxodisulfate may be added therein. Further, pipes of the automatic processor may be made of a material having a high oxygen permeability, such as a silicone rubber.

As the fixing agent in the fixer employed in the fixing process after the bleaching process, the combined use of a thiosulfate and a thiocyanate is preferred in order to maintain the fixing ability under ammonia-free conditions.

Setting the ammonium ion content of the fixer at 50 mol% or less, preferably 20 mol% or less and especially 0 to 10 mol% of the total cations is effective in preventing stains in the stabilizing process directly following the bleaching process and in reducing the pollution load due to decrease in ammonium ions, but the decrease in ammnoium ions may exert a harmful influence upon the fixing ability. Therefore, in a preferable embodiment of the invention, a thiocyanate is jointly used in the fixer at a concentration of 0.4 to 3.0 mol/l, or the concentration of a thiosulfate is set at not less than 0.5 mol/l, preferably not less than 1.0 mol/l and especially 1.2 to 2.5 mol/l.

The replenishing amount of the fixer or the bleach-fixer according to the invention is desirably not more than 900 ml, more desirably 20 to 750 ml and most desirably 50 to 620 ml per square meter of light-sensitive material.

The pH of the fixer or the bleach-fixer according to the invention is preferably 4 to 8.

The fixer or the bleach-fixer may contain the compounds represented by Formula (FA) described on page 56 of Japanese Pat. O.P.I. Pub. No. 295258/1989 or the exemplified compounds thereof, or the compounds represented by Formula (1) or (2) described on pages 5-10 of International Pat. Pub. No. W091/08517. The addition of these compounds has the effect of minimizing formation of sludges when the fixer or the bleach-fixer are used for a long time to process small batches of light-sensitive materials.

Favorable results can be obtained when these compounds represented by Formula (FA) or those represented by Formula (1) or (2) are added in an amount of 0.1 to 200 g per liter of processing solution.

The fixer or the bleach-fixer may use a sulfite or a sulfurous-acid-releasing compound. Typical examples thereof include potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogen sulfite, sodium hydrogensulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. Further, there may also be used the compounds represented by Formula (B-1) or (B-2) described on page 60 of Japanese Pat. O.P.I. Pub. No. 295258/1989.

These sulfites and sulfurous-acid-releasing compounds are required to be present in the fixer at a concentration of 0.05 mol/l or more in terms of sulfurous ions. This sulfurous ion concentration is desirably in a range of 0.08 to 0.65 mol/l, more desirably 0.10 to 0.50 mol/l and most desirably 0.12 to 0.40 mol/l.

In the invention, the processing time with the bleacher and that with the fixer may be arbitrarily selected; but, these are desirably not more than 6 min and 30 sec, more desirably ten sec to 4 min and 20 sec, and most desirably 20 sec to 3 min and 20 sec, respectively.

In one preferable embodiment of the invention, it is preferable that the bleacher and the fixer be subjected to forced stirring while used in processing, for the purpose of bringing out the effect of the

invention fully and enhancing the rapid processing capability. "Forced stirring" means to carry out stirring forcedly with the aid of a stirring means, not the usual diffusive movement of liquid. As the means for the forced stirring, the means disclosed in Japanese Pat. O.P.I. Pub. Nos. 222259/1989 and 206343/1989 can be employed.

In the invention, the crossover time between the tanks, such as that between the color developer tank and the bleacher tank, is not more than 10 sec, preferably not more than 7 sec. Setting the crossover time as the above exerts a favorable influence upon bleach foggs, besides the effect of the invention. Minimizing the amount of a processing solution brought in together with a light-sensitive material by providing duckbill valves is also a preferable embodiment of the invention.

Silver halide grains used in the silver halide color photographic light-sensitive material (hereinafter abbreviated as light-sensitive material) may be any of silver chloride, silver chlorobromide, silver iodobromide and silver chloroiodobromide, and silver iodobromide is preferably used in view of the effect of the invention.

The average silver iodide content of all the silver halide emulsions used in the light-sensitive material is desirably 0.1 to 15 mol%, more desirably 0.5 to 12 mol% and most desirably 1 to 10 mol%.

The average size of the grains in all the silver halide emulsions used in the light-sensitive material is desirably not more than 2.0 μm, more desirably 0.1 to 1.0 μm.

When the silver halide emulsion contains grains having an average (grain size)/(grain thickness) ratio not larger than 5, it is preferable that the grain size distribution be monodispersed in view of desilverizability.

"A monodispersed silver halide emulsion" indicates a silver halide emulsion in which silver halide grains having a grain size of average grain size ± 20% amount to 60% or more, preferably 70% or more, and especially 80% or more of the total weight of the silver halide grains.

Here, "average grain size" is defined by the grain size at which the product of the frequency ni of grains having a grain size ri and ri^3, ni × ri^3, becomes the maximum (three significant figures, the least figure is rounded to the nearest whole number).

The term "grain size" used here means the diameter for a spherical silver halide grain, and the diameter of a circle converted, in the same surface area, from a grain's projected figure for a non-spherical grain.

The grain size can be determined, for example, by the steps of photographing a grain at a magnification of 10,000 to 50,000 with an electron microscope, and measuring the grain diameter or the projected area on the print (the number of the measured grains should be at least 1,000 at random).

A particularly preferable and highly monodispersed emulsion is comprised of grains having a grain size distribution extent not more than 20% and especially not more than 15%, when said distribution extent is defined by

$$\frac{\text{standard deviation of grain sizes}}{\text{average grain size}} \times 100 = \text{distribution extent (\%)}.$$

Silver halide grains used in the invention may be regular crystal grains or twin crystal grains, and the ratio of (1.0.0) faces to (1.1.1) faces of them may be arbitrarily selected. In addition, the crystal structure of these silver halide grains may be uniform from the inner part to the outer part of grains, or may be a layer structure (core/shell structure) in which the inner part is different from the outer part in composition. There can also be used silver halide grains which form latent images mainly on their surfaces, or those which form latent images inside of grains. Moreover, tabular silver halide grains (see Japanese Pat. O.P.I. Pub. No. 113934/1983, Japanese Pat. Appl. No. 170070/1984) can be employed.

