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Formaldehyde-free stabilizing process.

Process of preparing a silver halide photographic light-sensitive material which is capable of stable processing with a low replenishment of a stabilizing solution containing aromatic or heterocyclic aldehydes, acetals or hemiacetals, is disclosed. The process is capable of positively preventing the production of any sulfide precipitates, any tar, scratches and foreign matter adhesion after completing drying step.

FIELD OF THE INVENTION

This invention relates to a process of preparing a silver halide color photographic light sensitive material and, particularly, to a process of preparing a silver halide color photographic light sensitive material, which is capable of performing a stable processing treatments without producing any precipitates but with inhibiting any dyes from being discolored.

BACKGROUND OF THE INVENTION

Generally, a silver halide color photographic light sensitive material is processed in the following procedures. After exposing it imagewise to light, it is processed in a color developing step and then in a processing step such as a bleaching step and a fixing step or a bleach-fixing step each having a fixing function. Next, it is processed in a stabilizing step and then in a washing step. In the washing step following the processing step carried out with a processing solution having the fixing function, the following compounds are either contained in or adhered to a subject light sensitive material so that the compounds can be brought into the light sensitive material; namely, the compounds capable of producing a water-soluble silver salt upon reaction with a silver halide, such as a thiosulfate or other water-soluble silver complex salts and, further, a sulfite or a metabisulfite as a preservative. In this case, it has been known that an image preservability is affected by the shortage of washing water.

The actual circumstances have been that, for solving the above-mentioned defects, the above-mentioned salts have been washed away from a subject light sensitive material by flowing a large amount of water. However, it has been demanded to carry out the processing steps in which washing water can be reduced and every antipollution measure can be taken, because of the economical reasons such as the shortage of natural water resources, the increases of water service/drainage rates and of heat/light expenses and the antipollutive reasons.

There have been some measures for solving the above-mentioned defects including, for example, those described in West German Patent No. 2,920,222 and in S.R. Goldwasser, 'Water Flow Rate in Immersion-Washing of Motion-Picture Film', SMPTE, Vol.64, pp.248-253, May (1955).

Besides the above, there is a known process in which a preliminary washing step is provided right behind the fixing bath so that every pollutant component either contained in or adhered to a light sensitive material may be reduced from the washing bath and a washing water consumption may also be economized. However, the above-mentioned techniques have not been satisfactory at all to eliminate any washing water.

Therefore, the above-mentioned techniques have been getting seriously problematic in the circumstances where the expenses for washing water is getting increased because, in recent years, the natural water resources have scarcely been left and the crude oil price has been increased.

On the other hand, there are also some known techniques in which a stabilizing step is carried out immediately after completing a photographic process without making any washing treatment. These techniques include, for example, those in which a silver stabilizing step is carried out with a thiocyanate immediately after completing the photographic process without carrying out any washing step, as described in U.S. Patent No. 3,335,004. However, the above-mentioned techniques have the defect that the surface of a subject light sensitive material is stained after drying the surface thereof, because a large amount of inorganic salts are contained in the stabilizing bath.

Also, when carrying out the stabilizing step, it was also found that the techniques have another defect that the resulting dye image is deteriorated while storing it for a long time.

On the other hand, when processing a color photographic light sensitive material for taking pictures typified by a photographic light sensitive material containing silver halide that is silver iodobromide, a stabilizing bath is generally used by containing formaldehyde in the final processing step following after a washing bath.

Formaldehyde applicable to the above-mentioned stabilizing bath has the effects of keeping the physical properties of a color photographic light sensitive material and, particularly, formaldehyde has the effects of preventing the color photographic light sensitive material from scratching the surface thereof and of preventing a gradation from being deteriorated by gradually hardening the photographic light sensitive material in allowing it to stand. In addition to the above, it is also known that formaldehyde has another effect of preventing the stability of a dye image from being deteriorated by an unreacted coupler remaining in the color photographic light sensitive material.

However, formaldehyde added into a stabilizing bath, for the purpose of stabilizing a dye image and so forth, has the defects not only that the originally aimed dye image stabilizing effect is degraded by making it adhered to a light sensitive material so as to produce an adduct together with sulfurous acid ions brought-in from the preceding bath (that is a processing solution having a fixing function), but also that a sulfurization is

accelerated. For solving the above-mentioned defects, U.S. Patent No. 4,786,583 proposes to use alkanol amine. When making use of alkanol amine, yellow stains produced in unexposed areas tend to be affected and, therefore, it could not be said that the sulfurization prevention effect is satisfactory.

Concerning formaldehyde, the CIIT (The Chemical Institute of Industrial Toxicity) of the U.S.A announced that rats had each a rhinal cancer with 15 ppm of formaldehyde, and NIOSH (The National Institute of Safety and Health) and ACGIH (The Authorized Committee of the Government for Industrial Hygiene) acknowledged each that a carcinogenesis may possibly be realized.

In Europe, formaldehyde is severely regulated and, particularly, in Germany, it has been regulated from 10 years ago that formaldehyde should be not more than 0.1 ppm in every residence.

Further in Japan, formaldehyde has been variously regulated, because of the toxicity thereof. The regulations include; for example, the laws regulating the specified poisonous substances or violent poisons each stimulating mucous membrane; the regulations for preventing any organic solvent toxicosis or for the articles for house-hold use, each specified in the chemical regulations attached to the OSHA (Occupational Safety and Health Administration Laws); the regulations for fibers and plywoods; and the formaldehyde regulations for underwear and baby-clothes. Accordingly, a technique for reducing formaldehyde application has been long-awaited for.

In recent years, there have also been the known processes for color negative films named Processes C-41B and C-41RA which were developed by Eastman Kodak Company with the purpose of making a process more rapid and saving the bath treatments. These processes are each comprised of the steps, namely, (Color developing step) - (Bleaching step) - (Fixing step) - (Stabilizing step) - (Drying step), which are rapid processes without substantially carrying out any washing step.

As the alternative techniques for applying other compounds in place of formaldehyde to a stabilizer used in the above-mentioned stabilizing step, there have been the known techniques in which hexamethylene tetramine type compounds or hexahydrotriazine type compounds are used, such as the techniques described in, for example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as 'JP OPI Publication') Nos. 63-244036/1988, 62-27742/1987 and 61-151538/1986.

On the other hand, in the industry skilled in the art, it has seriously been requested to save the amounts of every replenisher through the measures for saving the frequency of dissolving processing solutions by every operator in photofinishing laboratories (especially in large-scaled laboratories), for saving the space for storing processing solutions, for reducing the antipollution loads with cutting down waste liquids, and for improving every work environment.

However, when reducing the replenisher for the stabilizing solutions, the following problems have been in the limelight. The stabilizing solution has to stay longer in the stabilizing tank of an automatic developing machine; a thiosulfate is liable to be decomposed by air-oxidation and so forth; the finely granulated black precipitates of a sulfide are produced; a cotton waste-like suspended matter is produced; a matter is fixed to the tank walls; and tar is produced.

When making use of the above-mentioned processing solutions, there have further often raised the seriously irreparable troubles, after a drying step is completed, that tar may adhere to a subject film and that the film may be scratched or a foreign matter adheres to the film.

The techniques for solving the above-mentioned troubles are proposed in, for example, JP OPI Publication No. 2-153348/1990. The technique proposed therein is to prevent a subject light sensitive material from being stained in a process in the following manner. After processing the light sensitive material with a processing solution comprising a fixing agent containing a thiosulfate in a proportion within the range of 1.1 to 2.0 mols per liter so as to have a fixing function and, then, when processing the light sensitive material with a stabilizing solution containing at least one of hexamethylene tetramine and the derivatives thereof, hexahydrotriazine and the derivatives thereof and N-methylol compounds, the stains can be prevented from producing.

However, the above-proposed technique only suggests a possibility of a stain prevention and, when actually applying this technique to the low replenished process for light sensitive materials, it is proved that the troubles of producing the black precipitates of a sulfide and cotton waste-like suspended matters could not satisfactorily be eliminated.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a silver halide color photographic light sensitive material wherein a stable processing characteristics can be displayed even if a replenishment to a stabilizing solution is made in a relatively small amount and, while not only any conventional formaldehyde application can be made unused but also any dye discoloration can be inhibited, any sulfide precipitate production, any cotton waste-like suspended matter production and any tar production can be each prevented, any fixed matter adhesion to the

stabilizing tank walls, and any tar adhesion to, any scratches on and any foreign matter adhesion to a light sensitive material can also be prevented, respectively.

Other objects of the invention can be made apparent in the following descriptions.

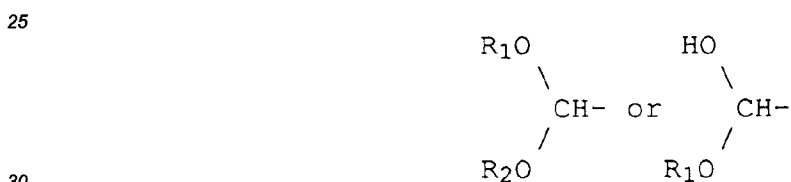
5 [Means for solving the problems]

The present inventors have energetically studied to satisfy the above-mentioned objects, they have finally achieved the invention. To be more concrete, the processing method for a silver halide color photographic light sensitive material relating to the invention comprises the steps of processing the silver halide color photographic light sensitive material with a processing solution having a fixing function and then processing the light sensitive material with a stabilizing solution, wherein the stabilizing solution contains a compound selected from the group consisting of the compounds represented by the following Formula [F] and the replenished amount of the stabilizing solution is not more than 670 ml/m².

15 Formula [F]



wherein Z represents the group consisting of the atoms necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring; X represents an aldehyde group,



wherein R₁ and R₂ represent each a lower alkyl group; and n is an integer of 1 to 4.

35 DETAILED DESCRIPTION OF THE INVENTION

From the results of the various studies made by the present inventors, it was proved that, when a compound represented by the above-given Formula [F] is used in a stabilizing solution, a dye image can be stabilized even if any conventional type formalin is not used. However, when continuously carrying out low replenished running treatments for a long time, the stabilizing solution was found to raise the troubles of producing a black sulfide precipitate, a cotton waste-like suspended matter, tar and a fixed matter adhering to tank walls, similar to the case of formalin.

The present inventors considered that the above-mentioned troubles will become more serious, because the more an automatic processing machine is made compact in size, the more the machine used therein can hardly be maintained. For solving the above-mentioned problems, the inventors have studied of the technique described in the foregoing JP OPI Publication No. 2-153348/1990. However, it was proved that any complete solution of the problems cannot be expected within the scope of the technique described therein.