These silver halide grains may be prepared by any of the acid method, the neutral method and the ammoniacal method.

There may also be used a method comprising the steps of forming seed grains by the acid method and then growing them to a prescribed size by the ammoniacal method which provides a higher growth speed. In growing silver halide grains, it is preferable that the pH and the pAg in the reaction vessel be controlled, and that silver ions and halide ions be sequentially and simultaneously added thereto in amounts corresponding to the growth rate of silver halide grains as described, for example, in Japanese Pat. O.P.I. Pub. No. 4852/1979.

The silver halide grains used in the invention are favorably prepared as described above. A composition containing the silver halide grains thus obtained is called a silver halide emulsion in this patent specification.

The method for processing a light-sensitive material according to the invention can be applied to any of color negative films, color papers, color positive films, color reversal films for slides, color reversal films for movies, color reversal films for TVs and reversal color papers, as far as these light-sensitive materials are of coupler-in-emulsion type containing couplers in themselves.

EXAMPLES

Typical examples of the present invention are described hereunder, but the embodiment of the invention is not limited to them.

Example 1

A multilayered color photographic light-sensitive material was prepared by forming sequentially the layers of the following compositions on a triacetylcellulose film base.

Addition amounts of respective components are in grams per square meter unless otherwise indicated. Amounts of silver halide emulsions and colloidal silvers are given in amounts of silver present. But those of sensitizing dyes are shown in moles per mole of silver halide contained in the same layer.

(Light-sensitive material sample)

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: 0.4 μm, AGI content: 2.0 mol%)	1.0
Sensitizing dye (SD-1)	1.8×10^{-5} (mol/mol AgX)
Sensitizing dye (SD-2)	2.8×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-3)	3.0×10^{-4} (mol/mol AgX)
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 emulsion layer	
Silver iodobromide emulsion (average grain size: 0.7 μm, AgI content: 8.0 mol%)	0.8
Sensitizing dye (SD-1)	2.1×10^{-5} (mol/mol AgX)
Sensitizing dye (SD-2)	1.9×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-3)	1.9×10^{-4} (mol/mol AgX)
Cyan coupler (C-2)	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 emulsion layer	
Silver iodobromide emulsion (average grain size: 0.8 μm, AgI content: 8.0 mol%)	1.70
Sensitizing dye (SD-1)	1.9×10^{-5} (mol/mol AgX)
Sensitizing dye (SD-2)	1.7×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-3)	1.7×10^{-4} (mol/mol AgX)
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)	6.8×10^{-5} (mol/mol AgX)
Sensitizing dye (SD-5)	6.2×10^{-4} (mol/mol AgX)
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)	1.9×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-7)	1.2×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-8)	1.5×10^{-5} (mol/mol AgX)
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 AgX)
Sensitizing dye (SD-7)	1.0×10^{-4} (mol/mol AgX)
Sensitizing dye (SD-8)	3.4×10^{-6} (mol/mol AgX)
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%)	0.5
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 AgX)
Sensitizing dye (SD-10)	1.9×10^{-5} (mol/mol AgX)
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 AgX)
Sensitizing dye (SD-10)	7.9×10^{-5} (mol/mol AgX)
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

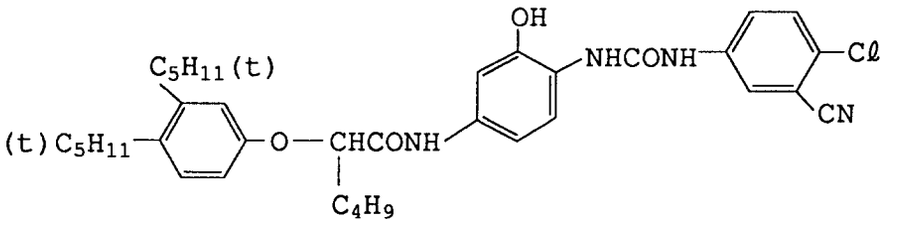
13th layer: 1st protective layer	
Fine grain silver iodobromide emulsion (average grain size: 0.08 μm, AgI content: 1.0 mol%)	0.4
UV absorbent (UV-1)	0.07
UV absorbent (UV-2)	0.10
High boiling solvent (Oil-1)	0.07
High boiling solvent (Oil-3)	0.07
Formalin scavenger (HS-1)	0.13
Formalin scavenger (HS-2)	0.37
Gelatin	1.3

14th layer: 2nd protective layer	
Alkali-soluble matting agent (average particle size: 2 μm)	0.13
Polymethylmethacrylate (average particle size: 3 μm)	0.02
Lubricant (WAX-1)	0.04
Gelatin	0.6

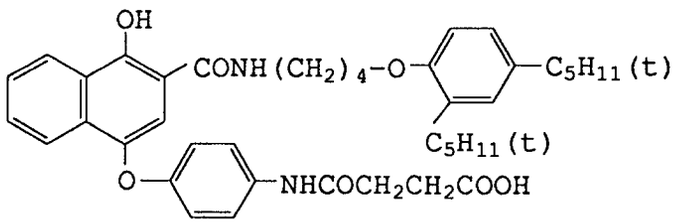
Besides the above compositions, coating aid Su-1, dispersant Su-2, a viscosity regulator, hardeners H-1 and H-2, stabilizer ST-1 and antifoggants AF-1 (Mw: 10,000) and AF-2 (Mw: 1,100,000) were added.