It was further proved that the above-mentioned problems can be solved to effectively achieve the objects of the invention when the compositions of not only the stabilizing solution but also those of a fixing solution itself are changed. To be more concrete, in the foregoing JP OPI Publication No. 2-153348/1990, only a thio-sulfate is used as a fixing solution and, in contrast to the above, it was found by the inventors that the objects of the invention can effectively be achieved by making combination use of a thiosulfate and a thiocyanate, that is, one of the preferred embodiments of the invention.

In the compounds represented by the foregoing Formula [F], the preferred embodiments include that the substituents for the above-denoted Z are to be an aldehyde group, a hydroxyl group, an alkyl group, an alkoxy group, a halogen atom, a nitro group, a sulfo group, a carboxy 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.

Now, the compounds relating to the invention, represented by Formula [F], will be detailed.

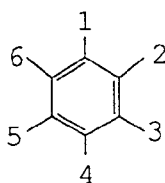
In Formula [F], Z represents the group consisting of the atoms necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring. The carbon rings and heterocyclic rings may be either single rings or condensed rings. Preferably, Z represents an aromatic carbon ring having a substituent or a heterocyclic ring. It is also preferable that the substituents for Z are to be the following groups.

5 Namely, an aldehyde group, a hydroxyl group, an alkyl group (such as a methyl, ethyl, methoxyethyl, benzyl, carboxymethyl or sulfopropyl group), an aralkyl group, an alkoxy group (such as a methoxy, ethoxy or methoxyethoxy group), a halogen atom, a nitro group, a sulfo group, a carboxy group, an amino group (such as an N,N-dimethylamino, N-ethylamino or N-phenylamino group), a hydroxyalkyl group, an aryl group (such as a phenyl or p-carboxyphenyl group), a cyano group, an aryloxy group (such as a phenoxy or p-carboxyphenyl group), an acyloxy group, an acylamino group, a sulfonamido group, a sulfamoyl group (such as an N-ethylsulfamoyl or N,N-dimethylsulfamoyl group), a carbamoyl group (such as a carbamoyl, N-methylcarbamoyl or N,N-tetramethylenecarbamoyl group), or a sulfonyl group (such as a methanesulfonyl, ethanesulfonyl, benzenesulfonyl or p-toluenesulfonyl group).

The carbon rings represented by Z include, preferably, a benzene ring and the heterocyclic rings represented thereby include, preferably, a 5- or 6-membered heterocyclic ring. The 5-membered rings include, for example, a thiophene, pyrrole, furan, thiazole, imidazole, pyrazole, succinimido, triazole or tetrazole ring. The 6-membered rings include, for example, a pyridine, pyrimidine, triazine or thiadiazine ring.

The condensed rings include, for example, a naphthalene, benzofuran, indole, thionaphthalene, benzimidazole, benzotriazole or quinoline ring.

The compounds preferably exemplified for the compounds represented by Formula [F] will be given below.



Exemplified compounds (F-1) through (F-52) can be prepared by inserting various kinds of substituents shown in the following table into the positions 1 through 6 indicated in the above-given formula.

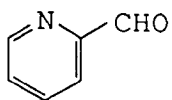
Table-1

	No	1	2	3	4	5	6
5	(F-1)	-CHO	H	H	H	H	H
	(F-2)	-CHO	H	H	-OH	H	H
	(F-3)	-CHO	H	-OH	H	H	H
10	(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
15	(F-8)	-CHO	H	-CHO	H	-OH	H
	(F-9)	-CHO	H	-CHO	H	H	-OH
	(F-10)	-CHO	-OH	-CHO	H	H	H
20	(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
25	(F-15)	-CH(OCH ₃) ₂	H	-OH	H	-OH	H
	(F-16)	-CHO	H	-NO ₂	H	H	H
	(F-17)	-CHO	H	H	-NO ₂	H	H
30	(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	-OH	H
35	(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
40	(F-25)	-CHO	H	Cl	H	H	H
	(F-26)	-CHO	H	H	Cl	H	H
	(F-27)	-CHO	H	Cl	H	Cl	H
	(F-28)	-CHO	H	-COOH	-COOH	H	H
45	(F-29)	-CHO	H	Br	H	H	H
	(F-30)	-CHO	H	H	Br	H	H
	(F-31)	-CHO	H	-OH	-SO ₃ H	H	H
50	(F-32)	-CHO	H	H	-NH ₂	H	H

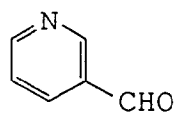
Table-1 (cont'd)

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 ₂ H ₅) ₂	H	H
(F-35)	-CHO	H	H	-CONH ₂	H	H
(F-36)	-CHO	H	H	-SO ₂ NH ₂	H	H
(F-37)	-CHO	H	H	-SO ₃ H	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 ₃ H	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)	$\begin{array}{c} \text{OH} \\ -\text{CH} \\ \text{OCH}_3 \end{array}$	H	-OH	H	H	H
(F-47)	$\begin{array}{c} \text{OH} \\ -\text{CH} \\ \text{OCH}_3 \end{array}$	H	H	-OH	H	H
(F-48)	-CHO	H	-OH	-CH ₃	H	H
(F-49)	-CHO	-SO ₃ Na	H	H	H	H
(F-50)	-CHO	H	$\begin{array}{c} -\text{O}(\text{CH}_2)_3 \\ \text{SO}_3\text{Na} \end{array}$	H	H	H
(F-51)	-CHO	H	-CH ₂ SO ₃ Na	H	H	H
(F-52)	-CHO	-OH	-OH	-CHO	H	H

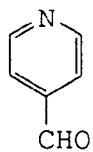
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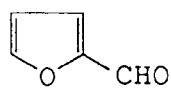
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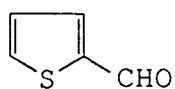
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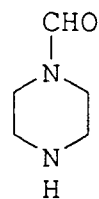
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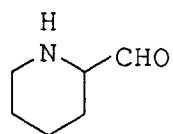
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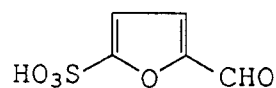
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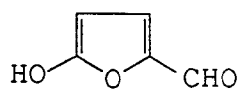
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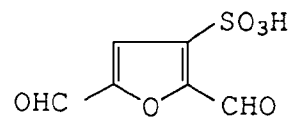
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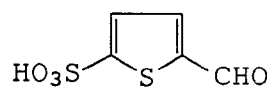
(F-61)



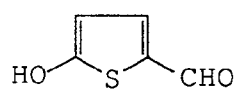
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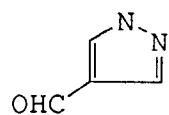
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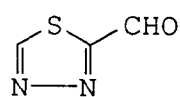
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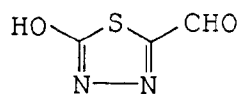
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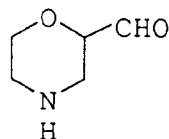
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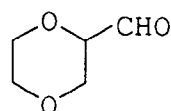
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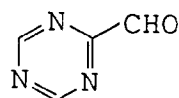
(F-68)



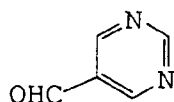
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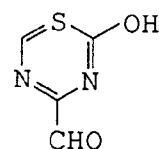
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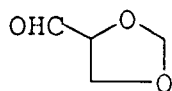
(F-71)



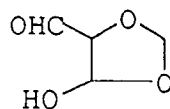
(F-72)



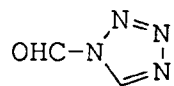
(F-73)



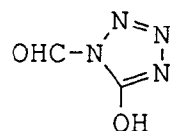
(F-74)



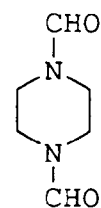
(F-75)



(F-76)



(F-77)



Besides the above compounds, the other typically exemplified compounds include the exemplified compounds (76) through (90) given in Japanese Patent Application No. 3-89686/1991, pp.13-14.

Among the typical examples of the compounds represented by Formula [F], the desirable compounds include, for example, those of (F-2), (F-3), (F-4), (F-6), (F-23), (F-24), (F-52) and (F-61) and the preferable compounds include those of (F-3).

The compounds represented by Formula [F] can readily be obtained from the commercial products available on the market.

The compounds represented by Formula [F] are contained in a stabilizing solution applicable to silver halide color photographic light sensitive materials. the compounds may also be contained in a processing solution

applicable to the preceding bath to a processing bath having a bleaching function, a processing solution having a bleaching function and a processing solution having a fixing function, as well as in a stabilizing solution, provided, the effects of the invention cannot be spoiled.

5 The compounds represented by Formula [F] may be added to a stabilizing solution, in an amount within the range of desirably 0.05 to 20 g, more desirably 0.1 to 15 g and preferably 0.5 to 10 g per liter of a stabilizing solution used therein.

The compounds represented by Formula [F] are characterized in that the image preservability can be more excellent, particularly, even under the low humidity conditions, as compared to the known compounds substitutable for formaldehyde.

10 The stabilizing solutions may be replenished in an amount of not more than 670 ml, desirably within the range of not less than 100 ml to not more than 500 ml and, particularly 160 ml to 460 ml per sq. meter of a light sensitive material used. When the stabilizing solution is replenished in an amount exceeding 670 ml, the waste solution is increased resultingly, so that it may not be desired from the social environmental and economical viewpoints and the effects of the invention may not remarkably be displayed. Therefore, the less a replenishment thereof is so made as not to exceed the limited amount of 100 ml/m², the more the effects of the invention can be remarkably displayed.

The expression, 'an amount replenished', stated in this invention means a substantial amount replenished. When reclaiming a solution, the amounts of a reclaiming agents replenished means the amounts replenished.

20 In the invention, the pH value of a stabilizing solution is to be not lower than 6.0, desirably not lower than 7.0 and preferably within the range of 7.5 to 9.0. The pH controllers which may be contained in a stabilizing solution include also any types of alkalizing agent or an acidifying agent, which are generally known.

In the invention, it is desirable that a stabilizing solution contains a chelating agent having a chelating stability constant of not less than 8 to iron ions. The term, 'a chelating stability constant', means a constant well-known from L.G. Sillen · A.E. Martell, "Stability Constants of Metal-ion Complexes", The Chemical Society, London (1964) and S. Chaberek · A.E. Martell, "Organic Sequestering Agents", Wiley (1959).