The emulsions used in preparing the above sample, which were comprised of monodispersed grains having a surface low silver iodide portion, were subjected to optimum gold and sulfur sensitization according to the usual method. The average grain sizes are shown by diameters of converted cubes.

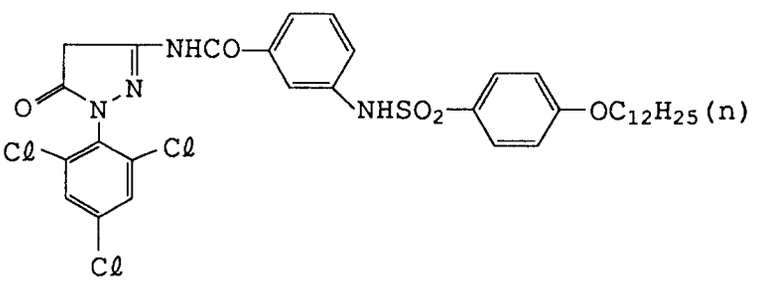
C-1



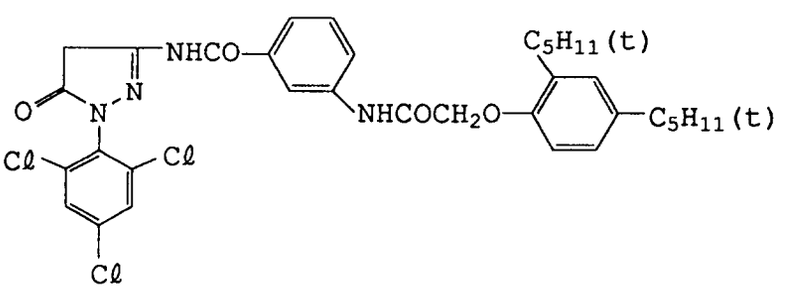
C-2



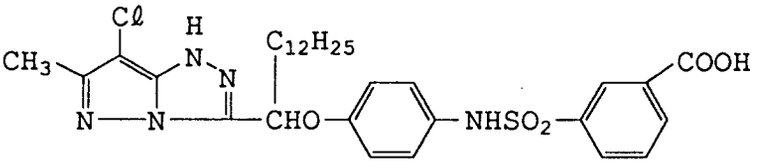
M-1



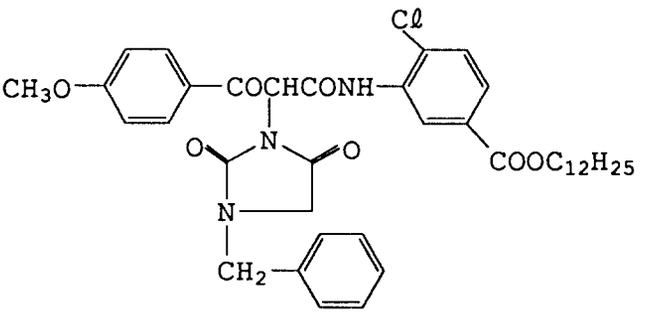
M-2



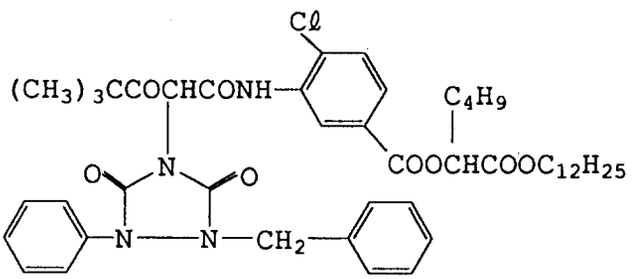
M-3



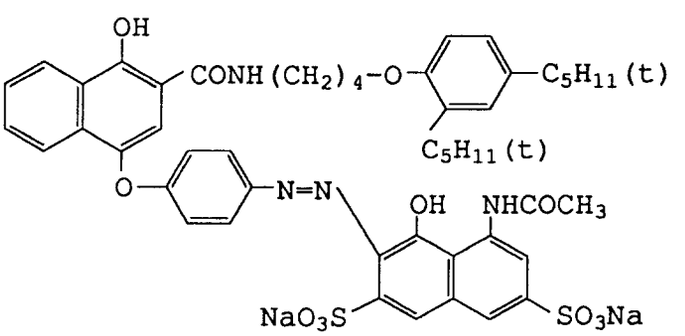
Y-1



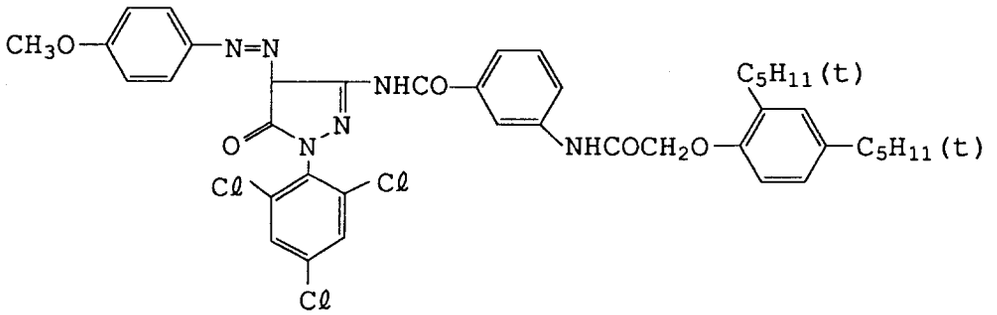
Y-2



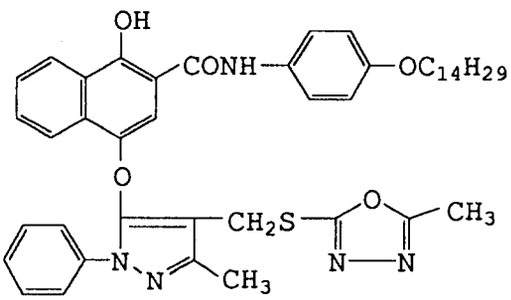
CC-1



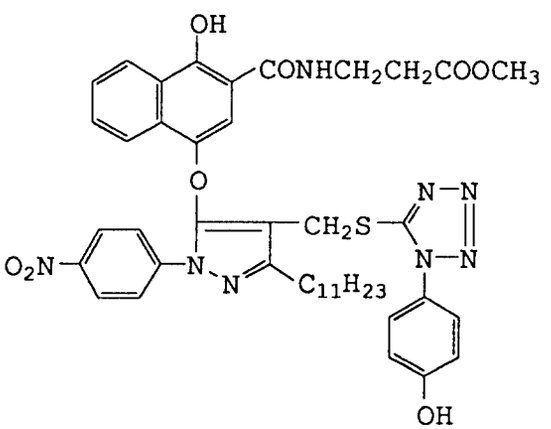
CM-1



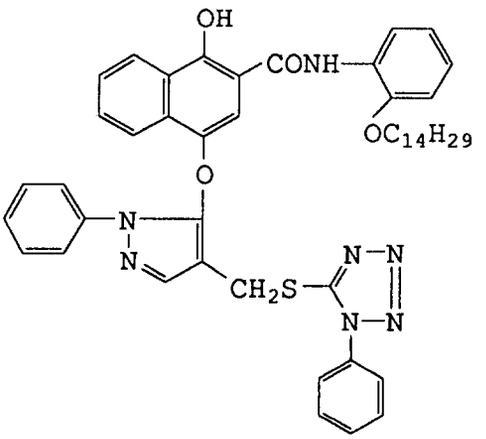
D-1



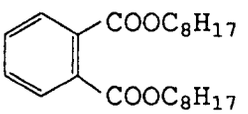