25 The chelating agents having a chelating stability constant of not less than 8 to iron ions include, for example, an organic carboxylic acid chelating agent, an organic phosphoric acid chelating agent, an inorganic phosphoric acid chelating agent and a polyhydroxy compound. The above-mention iron ions mean each a ferric ion (Fe³⁺).

30 The examples of the typical compounds for the chelating agents having a chelating stability constant of not less than 8 to ferric ions include those given below, provide however that the chelating agents shall have no special limitation thereto. Namely, ethylenediamine diorthohydroxy phenyl acetic acid, diaminopropane tetraacetic acid, nitrilotriacetic acid, hydroxyethylenediamine triacetic acid, dihydroxyethyl glycine, ethylenediamine diacetic acid, ethylenediamine dipropionic acid, iminodiacetic acid, diethylenetriamine pentaacetic acid, 35 hydroxyethyl iminodiacetic acid, diaminopropanol tetraacetic acid, transcyclohexanediamine tetraacetic acid, glycoether diamine tetraacetic acid, ethylenediamine tetrakis(methylene phosphonic acid, nitrilotrimethylene phosphonic 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. 40 Among them, it is desirable to use diethylenetriamine pentaacetic acid, nitrilotriacetic acid, nitrilotrimethylene phosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid and, inter alia, it is preferable to use 1-hydroxyethylidene-1,1-diphosphonic acid.

45 The above-given chelating agents may be used in an amount within the range of, desirably 0.01 to 50 g and, preferably 0.05 to 20 g per liter of a stabilizing solution used. When this is the case, every excellent result can be enjoyed.

The compounds desirably added to a stabilizing solution include, for example, an ammonium compound. These compounds may be supplied from the ammonium salts of various kinds of inorganic compounds. The ammonium salts thereof include, typically, ammonium hydroxide, ammonium bromide, ammonium chloride and ammonium phosphate. These salts may be used independently or in combination. The ammonium compounds 50 may be used within the range of, desirably, 0.001 to 1.0 mols and, preferably, 0.002 to 2.0 mols per liter of a stabilizer used.

It is desirable that the stabilizing solution contains any one of sulfites regardless of either organic or inorganic sulfites, provided they are able to release sulfite ions. The inorganic sulfite salts are preferably used. The typical compounds thereof include, desirably, sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. 55

The above-given sulfites may be added to a stabilizing solution in such an amount, desirably, so as to be at least 1×10^{-3} mols/liter and, preferably, within the range of 5×10^{-3} to 10^{-1} mols/liter. When this is the case,

a stain prevention effect can be displayed thereby. The sulfites may be added directly to a stabilizing solution or, preferably, to a stabilizing replenisher.

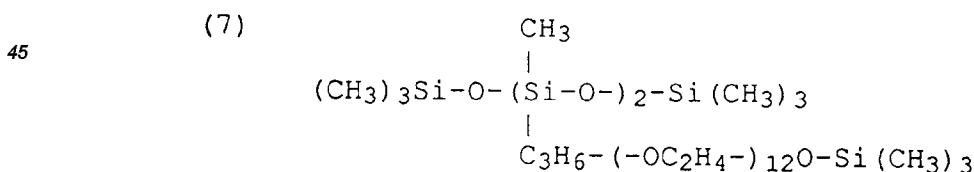
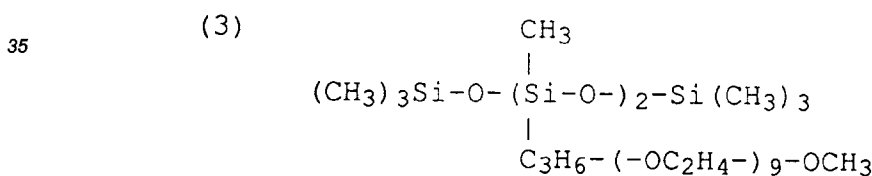
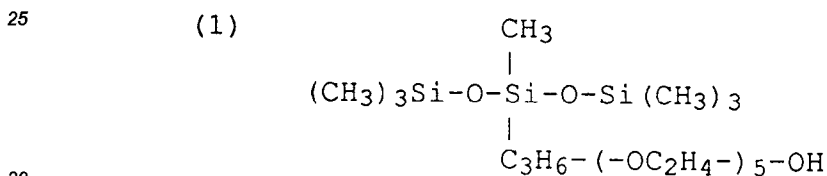
It is desirable that the stabilizing solutions contain the above-mentioned chelating agents and a metal salt in combination. The metal salts include, for example, those of Ba, Ca, Ce, Co, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al or Sr. These metal salts may be supplied in the form of the inorganic salts such as those of a halide, hydroxide, sulfate, carbonate, phosphate or acetate or a water-soluble chelating agent. These metal salts may be added in an amount within the range of, desirably 1×10^{-4} to 1×10^{-1} mols/liter of a stabilizer and, preferably 4×10^{-4} to 2×10^{-2} mols/liter thereof.

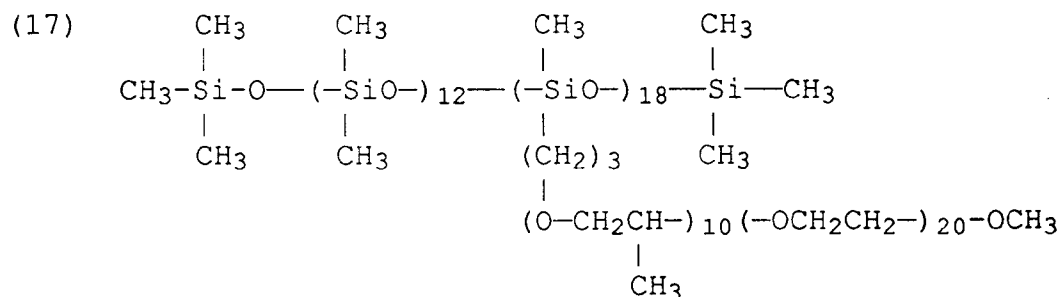
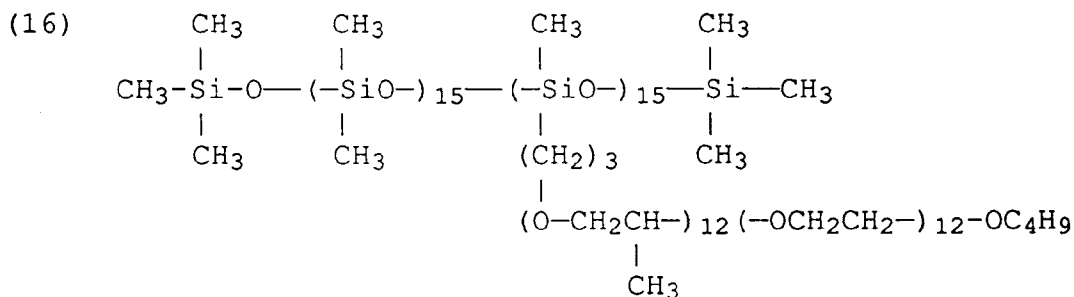
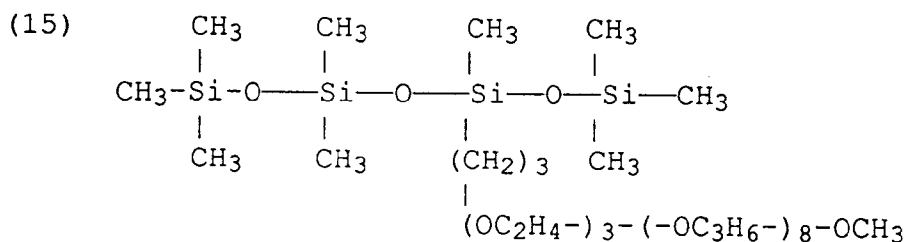
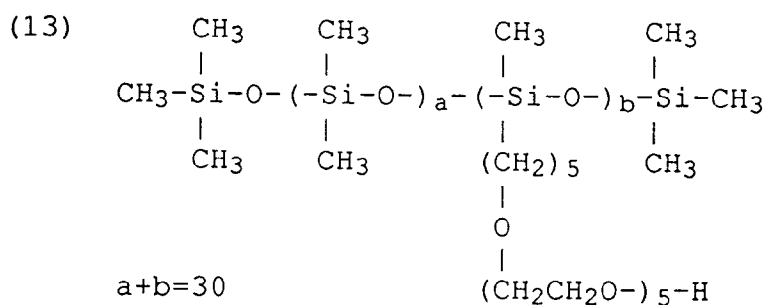
It is allowed that a stabilizing solution may contain organic acid salts (such as citrate, acetate, succinate, oxalate and benzoate) and pH controllers (such as phosphate, borate, hydrochloric acid and sulfate). The above-mentioned compounds may be added in an amount within the range that the pH of a stabilizing bath can necessarily be maintained, but the stability of a color photographic image and the production of precipitates may not be affected, provided that the compounds may be used in any combination.

In the invention, it is also allowed to make combination use of well-known antimolds such as 5-chloro-2-methylisothiazoline-3-one and benzisothiazoline in the stabilizing solutions of the invention, provided that the effects of the invention cannot be spoiled.

The stabilizing solutions may preferably contain a surfactant including, particularly, the compounds represented by Formula [II] given in Japanese Patent Application No. 2274026/1990, p.6. The typical and particularly desirable examples thereof include the following water-soluble organic siloxane type compounds and, besides, it is also allowed to use the compounds represented by Formulas [I] and [II] given in JP OPI Publication No. 62-250449/1987.

(Water-soluble organic siloxane type compounds)





Besides the above-given compounds, the other typical examples of them also include those of (II-2), (II-4) through (II-6), (II-8) through (II-12) and (II-14).

The water-soluble organic siloxane type compounds containing polyoxyalkylene groups may be added in an amount within the range of 0.01 to 20 g per liter of a stabilizing solution. In that case, they can display excellent effects.

If they are added in an amount of less than 0.01 g, the surface of a subject light sensitive material is dis-

tinctively stained. If exceeding 20 g, a large amount of the organic siloxane type compounds adhere to the surface of a subject light sensitive material, so that the stains may resultingly be increased.

In the process of the invention, silver may be recovered from a stabilizing solution used. It is also a desirable embodiment for embodying the invention to treat a stabilizing solution in an ion-exchange treatment, an electro dialysis treatment (for the details, refer to JP OPI Publication No. 61-28949/1986) or a back permeation treatment (for the details, refer to JP OPI Publication Nos. 60-241053/1985, 62-254151/1987 and 2-132440/1990). It is also desirable to use water demineralized in advance in a stabilizing solution, because the antimolding, stabilizing and image preserving properties of the stabilizing solution can be improved thereby.

The means for the demineralizing treatments may include any one, provided that washing water can keep the Ca and Mg ions thereof having not more than 5 ppm after completing the treatment. For example, the treatments are desirably carried out, independently or in combination, with an ion-exchange resin or a back permeating membrane. The ion-exchange resins and back permeating membranes are detailed in, for example, Open Technical Bulletin No.87-1984.

In the stabilizing solutions, the salt concentration is desirably not more than 1000 ppm and preferably not more than 800 ppm, from the viewpoint of displaying the effects of the invention.

A soluble iron salt is desirably made present in the stabilizing solutions, from the viewpoint of displaying the effects of the invention.

In the stabilizers, the above-mentioned soluble iron salts may be used in a concentration of at least 5×10^{-3} mols/liter or within the range of, desirably, 8×10^{-3} to 150×10^{-3} mols/liter and, preferably, 12×10^{-3} to 100×10^{-3} mols/liter.

In a stabilizing treatment, the treating temperature is within the range of, desirably, 15 to 70°C and, preferably, 20 to 55°C. The treating time is desirably not longer than 150 seconds or within the range of, more desirably, 3 to 120 seconds and, preferably, 6 to 90 seconds.

A stabilizing tank may be comprised of a plurality of tanks. The numbers of the tanks are, desirably, not less than 2 tanks to not more than 6 tanks and, more desirably, 2 to 3 tanks. The stabilizing tank is preferably comprised of 2 tanks and so arranged as to be a counter-current system (that is a system in which a stabilizer is supplied from a bath behind and is then overflowed from a bath forward.)

In the invention, there displays the effect that any sulfurization can hardly be produced even if the aperture area of a stabilizing tank should be widened, despite of that it has been considered to be liable to produce a sulfurization when the aperture area of a stabilizing tank is widened. However, in accordance with the invention, any sulfurization can hardly be produced even if the aperture area should be widened.

Any washing treatment is not required at all after completing the above-mentioned stabilizing treatment. However, it is allowed, if intended, to carry out a surface rinsing treatment with a small amount of washing water for a substantially short time.

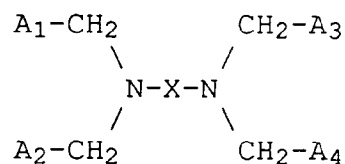
In the processes applied with the processing solutions of the invention, the desired processing steps may be given as follows;

- (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 above-given processing steps, the steps of (1), (2) and (3) are desirable and, particularly, step (2) is preferable. In other words, 'the processing solutions each having a fixing function', stated in the invention, include for example, various independent or combined processing solutions such as a bleach-fixing solution, a bleaching solution and a fixing solution, a bleaching solution and a bleach-fixing solution, a bleach-fixing solution and a fixing solution and a bleach-fixing solution and another bleach-fixing solution, as mentioned in the above-given processing steps. Among the processing solutions each having a fixing function preferable for the invention is a fixing solution.

In the invention, the bleaching agents desirably applicable to a bleaching solution or a bleach-fixing solution include, for example, the ferric complex salts of an organic acid represented by Formula [A] given below.

Formula [A]



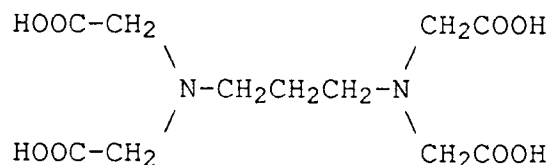
wherein A_1 through A_4 may be the same with or the different from each other and represent each -CH₂OH, -COOM or -PO₃M₁M₂ in which M, M₁ and M₂ represent each a hydrogen atom, an alkali metal atom or an ammonium group; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms.

Now, the compounds represented by Formula [A] will be detailed below.

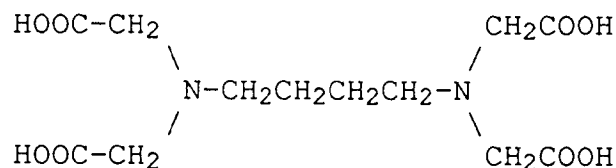
A_1 through A_4 may be the same with or the different from each other and represent each -CH₂OH, -COOM or -PO₃M₁M₂ in which M, M₁ and M₂ represent each a hydrogen atom, an alkali metal atom (such as a sodium atom or a potassium atom) or an ammonium group; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms (such as a trimethylene, tetramethylene or pentamethylene group). The substituents for the above-mentioned alkylene groups include, for example, a hydroxyl group and an alkyl group having 1 to 3 carbon atoms.

The typical compounds desirably represented by the foregoing Formula [A] will be given below.

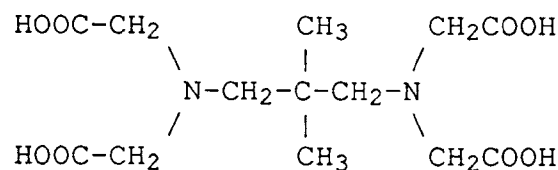
(A-1)



(A-4)



(A-9)



Besides the above, the other typical examples of the compounds further include those of (A-2), (A-3), (A-5) through (A-8) and (A-10) through (A-12) given in JP Application No. 2-274026/1990, pp.89-90.

As for the ferric iron complex salts of the above-given (A-1) through (A-12), the sodium salts, potassium salts or ammonium salts of these ferric iron complex salts may be used without limitation. From the viewpoints

of the effects of the objects of the invention and the solubility, the ammonium salts of the ferric iron complex salts may preferably be used.

Among the above-given examples of the compounds, the particularly preferable compound is A-1).

In the other desirable embodiments of the invention, the ammonium salts may be used in a proportion of not more than 50 mol%, desirably not more than 20 mol% and preferably not more than 10 mol%, because the oxidation of the foregoing bleaching agents are high enough and a bleach-fog is liable to produce in the case of using the ammonium salts.

The above-mentioned organic acid ferric iron complex salts may be added in an amount within the range of, desirably, 0.1 to 2.0 mols per liter of a bleaching solution used and, preferably, 0.15 to 1.5 mols.

When making combination use of the ferric iron complex salts of an organic acid, represented by the foregoing Formula [A] and two or more kinds of other organic acid ferric complex salts such as ethylenediamine tetraacetic acid, the ferric complex salts of the compounds represented by Formula [A] are to occupy desirably not less than 70% (in terms of mols), more desirably not less than 80%, particularly not less than 90% and preferably not less than 95%.

The organic acid iron (III) complex salts may also be used either in the form of a complex salt or after the iron (III) ion complex salts are formed in a solution by making use of an iron (III) salt such as ferric sulfate, ferric chloride, ferric acetate, ferric ammonium sulfate or ferric phosphate and aminopolycarboxylic acid or the salts thereof. When the organic iron (III) complex salts are used in the form of a complex salt, the complex salts may be used independently or in combination. Also, when the complex salts are formed in a solution by making use of ferric complex salts and aminopolycarboxylic acid, the ferric salts may be used independently or in combination. Further, it is allowed to use the aminopolycarboxylic acids independently or in combination.

In either cases mentioned above, aminopolycarboxylic acids may be used in an excess amount more than for forming iron (III) ion complex salts.

When the bleaching solution or bleach-fixing solution contains at least one of the imidazole and the derivatives thereof given in JP Application No. 63-48931/1988 or the compounds represented by Formulas [I] through [IX] and the exemplified compounds thereof each also given in the same application, the effects of the rapid bleaching or bleach-fixing property can be displayed.

Besides the above-given bleach accelerators, the following compounds may also similarly be used. Namely, the exemplified compounds given in JP Application No. 60-263568/1985, pp.51~115; the exemplified compounds given in JP OPI Publication No. 63-17445/1988, pp.22~25; and the compounds given in JP OPI Publication No. 53-95630/1975 and 53-28426/1975.

The above-given bleach accelerators may be used independently or in combination. They may be added in an amount within the range of, generally 0.01 to 100 g per liter of a bleaching solution used, desirably 0.05 to 50 g and, preferably 0.05 to 15 g.

When adding the bleach accelerators, they may be added as they are. However, they may generally be added after they are dissolved in advance in an organic acid or the like. They may also be added, if required, after dissolving them with an organic solvent such as methanol, ethanol and acetone.

The bleaching solutions or bleach-fixing solutions may be used at a temperature within the range of 20 to 50°C and desirably 25 to 45°C.

The pH values of the bleaching solutions may be, desirably, not higher than 6.0 and, preferably, within the range of not lower than 1.0 to not higher than 5.5.

The pH values of the bleaching solutions are each defined as a pH of the content of a processing tank when processing a silver halide photographic light sensitive material, these pH values can clearly be distinguished from the pH values of the so-called replenishers.

The bleaching solutions or bleach-fixing solutions are ordinarily used upon adding thereto a halide such as ammonium bromide, potassium bromide and sodium bromide. It is also allowed to contain thereto a variety of fluorescent whitening agents and defoaming agents.

The bleaching solution may be replenished in an amount of, desirably not more than 500 ml per sq. meter of a silver halide color photographic light sensitive material used, more desirably within the range of 20 ml to 400 ml and, preferably 40 ml to 350 ml. The lower the replenished amount is, the more the effects of the invention can be remarkable.

In the invention, it is allowed, if desired, to blow the air or oxygen into a processing bath or a reservoir tank for a processing replenishing solution, or to appropriately add a suitable oxidizer such as hydrogen peroxide, a bromate and a persulfate.

It is also allowed to use a relatively high oxygen-permeative member such as silicone rubber for serving as the pipes of an automatic processing machine.

Next, in a fixing step applied after a bleaching step, a fixing solution or a bleach-fixing solution may desirably contain at least a thiocyanate for serving as a fixing agent, and a thiosulfate and the thiocyanate may

also be used in combination. The thiocyanates may be used in an amount of, desirably not less than 0.3 mols/liter and, preferably within the range of 0.5 to 3.0 mols/liter.

The fixing solutions or bleach-fixing solutions each relating to the invention may be replenished in an amount of, desirably, not more than 900 ml per sq. meter of a subject light sensitive material, or within the range of, more desirably, 20 to 750 ml per sq. meter thereof and, preferably, 50 to 620 ml per sq. meter thereof.

The pH values of the fixing solutions or bleach-fixing solutions each relating to the invention is preferably within the range of 4 to 8.