D-2



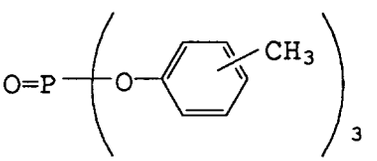
D-3



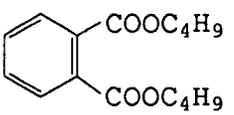
Oil-1



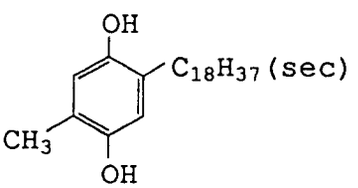
Oil-2



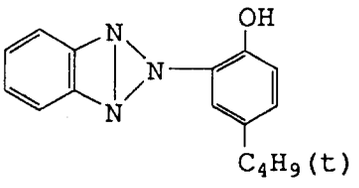
Oil-3



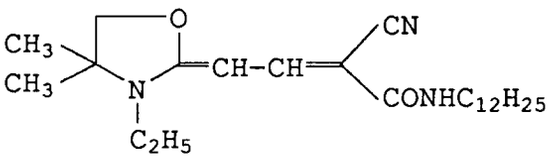
SC-1



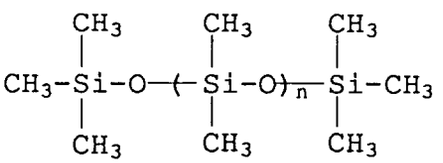
UV-1



UV-2

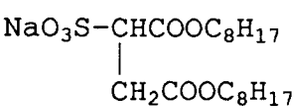


WAX-1

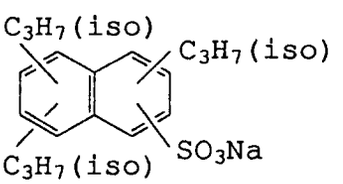


Mw=3,000 (weight-average molecular weight)

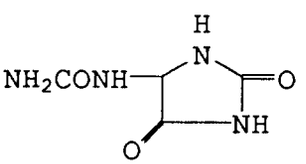
Su-1



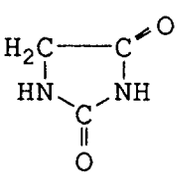
Su-2



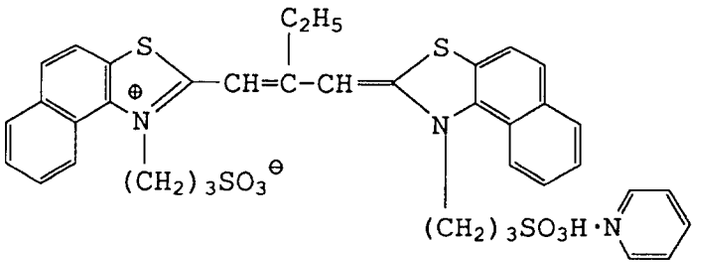
HS-1



HS-2



SD-1



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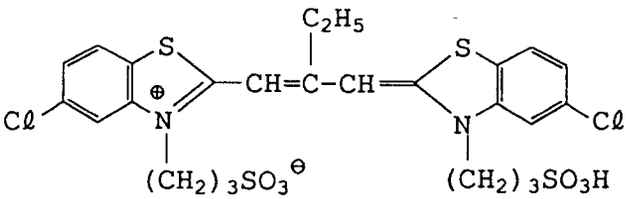
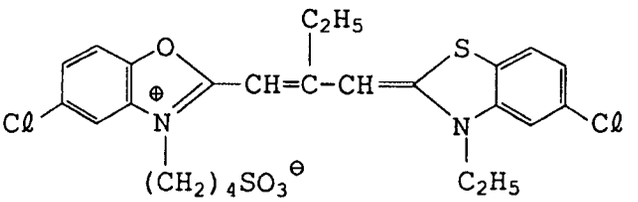
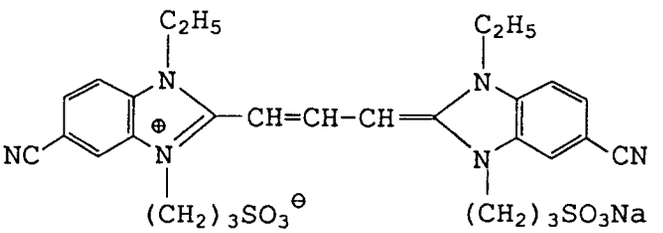


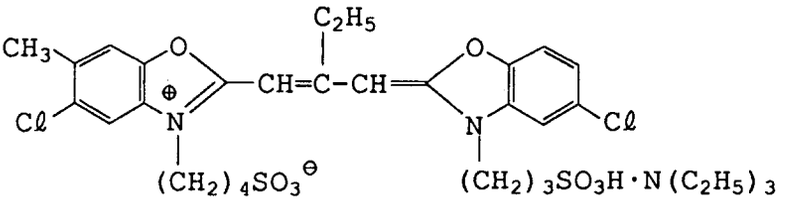
SD-3



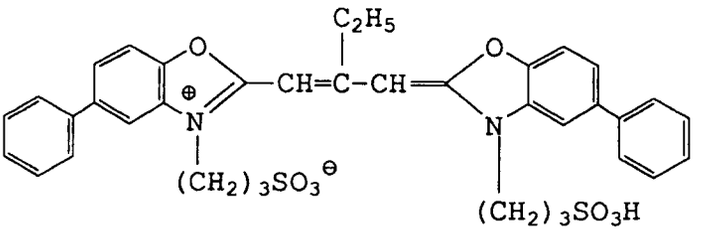
SD-4



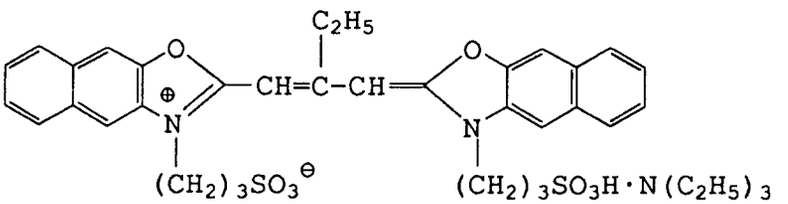
SD-5



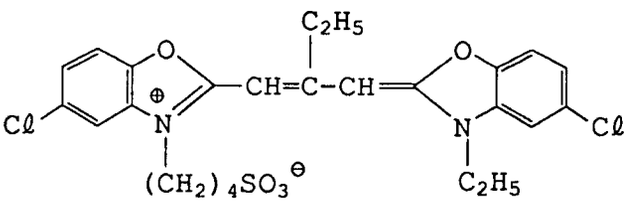
SD-6



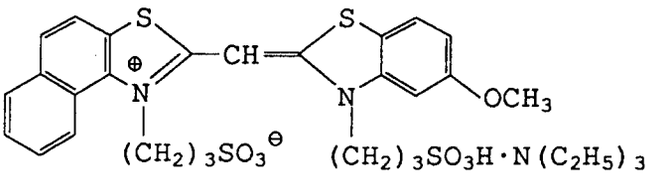
SD-7



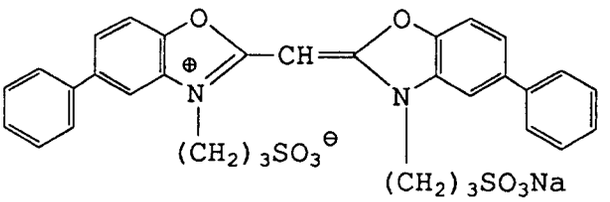
SD-8



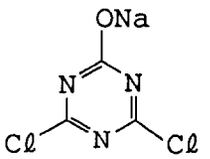
SD-9



SD-10



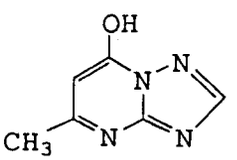
H-1



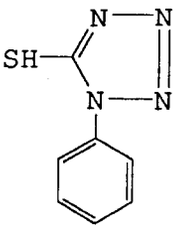
H-2

$(CH_2=CHSO_2CH_2)_2O$

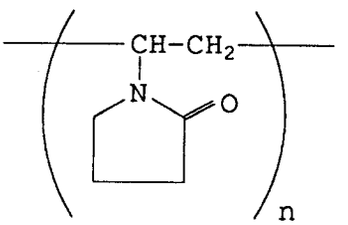
ST-1



AF-1



AF-2



n: degree of polymerization

The samples thus obtained were exposed by actual photographing and then processed under the following conditions:

Process	Processing Time	Processing Temp	Replenishing *Amount
Color developing	3 min 15 sec	38 ° C	536 ml
Bleaching	45 sec	38 ° C	134 ml
Fixing	1min 30 sec	38 ° C	536 ml
**Stabilizing	90 sec	38 ° C	536 ml
Drying	1 min	40 to 70 ° C	-

* Replenishing amounts are in amounts per square meter of light-sensitive material.

** Stabilizing was performed in a 3-tank countercurrent mode by feeding a replenisher to the final tank.

Compositions of the processing solutions used in the above processes are as follows:

Color developing 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
Diethylenetriaminepentacetic acid	3.0 g
Potassium hydroxide	1.2 g

Water was added to make 1 liter, and the pH is adjusted to 10.08 with potassium hydroxide and 20% sulfuric acid.