The fixing solutions or bleach-fixing solutions are allowed to contain the compounds represented by Formula [FA] given in JP Application No. 63-48931/1988, p.56 and the exemplified compounds and, further, the compounds represented by Formula (1) or (2) given in International Publication No. WO91/08517, pp.5~10. In the cases mentioned above, the other effects can be so displayed as to remarkably reduce a sludge produced when a small quantity of light sensitive material is processed extending for a long time with a bleach-fixing solution or a fixing solution.

An excellent effect can be displayed when the compounds represented by the foregoing Formula [FA] and Formula (1) or (2) are added in an amount within the range of 0.1 to 200 g per liter of a processing solution used.

The fixing solutions or bleach-fixing solutions may also be applied with a sulfite or a sulfite-releasing compound. The typical exemplified compounds thereof include, for example, potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, potassium methabisulfite, sodium metabisulfite and ammonium metabisulfite. In addition, the compounds represented by Formula [B-1] or [B-2] given in JP Application No. 63-48931/1988, p.60 may also be included therein.

In the sulfites and sulfite releasing compounds, the sulfurous acid ions thereof are required to be in an amount of at least 0.05 mols per liter of a fixing solution used or within the range of, desirably 0.10 to 0.50 mols/liter and, preferably 0.12 to 0.40 mols/liter.

When making use of each of the processing solutions relating to the invention each having a fixing function, any processing time may be selected. However, it is desirably within 3 minutes 30 seconds or within the range of, more desirably 10 to 20 seconds and, preferably 20 seconds to 3 minutes.

In the embodiments of the invention, it is preferred to forcibly stir a stabilizing solution, a processing solution having a fixing function and a bleaching solution. The reasons thereof are that the stirring treatments are carried out from the viewpoints not only for more excellently displaying the effects of the objects of the invention, but also for providing a rapid processing aptitude. The expression, '--- to forcibly stir ---', does not mean herein any ordinary liquid diffusion/transfer, but means a forcible stirring made by attaching with a stirring means. As for the stirring means, the means given in JP OPI Publication Nos. 64-222259/1989 and 1-206343/1990 may be adopted.

In the invention, when a cross-over time between each of the tanks such as between a fixing tank and a stabilizing tank is not longer than 10 seconds and desirably not longer than 7 seconds, another effect different from those of the invention, that is an effect on a bleaching fog prevention, can be displayed. In addition to the above, it is an desirable embodiment, from the viewpoint of embodying the invention, to provide a method for reducing a processing solution brought-in from a light sensitive material upon providing a duckbill valve, for example.

As for the silver halide grains applicable to silver halide color photographic light sensitive materials applicable to the processes of the invention (hereinafter abbreviated to as 'light sensitive materials', if required), any one of silver chloride, silver chlorobromide, silver iodobromide and silver chloriodobromide. Among these silver halide grains, silver iodobromide grains can desirably be used.

In the above-mentioned light sensitive materials, the average silver iodide content of the whole silver halide emulsion is to be within the range of, desirably 0.1 to 15 mol%, more desirably 0.5 to 12 mol% and, preferably 1 to 10 mol%.

In the light sensitive materials, the average grain size of the whole silver halide emulsion is to be not larger than 2.0 μm and, preferably within the range of 0.1 to 1.0 μm .

When a silver halide emulsion contains the grains having an average value of (the grain sizes/the grain thicknesses) of less than 5, it is desirable from the desilvering viewpoint that the grain size distribution thereof is monodispersive.

A monodisperse type silver halide emulsion means that the silver halide grains, which have the grain sizes within the range of $\pm 20\%$ of the average grain size, occupy not less than 60%, desirably not less than 70% and preferably not less than 80% by weight of the whole silver halide grains.

The term, 'an average grain size', is herein defined as a grain size r_i obtained when a product $n_i \times r_i^3$ is maximized, in which r_i represents a grain size and n_i represents a frequency of the grains having a grain size r_i ; (wherein the significant figures have each three figures and the number of the lowest figure is rounded by

the fractions of 5 and over as a unit and cut away the rest.)

In the case of globular-shaped silver halide grains, the term, 'a grain size', means a grain diameter and, in the case of the other shaped grains than the globular-shaped, it means a diameter of the grain obtained when the projective image area thereof is converted into a circle having the same area.

5 The above-mentioned grain sizes can be obtained in the manner, for example, that a subject grain is magnified by 10,000 to 50,000 times through an electron microscope, the magnified image thereof is photographed and either one of the printed grain diameter or the projected grain area is practically measured; (provided that the numbers of the grains subject to measurement are to be not less than 1000 pieces.

10 The particularly desirable highly monodisperse type emulsions have each the following defined distribution range of not more than 20% and preferably not more than 15%;

$$(\text{Standard deviation/Average grain size}) = \text{Distribution range (\%)}$$

15 The crystals of silver halide grains may be either regular crystals or twinned crystals and may also be those having any ratios of [1.0.0] planes to [1.1.1] planes. Further, the crystal structures of the silver halide grains may be either those uniform from the inside to the outside or the layered structures different between the inside and the outside (that is so-called a core-shell type structure). Still further, the silver halides may also be either a type of forming a latent image mainly on the surfaces of the grains thereof or another type of forming a latent image inside the grains. In addition, the so-called tabular-shaped silver halide grains may also be used; (for the details, refer to JP OPI Publication No. 58-113934/1983 and JP Application No. 59-170070/1984).

20 Any silver halide grains can be used therein, provided that they are prepared in any one of the preparation processes, such as an acidic process, a neutralizing process and an ammoniacal process.

It is, further, allowed to use the process comprising, for example, preparing seed grains in an acidic process, growing the resulting seed grains in an ammoniacal process which is capable of making a growing rate faster and then further growing the grown grains up so as to have a specific size. When growing silver halide grains, it is desirable that silver ions and halide ions are gradually poured into a reaction chamber at the same time and mixed together, with controlling the pH, pAg and so forth in the reaction chamber so that the amounts of the both ions can meet the silver halide grain growing rate as described in, for example, JP OPI Publication No. 54-48521/1979.

It is preferred to prepare silver halide grains in the following manner. In the invention, the compositions containing the above-described silver halide grains are called the silver halide emulsions.

30 In the silver halide color photographic light sensitive materials of the invention, the silver halide emulsions given in Research Disclosure No. 308119 (hereinafter abbreviated to as RD308119) may be used therein. The following table indicates where the silver halide emulsions are given in RD308119.

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	[Item]	[Pages of RD308119]
5	Iodine composition	993 I-A
	Preparation processes	993 I-A and 994 E
	Crystal habit: Regular crystal	993 I-A
10	: Twinned crystal	-ditto-
	Epitaxial	-ditto-
15	Halogen composition: Uniform	993 I-B
	: Not uniform	-ditto-
	Halogen conversion	994 I-C
20	: Substituted	-ditto-
	Metal contents	994 I-D
25	Monodispersion	995 I-F
	Solvent addition	-ditto-
	Latent image formed position: Surface	995 I-G
30	: Inside	-ditto-
	Applicable light sensitive material:	
	Negative	995 I-H
35	Positive (containing internally fogged grains)	-ditto-
	Emulsions mixedly applied	995 I-J
40	Demineralization	995 II-A

In the invention, a physically ripened, chemically ripened and spectrally sensitized silver halide emulsion is used. The additives applicable to the above-mentioned processing steps are detailed in Research Disclosure
 45 Nos. 17643, 18716 and 308119 (hereinafter abbreviated to as RD17643, RD18716 and RD308119)
 The following table indicates where the additives are given.

50

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	[Item]	[Pages of RD308119]	[RD17643]	[RD18716]
5	Chemical sensitizer	996 III-A	23	648
	Spectral sensitizer	996 IV-A-A,B,C, D,E,H,I,J	23~24	648~9
10	Super sensitizer	996 IV-A-E,J	23~24	648~9
	Antifoggant	998 VI	24~25	649
	Stabilizer	998 VI	24~25	649

15

The well-known photographic additives applicable to the invention are also given in the above-mentioned Research Disclosures. The items relative thereto are indicated in the following table.

20

	[Item]	[Pages of RD308119]	[RD17643]	[RD18716]
25	Anti-color staining agent	1002 VII-I	25	650
	Dye image stabilizer	1001 VII-J	25	
	Whitening agent	998 V	24	
30	UV absorbent	1003 VIII C, XIII C	25~26	
	Light absorbent	1003 VIII	25~26	
35	Light scattering agent	1003 VIII		
40	Filtering dye	1003 VIII	25~26	
	Binder	1003 IX	26	651
	Antistatic agent	1006 XIII	27	650
45	Layer hardener	1004 X	26	651
	Plasticizer	1006 XII	27	650
50	Lubricant	1006 XII	27	650
	Activator-Coating aid	1005 XI	26~27	650
	Matting agent	1007 XVI		
55	Developing agent (contained in a light sensitive material)	1011 XX-B		

A variety of couplers may be used in the light sensitive materials applicable to the invention. The typical examples of the couplers are given in the above-mentioned Research Disclosures. The following table indicates where these couplers are given therein.

5	[Item]	[Pages of RD308119]	[RD17643]	[RD18716]
	Yellow coupler	1001 VII-D	VII C~G	
10	Magenta coupler	1001 VII-D	VII C~G	
	Cyan coupler	1001 VII-D	VII C~G	
	DIR coupler	1001 VII-F	VII F	
15	BAR coupler	1002 VII-F		
	Other useful residual group releasing coupler	1001 VII-F		
20	Alkali-soluble coupler	1001 VII-E		

The additives applicable to the invention may be added in a dispersion method detailed in RD308119, XIV and so forth.

25 In the invention, the supports given in the foregoing RD17643, p.28; RD18716, pp.647~648; and RD308119, XIX can be used.

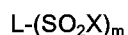
A light sensitive material may be provided with the filtering layers and interlayers given in the foregoing RD308119, VII-K and may also have various layer arrangements such as the normal layer arrangements, inverted layer arrangements and unit arrangements each given in the foregoing RD308119, VII-K.

30 In the invention, when making use of a vinyl sulfone type layer hardener in a light sensitive material, the effects of the invention can be displayed more excellently.

The above-mentioned vinyl sulfone type layer hardeners mean a compound having a vinyl group coupled to a sulfonyl group or a group capable of forming a vinyl group and, preferably, a compound having at least two vinyl groups each coupled to a sulfonyl group or at least two groups each capable of forming a vinyl group.