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

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

Bleaching tank solution	
Ammonium ferric 1,3-diaminopropanetetracetate	0.3 mol
Ethylenediaminetetracetic acid	2g
Bromide salt	1.81 mol
Glacial acetic acid	50 ml

The pH was adjusted to 4.5 with aqueous ammonia, aqueous caustic potash or glacial acetic acid, while controlling the concentration of ammonium ions at 20 mol% of the total cations. Then, water was added to make 1 liter.

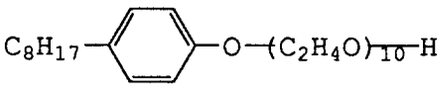
Bleaching replenisher	
Ammonium ferric 1,3-diaminopropanetetracetate	0.36 mol
Ethylenediaminetetracetic acid	2 g
Bromide salt	178 g
Glacial acetic acid	50 ml

The pH was adjusted to 4.0 with aqueous ammonia, aqueous caustic potash or glacial acetic acid, while controlling the concentration of ammonium ions at 20 mol% of the total cations. Then, water was added to make 1 liter.

Fixing tank solution and fixing replenisher	
Thiosulfate	0.3 mol
Thiocyanate	0.2 mol
Metabisulfite	3 g
Ethylenediaminetetracetic acid	0.8 g

Water was added to make 1 liter, then the pH was adjusted to 6.5 with acetic acid, aqueous ammonia and aqueous caustic potash and, at the same time, the ratio of ammonium ions to the total cations was adjusted as shown in Table 4 by changing kinds of salts (e.g., ammonium salt, potassium salt) Stabilizing tank solution and stabilizing replenisher

Surfactant 0.1 g



Dearcide 702 (product of Dearborn Co.) 1.0 ml

Formalin or a compound of Formula (F)

Shown in Table 4

Water was added to make 1 liter, then the pH was adjusted to 7.0 with potassium hydroxide and 20% sulfuric acid.

A continuous processing was run with a small automatic processor for experimental continuous processing till the amount of stabilizing replenisher fed reached 10 times the capacity of the stabilizing bath.

After completion of the continuous processing, the stabilizing bath was examined if there was any sulfide precipitate, and the maximum magenta density of the processed film sample was measured. The sample was then stored for 3 weeks at 70 °C and 70% relative humidity, and the maximum magenta density after storing was measured to determine color fading of the dye. Further, the processed sample was visually checked for backside stains, scratches and adhesion of foreign matters. The results of the evaluation are shown in Table 5.

The meaning of alphabetical signs in Table 5 are as follows:

Sulfide precipitation

A no precipitates occur
B precipitates occur slightly
C precipitates occur in a large amount

The amount of precipitates increases as the number of C's increases.

Backside stains

A no stains occur
B stains occur slightly
C stains occur

The degree of stains becomes heavier as the number of C's increases.

Scratches and adhesion of foreign matters

A not observed
B slightly observed
C apparently observed

The degree of scratches and adhesion of foreign matters becomes heavier as the number of C's increases.

Table 4

Experiment No.	Ratio of Ammonium Ions to the Total Cations in Stabilizer (mol%)	Formalin or Compound of Formula (F)		Remarks
		Compound No.	Addition Amount (g/l)	
1-1	20	-	-	Comparison
1-2	20	formalin (37%)	3.5	Comparison
1-3	20	F-1	3.5	Invention
1-4	20	F-2	3.5	Invention
1-5	20	F-3	3.5	Invention
1-6	20	F-4	3.5	Invention
1-7	20	F-6	3.5	Invention
1-8	20	F-23	3.5	Invention
1-9	20	F-24	3.5	Invention
1-10	20	F-52	3.5	Invention
1-11	20	F-61	3.5	Invention
1-12	20	F-62	3.5	Invention
1-13	0	formalin (37%)	3.5	Comparison
1-14	30	formalin (37%)	3.5	Comparison
1-15	50	formalin (37%)	3.5	Comparison
1-16	60	formalin (37%)	3.5	Comparison
1-17	80	formalin (37%)	3.5	Comparison
1-18	0	F-3	3.5	Invention
1-19	30	F-3	3.5	Invention
1-20	50	F-3	3.5	Invention
1-21	60	F-3	3.5	Comparison
1-22	80	F-3	3.5	Comparison
1-23	20	F-3/F-2	1.5/2.0	Invention
1-24	20	F-3/F-62	1.5/2.0	Invention
1-25	20	F-2/F-62	1.5/2.0	Invention

Table 5

Experiment No.	Color Fading Ratio(%)	Sulfide Precipi tates	Back side Stains	Scratches and Adhesion of Foreign Matters	Remarks
1-1	39.8	B	A	C	Comparison
1-2	4.3	C	A	A	Comparison
1-3	3.4	A	A	A	Invention
1-4	3.2	A	A	A	Invention
1-5	3.0	A	A	A	Invention
1-6	3.9	B	A	A	Invention
1-7	4.1	B	A	A	Invention
1-8	4.2	A-B	A	A	Invention
1-9	4.1	B	A	A	Invention
1-10	3.8	A	A	A	Invention
1-11	3.6	B	A	A	Invention
1-12	3.5	A	A	A	Invention
1-13	4.3	C-B	A	A	Comparison
1-14	4.0	C	A	A	Comparison
1-15	4.1	D	A	A	Comparison
1-16	4.1	D	A	A	Comparison
1-17	4.0	D	A	A	Comparison
1-18	2.9	A	A	A	Invention
1-19	3.0	B	B	A	Invention
1-20	3.0	B	B	A	Invention
1-21	3.1	B-C	B-C	B-C	Comparison
1-22	3.3	C	C	C-D	Comparison
1-23	3.0	A	A	A	Invention
1-24	3.2	A	A	A	Invention
1-25	3.1	A	A	A	Invention

It is understood from the results shown in Table 5 that the present invention is effective in improving image preservability, solution preservability and in preventing film stains, adhesion of foreign matters, in addition to the capability of minimizing pollution load.