35 For example, the compounds having the following Formula [VS-I] can preferably be used in the invention.

Formula [VS-I]



40 In the above-given Formula [VS-I], L represents a bonding group having m valencies; X represents -CH=CH₂ or -CH₂CH₂Y in which Y represents a group capable of splitting off in the form of HY with a base, such as a halogen atom, a sulfonyloxy group, a sulfoxy group (including the salts thereof) and a tertiary amine residual group; and m is an integer of 2 to 10, provided, when m is not less than 2, -SO₂X may be the same with or the different from each other.

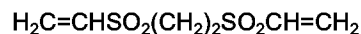
45 The bonding group L having m valencies is an m valent group formed by a single bond or the combinations of the plural bonds represented by, for example, an aliphatic hydrocarbon group (such as an alkylene group, an alkylidene group, and alkylidene group or the group formed by bonding the above-given groups, an aromatic hydrocarbon group (such as an arylene group or the group formed by bonding the above-given group), -O-, -'- (in which R' represents a hydrogen atom or, preferably, an alkyl group having 1 to 15 carbon atoms), -S-, >N-, 50 -CO-, -SO-, -SO₂- or -SO₃-; provided that, when a bonding group L contains 2 or more -NR'-, these R's may be bonded together to form a ring.

The bonding group L may include further those having a substituent such as a hydroxy group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an alkyl group or an aryl group.

The typical examples of X include, preferably, -CH=CH₂ or -CH₂CH₂Cl.

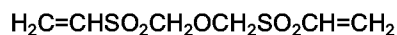
55 The typical examples of the vinyl sulfone type layer hardeners will be given below.

(VS-2)

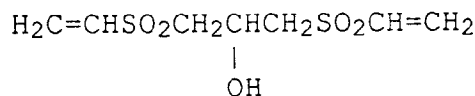


(VS-4)

(VS-6)

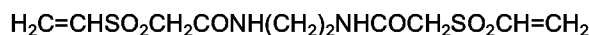


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(VS-9)



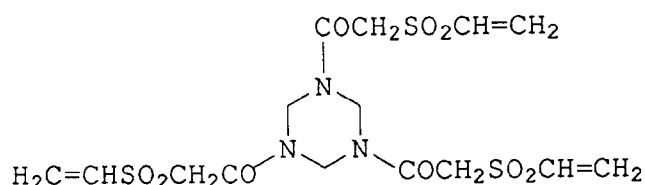
(VS-10)



(VS-12)

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20



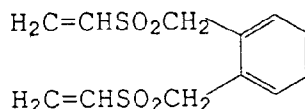
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(VS-22)



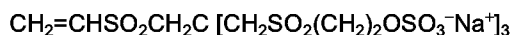
(VS-33)

30



35

(VS-54)



40

The other typical exemplified compounds include (VS-1), (VS-3), (VS-5), (VS-7), (VS-8), (VS-11), (VS-13), (VS-21), (VS-23) through (VS-32), (VS-34) through (VS-53) and (VS-55) through (VS-57) each given in JP Application No. 2-274026/1990, pp.122~128.

45

The vinyl sulfone type layer hardeners applicable to the invention include, for example; the aromatic type compounds such as those given in German Patent No. 1,100,942 and U.S. Patent No. 3,490,911; the alkyl compounds bonded to a heteroatom, such as those given in JP Examined Publication No. 44-29622/1969, 47-25373/1972 and 47-24259/1972; the sulfonamide ester type compounds such as those given in JP Examined Publication No. 47-8736/1972; 1,3,5-tris[β-(vinyl sulfonyl)propionyl]-hexahydro-s-triazine such as those given in JP OPI Publication No. 49-24435/1974; the alkyl type compounds such as those given in JP Examined Publication No. 50-35807/1975 and JP OPI Publication No. 51-44164/1976; and the compounds such as those given in JP OPI Publication No. 59-18944/1984.

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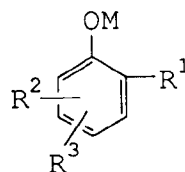
The above-given vinyl sulfone type layer hardeners may be dissolved in water or an organic solvent and then used in a proportion within the range of 0.005 to 20% by weight and, preferably, 0.02 to 10% by weight of a binder (such as gelatin) used. These hardeners may be added into a photographic layer in a batch system or an in-line addition system.

55

There is no special limitation to the additions of these hardeners to the photographic layers. For example, the uppermost single layer, the lowermost single layer or every one of the photographic layers may be added thereby.

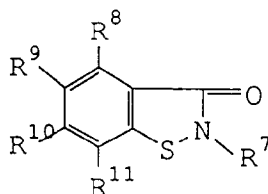
In the invention, it is preferred that a silver halide color photographic light sensitive material contains at least one kind of the compounds represented by the following Formulas [B-1] through [B-3].

Formula [B-1]

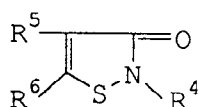


wherein R¹ represents an alkyl group, a cycloalkyl group, an aryl group, a hydroxyl group, an alkoxy-carbonyl group, an amino group, a carboxylic acid group (including the salts thereof) or a sulfonic acid group (including the salts thereof); R² and R³ represent each a hydrogen atom, a halogen atom, an amino group, a nitro group, a hydroxyl group, an alkoxy-carbonyl group, a carboxylic acid group (including the salts thereof) or a sulfonic acid group (including the salts thereof); and M represents a hydrogen atom, an alkali metal atom or an ammonium group.

Formula [B-2]



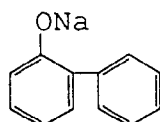
Formula [B-3]



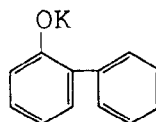
wherein R⁴ represents a hydrogen atom, an alkyl group, an aryl group, a halogenoalkyl group, -R¹²-OR¹³, -CONHR¹⁴ (in which R¹² represents an alkylene group and R¹³ and R¹⁴ represent each a hydrogen atom, an alkyl group or an arylalkyl group) or an arylalkyl group; R⁵ and R⁶ represent each a hydrogen atom, a halogen atom, a halogenoalkyl group or an alkyl group; R⁷ represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a halogenoalkyl group, an arylalkyl group, -R¹⁵-OR¹⁶ or -CONHR¹⁷ (in which R¹⁵ represents an alkylene group; and R¹⁶ and R¹⁷ represent each a hydrogen atom or an alkyl group); and R⁸, R⁹, R¹⁰ and R¹¹ represent each a hydrogen atom, a halogen atom, a hydroxy group, an alkyl group, an amino group or a nitro group.

The typical examples of the compounds represented by Formula [B-1] include the following exemplified compounds.

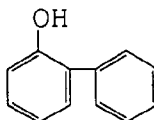
(B-1-1)



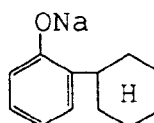
(B-1-2)



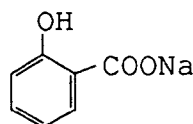
(B-1-3)



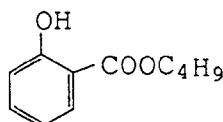
(B-1-16)



(B-1-18)



(B-1-19)



The other typical examples thereof further include (B-1-4) through (B-1-15) and (B-1-17) each given in JP Application No. 2-274026/1990, pp.130~132.

Among the compounds represented by the above-given Formula [B-1], there are some compounds are known as the antimolds for oranges and so forth and, therefore, they may readily be available to the persons skilled in the art.

The preferable compounds among the above-given exemplified compounds include, for example, (B-1-1), (B-1-2), (B-1-3), (B-1-4) and (B-1-5).

The compounds represented by Formula [B-1], which are applicable to the invention, may be used in an amount within the range of desirably 0.03 to 50 g per liter of the stabilizer of the invention used, more desirably, 0.12 to 10 g and, preferably, 0.15 to 5 g.

The typical examples of the compounds represented by the foregoing Formula [B-2] or [B-3] will be given below. It is, however, to be understood that the invention shall not be limited thereto.

(B-2-1) 2-methyl-4-isothiazoline-3-one

(B-2-2) 5-chloro-2-methyl-4-isothiazoline-3-one

(B-2-3) 2-methyl-5-phenyl-4-isothiazoline-3-one

(B-2-4) 4-bromo-5-chloro-2-methyl-4-isothiazoline-3-one

(B-2-5) 2-hydroxymethyl-4-isothiazoline-3-one

(B-2-6) 2-(2-ethoxyethyl)-4-isothiazoline-3-one

(B-2-7) 2-(N-methyl-carbamoyl)-4-isothiazoline-3-one

(B-2-8) 5-bromomethyl-2-(N-dichlorophenyl-carbamoyl)-4-isothiazoline-3-one

(B-2-9) 5-chloro-2-(2-phenylethyl)-4-isothiazoline-3-one

(B-2-10) 4-methyl-2-(3,4-dichlorophenyl)-4-isothiazoline-3-one

(B-3-1) 1,2-benzisothiazoline-3-one

(B-3-2) 2-(2-bromoethyl)-1,2-benzisothiazoline-3-one

(B-3-3) 2-methyl-1,2-benzisothiazoline-3-one

5 (B-3-4) 2-ethyl-5-nitro-1,2-benzisothiazoline-3-one

(B-3-5) 2-benzyl-1,2-benzisothiazoline-3-one

(B-3-6) 5-chloro-1,2-benzisothiazoline-3-one

10 The synthesizing processes of the above-given exemplified compounds and the other applications thereof are described in, for example, U.S. Patent Nos. 2,767,172, 2,767,173, 2,767,174 and 2,870,015, British Patent No. 848,130 and French Patent No. 1,555,416. Some of the exemplified compounds are available on the market and they are available under the trade names of, for example, Topside 300 and 600 (each manufactured by Permachem Asia Co.), Fineside J-700 (manufactured by Tokyo Fine Chemicals Co.) and Proxel GXL (manufactured by I.C.I.)

15 The compounds represented by Formulas [B-1] through [B-3] may be used in an amount within the range of 0.1 to 500 mg and, preferably, 0.5 to 100 mg per sq. meter of a light sensitive materials used.

The compounds represented by formulas [B-1] through [B-3] may be used independently or in combination.

20 The invention can be applied to color photographic light sensitive materials including, for example, a color paper, a color negative film, a color reversal film, a color reversal paper, a direct positive paper, a cinematographic color film and a TV color film, each for general or cinematographic use.

[EXAMPLES]

25 The typical examples of the invention will be detailed below. It is, however, to be understood that the embodiments of the invention shall not be limited thereto.

EXAMPLE 1

30 A multilayered color photographic light sensitive material was prepared by forming the layers having the following compositions on a triacetyl cellulose film support, in the order from the support side.

The amounts of the materials added to a subject silver halide photographic light sensitive material are indicated by grams per sq. meter unless otherwise expressly stated. The amounts of silver halide and colloidal silver are indicated by converting them into the silver contents. However, the sensitizing dyes used therein are indicated by the mol numbers per mol of silver halides contained in one and the same layer.

35

(Light sensitive material sample)

Layer 1 : An antihalation layer

40	Black colloidal silver	0.2
	UV absorbent (UV-1)	0.23
	High boiling solvent (Oil-1)	0.18
	Gelatin	1.4

45 Layer 2 : Interlayer 1

Gelatin 1.3

50

55

Layer 3 : A low-speed red-sensitive emulsion layer

5	Silver iodobromide emulsion (Average grain size: 0.4 μ m) (AgI: 2.0 mol%)	1.0
	Sensitizing dye (SD-1)	1.8x10 ⁻⁵ (mols/mol of Ag)
10	Sensitizing dye (SD-2)	2.8x10 ⁻⁴ (mols/mol of Ag)
	Sensitizing dye (SD-3)	3.0x10 ⁻⁴ (mols/mol of Ag)
	Cyan coupler (C-1)	0.70
15	Colored cyan coupler (CC-1)	0.066
	DIR compound (D-1)	0.03
20	DIR compound (D-3)	0.01
	High boiling solvent (Oil-1)	0.64
	Gelatin	1.2

25

Layer 4 : A medium-speed red-sensitive emulsion layer

30	Silver iodobromide emulsion (Average grain size: 0.7 μ m) (AgI: 8.0 mol%)	0.8
	Sensitizing dye (SD-1)	2.1x10 ⁻⁵ (mols/mol of Ag)
35	Sensitizing dye (SD-2)	1.9x10 ⁻⁴ (mols/mol of Ag)
	Sensitizing dye (SD-3)	1.9x10 ⁻⁴ (mols/mol of Ag)
40	Cyan coupler (C-2)	0.28
	Colored cyan coupler (CC-1)	0.027
	DIR compound (D-1)	0.01
45	High boiling solvent (Oil-1)	0.26
	Gelatin	0.6

50

55

Layer 5 : A high-speed red-sensitive emulsion layer

5	Silver iodobromide emulsion (Average grain size: 0.8 μ m) (AgI: 8.0 mol%)	1.70
	Sensitizing dye (SD-1)	1.9x10 ⁻⁵ (mols/mol of Ag)
10	Sensitizing dye (SD-2)	1.7x10 ⁻⁴ (mols/mol of Ag)
	Sensitizing dye (SD-3)	1.7x10 ⁻⁴ (mols/mol of Ag)
	Cyan coupler (C-1)	0.05
15	Cyan coupler (C-2)	0.10
	Colored cyan coupler (CC-1)	0.02
	DIR compound (D-1)	0.025
20	High boiling solvent (Oil-1)	0.17
	Gelatin	1.2

25

Layer 6 : Interlayer 2

Gelatin 0.8

30 Layer 7 : A low-speed green-sensitive emulsion layer

35	Silver iodobromide emulsion (Average grain size: 0.4 μ m) (AgI: 2.0 mol%)	1.1
	Sensitizing dye (SD-4)	6.8x10 ⁻⁵ (mols/mol of Ag)
	Sensitizing dye (SD-5)	6.2x10 ⁻⁴ (mols/mol of Ag)
40		
	Magenta coupler (M-1)	0.54
	Magenta coupler (M-2)	0.19
45	Colored magenta coupler (CM-1)	0.06
	DIR compound (D-2)	0.017
50	DIR compound (D-3)	0.01
	High boiling solvent (Oil-2)	0.81
	Gelatin	1.8

55

Layer 8 : A medium-speed green-sensitive emulsion layer

5	Silver iodobromide emulsion (Average grain size: 0.7 μ m) (AgI: 8.0 mol%)	0.7
	Sensitizing dye (SD-6)	1.9×10^{-4} (mols/mol of Ag)
10	Sensitizing dye (SD-7)	1.2×10^{-4} (mols/mol of Ag)
	Sensitizing dye (SD-8)	1.5×10^{-5} (mols/mol of Ag)
	Magenta coupler (M-1)	0.07
15	Magenta coupler (M-2)	0.03
	Colored magenta coupler (CM-1)	0.04
20	DIR compound (D-2)	0.018
	High boiling solvent (Oil-2)	0.30
	Gelatin	0.8

25

Layer 9 : A high-speed green-sensitive emulsion layer

30	Silver iodobromide emulsion (Average grain size: 1.0 μ m) (AgI: 8.0 mol%)	1.7
	Sensitizing dye (SD-6)	1.2×10^{-4} (mols/mol of Ag)
35	Sensitizing dye (SD-7)	1.0×10^{-4} (mols/mol of Ag)
	Sensitizing dye (SD-8)	3.4×10^{-6} (mols/mol of Ag)
	Magenta coupler (M-1)	0.09
40		
	Magenta coupler (M-3)	0.04
	Colored magenta coupler (CM-1)	0.04
45	High boiling solvent (Oil-2)	0.31
	Gelatin	1.2

50

55

Layer 10 : A yellow filter layer

	Yellow colloidal silver	0.05
5	Anti-color-staining agent (SC-1)	0.1
	High boiling solvent (Oil-2)	0.13
10	Gelatin	0.7
	Formalin scavenger (HS-1)	0.09
	Formalin Scavenger (HS-2)	0.07

15

Layer 11 : A low-speed blue-sensitive emulsion layer

20	Silver iodobromide emulsion (Average grain size: 0.4 μ m) (AgI: 2.0 mol%)	0.5
25	Silver iodobromide emulsion (Average grain size: 0.7 μ m) (AgI: 8.0 mol%)	0.5
	Sensitizing dye (SD-9)	5.2×10^{-4} (mols/mol of Ag)
	Sensitizing dye (SD-10)	1.9×10^{-5} (mols/mol of Ag)
30	Yellow coupler (Y-1)	0.65
	Yellow coupler (Y-2)	0.24
35	DIR compound (D-1)	0.03
	High boiling solvent (Oil-2)	0.18
	Gelatin	1.3
40	Formalin scavenger (HS-1)	0.08

45

50

55

Layer 12 : A high-speed blue-sensitive emulsion layer

5	Silver iodobromide emulsion (Average grain size: 1.0 μ m) (AgI: 8.0 mol%)	1.0
	Sensitizing dye (SD-9)	1.8×10^{-4} (mols/mol of Ag)
10	Sensitizing dye (SD-10)	7.9×10^{-5} (mols/mol of Ag)
	Yellow coupler (Y-1)	0.15
	Yellow coupler (Y-2)	0.05
15	High boiling solvent (Oil-2)	0.074
	Gelatin	1.30
20	Formalin scavenger (HS-1)	0.05
	Formalin scavenger (HS-2)	0.12

Layer 13 : Protective layer 1

25		
	Finely grained silver iodobromide emulsion (Average grain size: 0.08 μ m) (AgI: 1.0 mol%)	0.4
30	UV absorbent (UV-1)	0.07
	UV absorbent (UV-2)	0.10
35	High boiling solvent (Oil-1)	0.07
	High boiling solvent (Oil-3)	0.07
	Formalin scavenger (HS-1)	0.13
40	Formalin scavenger (HS-2)	0.37
	Gelatin	1.3

45 Layer 14 : Protective layer 2

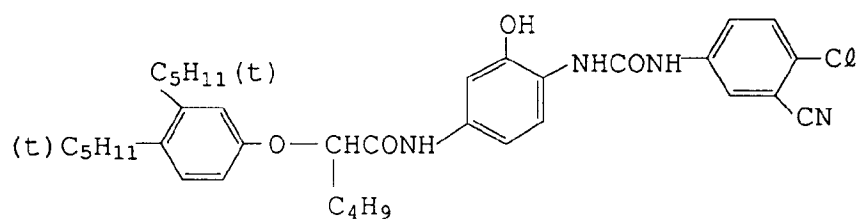
	Alkali-soluble matting agent (Average particle size: 2 μ m)	0.13
50	Polymethyl methacrylate (Average particle size: 3 μ m)	0.02
	Lubricant (WAX-1)	0.04
55	Gelatin	0.6

Besides the above-given compositions, coating aid Su-1, Dispersing aid Su-2, a viscosity controller, layer

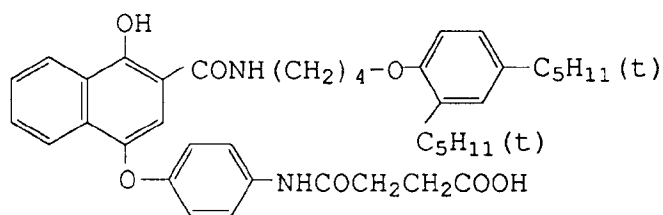
hardeners H-1 and H-2, stabilizer ST-1, antifoggant AF-1 and two kinds of antifoggant AF-2 having Mw: 100000 and Mw: 1100000 were each added.

The emulsions applied to the above-described samples were the monodisperse emulsions having a low silver iodide content on the surfaces of the emulsion grains and they were subjected to the optimum gold-sulfur sensitization in an ordinary method. The average grain size thereof were indicated by the grain sizes converted into a cube.