Example 2

The sample prepared in Example 1 was subjected to photographing as in Example 1 and then processed under the following conditions.

Process	Processing Time	Processing Temp	Replenishing *Amount
Color developing	3 min 15 sec	38 ° C	536 ml
Bleach-fixing	2 min 15 sec	38 ° C	790 ml
Stabilizing	90 sec	30 to 34 ° C	5 ml
Drying		40 to 60 ° C	-

The following color developing solution, bleach-fixer and stabilizer were used.

Color developing 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
Diethylenetriaminepentacetic acid	3.0 g
Potassium hydroxide	1.2 g

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

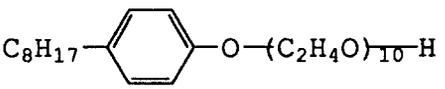
Color developing replenisher	
Potassium carbonate	35 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	5.8 g
Potassium hydroxide	2 g
Diethylenetriaminepentacetic acid	3.0 g

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

Bleach-fixing tank solution and bleach-fixing replenisher	
Complex salt of ferric ethylenediaminetetracetate	0.3 mol
Complex salt of ferric 1,3-diaminopropane-tetracetate	0.3 mol
Ethylenediaminetetracetic acid	2 g
Sulfite	12 g
Thiosulfate	0.3 mol
Thiocyanate	0.2 mol
Aqueous ammonia (28%)	10 ml

The pH was adjusted to 6.0 with aqueous ammonia, aqueous caustic potash and glacial acetic acid, and the concentration of ammonium ions in the total cations was adjusted as shown in Table 6 by changing kinds of salts (e.g., ammonium salt, potassium salt). Then, water was added to make 1 liter. Stabilizing tank solution and stabilizing replenisher

Dearcide 702 (product of Dearborn Co.)	1.0 ml
Surfactant	0.1 g



Formalin or compound of Formula(F) amount of shown in Table 6

Water was added to make 1 liter, and the pH was adjusted to 7.0 with potassium sulfite and 20% sulfuric acid.

Evaluation was carried out in the same manner and on the same items as in Example 1.

Table 6

Experiment No	Ratio of Ammonium Ions to the Total Cations in Stabilizer (mol%)	Formalin or of Formula	Compound (F) Addition	Remarks
		Compound No	Addition Amount (g/l)	
2-1	20	-	-	Comparison
2-2	20	formalin (37%)	3.0	Comparison
2-3	20	F-1	3.0	Invention
2-4	20	F-2	3.0	Invention
2-5	20	F-3	3.0	Invention
2-6	20	F-4	3.0	Invention
2-7	20	F-6	3.0	Invention
2-8	20	F-23	3.0	Invention
2-9	20	F-24	3.0	Invention
2-10	20	F-52	3.0	Invention
2-11	20	F-61	3.0	Invention
2-12	20	F-62	3.0	Invention
2-13	20	F-3/F-2	1.5/1.5	Invention
2-14	20	F-3/F-62	1.5/1.5	Invention
2-15	20	F-2/F-62	1.5/1.5	Invention
2-16	0	formalin (37%)	1.5/1.5	Comparison
2-17	30	formalin (37%)	1.5/1.5	Comparison
2-18	50	formalin (37%)	1.5/1.5	Comparison
2-19	60	formalin (37%)	1.5/1.5	Comparison
2-20	80	formalin (37%)	1.5/1.5	Comparison
2-21	0	F-3	3.0	Invention
2-22	30	F-3	3.0	Invention
2-23	50	F-3	3.0	Invention
2-24	60	F-3	3.0	Comparison
2-25	80	F-3	3.0	Comparison

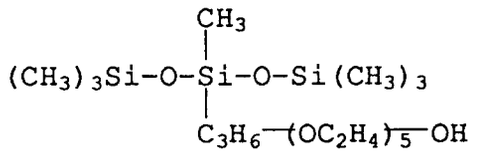
Table 7

Experiment No.	Color Fading Ratio (%)	Sulfide Precipit ates	Backside Stains	Scratches and Adhesion of Foreign Matters	Remarks
2-1	40.0	C	B	C	Comparison
2-2	4.5	C-D	A	A	Comparison
2-3	3.5	A	A	A	Invention
2-4	3.3	A	A	A	Invention
2-5	3.1	A	A	A	Invention
2-6	3.8	B	A	A	Invention
2-7	4.0	B	A	A	Invention
2-8	4.1	B	A	A	Invention
2-9	4.1	B	A	A	Invention
2-10	4.0	B	A	A	Invention
2-11	3.7	B	A	A	Invention
2-12	3.4	A	A	A	Invention
2-13	3.1	A	A	A	Invention
2-14	3.2	A	A	A	Invention
2-15	3.3	A	A	A	Invention
2-16	4.3	C	A	A	Comparison
2-17	4.3	D	A	A	Comparison
2-18	4.3	D	A	A	Comparison
2-19	4.3	D	A	A	Comparison
2-20	4.5	D	B-A	A	Comparison
2-21	3.0	A	A	A	Invention
2-22	3.1	B	B	A	Invention
2-23	3.0	B	B	A	Invention
2-24	3.1	B-C	B-C	B-C	Comparison
2-25	3.0	C	C	C-D	Comparison

It is apparent from the results in Table 7 that the present invention is effective in improving image preservability, solution preservability and in minimizing stains of film, adhesion of foreign matters, in addition to the capability of reducing pollution load.

Example 3

Using the sample prepared in Example 1, experiments were made in the same manner and in the same evaluation procedure as in Example 1, except that the following compound was added to the stabilizer.



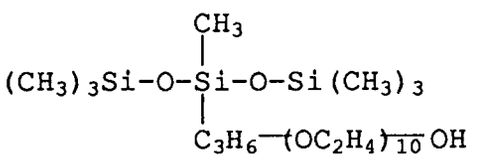
amount added

(exemplified compound (1)) 1.0 g/l

In the experiments, addition of the above exemplified compound to the stabilizer did not cause any change in color fading rate. And, though the backside stains on the test pieces of experiment Nos. 1-19 and 1-20 were rated B as shown in Table 5, the backside stains on the test pieces processed in the same procedures as in Nos. 1-19 and 1-20, except that the above exemplified compound (1) is added to the stabilizer were rated A; that is, the effect of the invention was much more enhanced. According to the evaluation method above described, adhesion of foreign matters was not observed at all on the test pieces stabilized with the stabilizer containing exemplified compound (1), in an environment of 25 °C and 10% relative humidity. The experiments respectively using exemplified compounds (3), (7), (13), (15), (16) and (17) in place of exemplified compound (1) gave much the same results as exemplified compound (1).

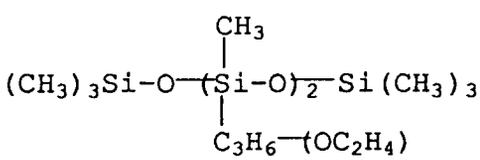
Example 4

Using the sample prepared in Example 1, experiments were conducted in the same manner and in the same evaluation procedure as in Example 2, except that the following compounds were added to the stabilizer.



amount added

(exemplified compound (1)) 0.5 g/l



(exemplified compound (3)) 0.5 g/l

In the experiments, though the color fading rate did not change, the backside stain was thoroughly prevented, exhibiting the effect of these exemplified compounds. Further, according to the evaluation method adhesion of foreingn matters was not observed at all on the test pieces processed with the stabilizer containing the above exemplified compounds, in an environment of 25 °C and 10% relative humidity. In the experiments in which exemplified compounds (7), (13), (15), (16) and (17) were respectively used in place of exemplified compounds (1) and (3), the results obtained were much the same as those with exemplified compounds (1) and (3).

Example 5

To the stabilizers of experiment Nos. 1-19 and 1-20 of Example 1 as well as experiment Nos. 2-22 and 2-23 was added 0.05 mol/l each of potassium sulfite, and running experiments were carried out in the same manner as in Example 1 or 2.

The results showed that though the color fading rate of the magenta dye as well as scratches and adhesion of foreign matters did not change, both the precipitation of sulfides and the backside stain were improved to A, enhancing the effect of the invention much more.

Claims

1. A method for processing a silver halide color photographic light-sensitive material, comprising the steps of

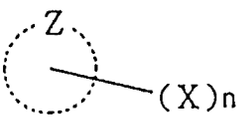
exposing the material,

developing the exposed material,

processing the developed material with a processing solution having a fixing ability, and

stabilizing the processed material with a stabilizer, wherein the concentration of ammonium ions in said processing solution is not more than 50 mol% of the total cations, and said stabilizer contains in an amount of 0.05 to 20g per litre at least one compound selected from those represented by the following Formula (F):

Formula (F)



wherein Z represents a group of atoms necessary to form a carbocycle or a heterocycle; X represents an aldehyde group, $(R_1O)(R_1O)CH$- or $(HO)(R_1O)CH$- (wherein R_1 and R_2 each represent a lower alkyl group); and n represents an integer of 1 to 4.

2. The method of claim 1, wherein the concentration of ammonium ions in said processing solution is not more than 20 mol% of the total cations.

3. The method of claim 1, wherein said processing solution is a fixing solution.

4. The method of claim 2, wherein said processing solution is a fixing solution.

5. The method of claim 1, wherein said processing solution is a fix-bleaching solution.

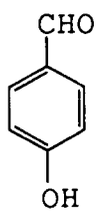
6. The method of claim 2, wherein said processing solution is a fix-bleaching solution.

7. The method of claim 1, wherein said Z in Formula (F) represents a benzene ring, thiophene ,pyrrole, furan, thiazole, imidazole, pyrazole, succinimide, triazole, tetrazole, pyridine, pyrimidine, triazine or thiadiazine.

8. The method of claim 1, wherein said stabilizer further contains 0.05 to 20g per litre of a surfactant having a polyoxyethylene or polyoxypropylene group.

9. The method of claim 1, wherein said stabilizer further contains in an amount of 0.01 to 20 g per litre a water-soluble organic siloxane compound having a polyoxyethylene or polyoxypropylene group.

10. The method of claim 1, wherein said compound includes a compound selected from the group consisting of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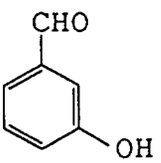
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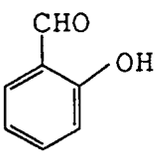
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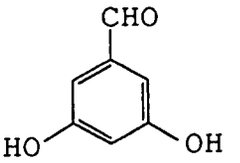
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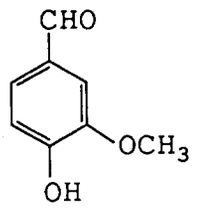
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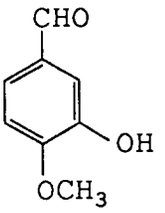
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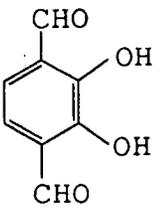
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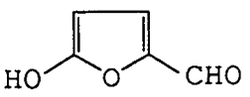
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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 5183

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)
E	EP-A-0 506 349 (KONICA) * page 3, line 14 - page 11, line 1 * * page 26, line 50 - page 32, line 56 * * page 75, line 37 - line 50 * -----	1-10	G03C7/42 G03C7/30 G03C7/407

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	09 NOVEMBER 1992	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

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

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