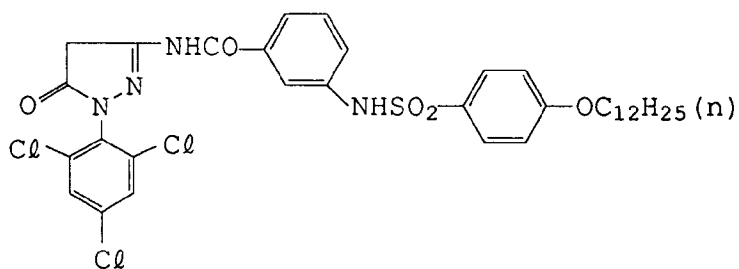
C-1



C-2



M-1

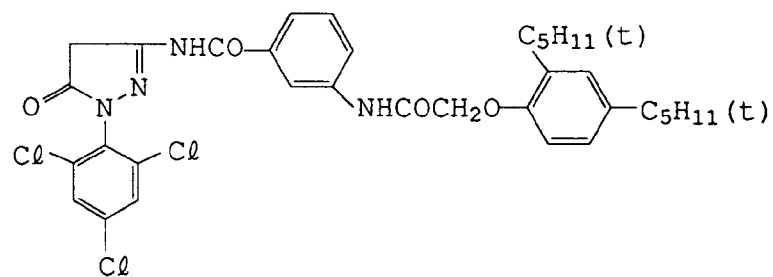


M-2

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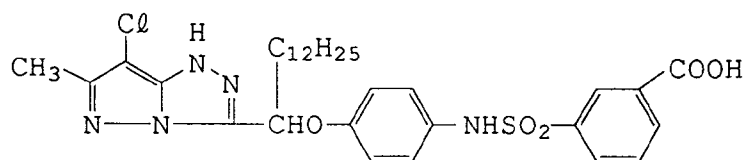
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M-3

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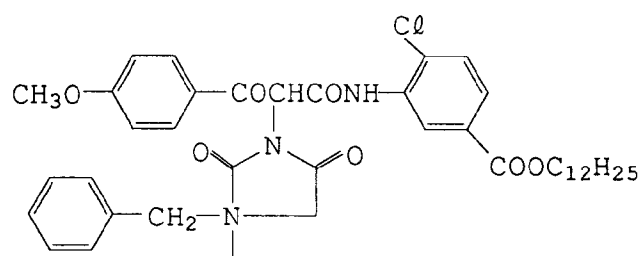
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Y-1

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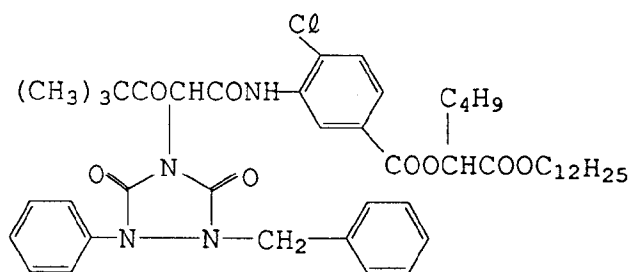
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Y-2

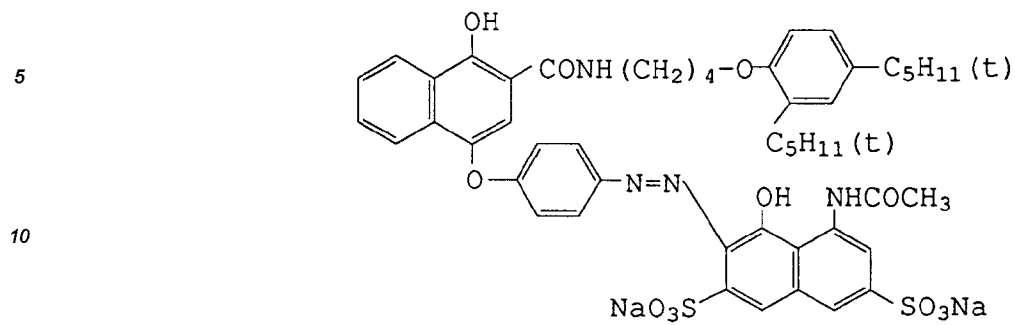
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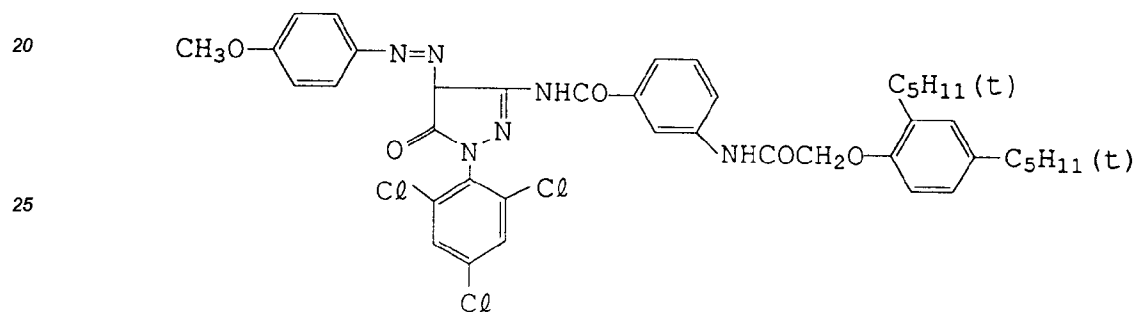
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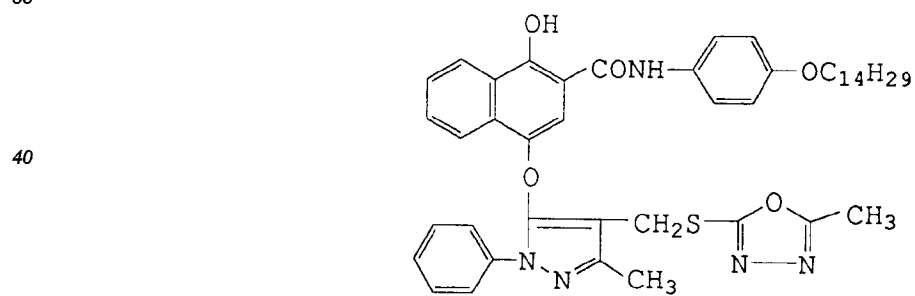
CC-1



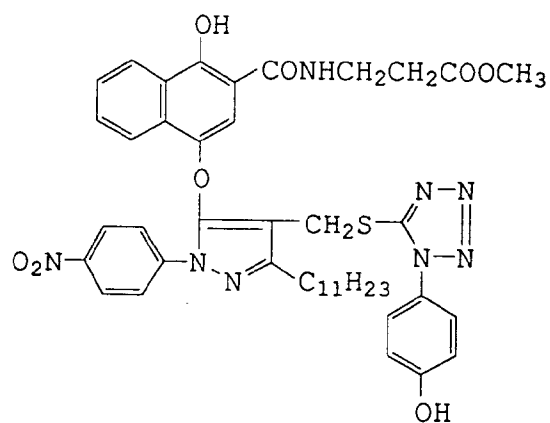
CM-1



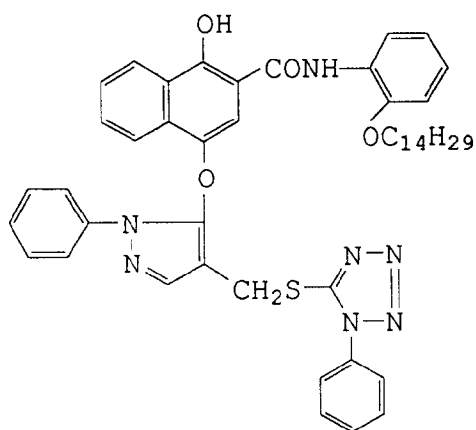
D-1



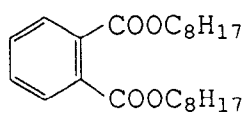
D-2



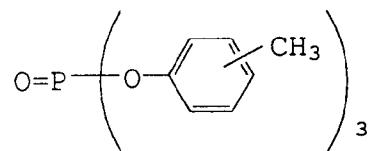
D-3



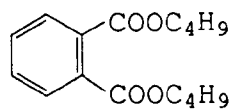
Oil-1



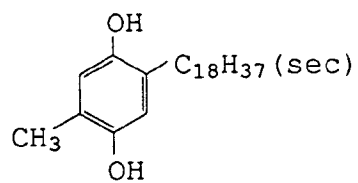
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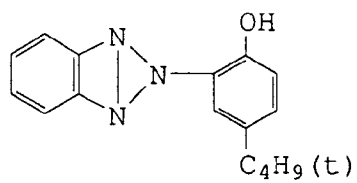
Oil-3



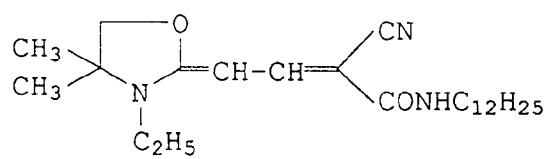
SC-1



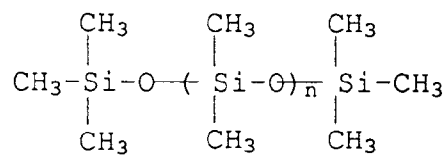
UV-1



UV-2



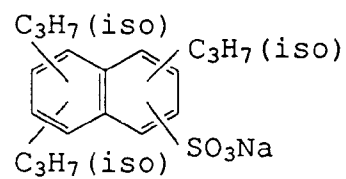
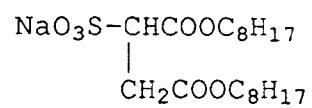
WAX-1



Weight average molecular weight: Mw=3000

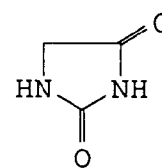
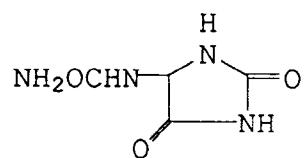
Su-1

Su-2

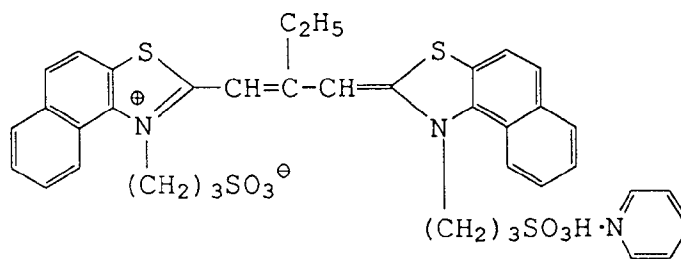


HS-1

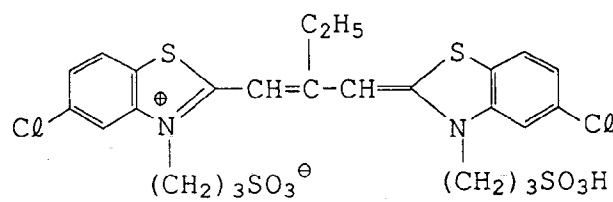
HS-2



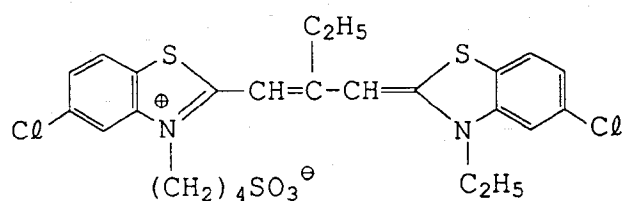
SD-1



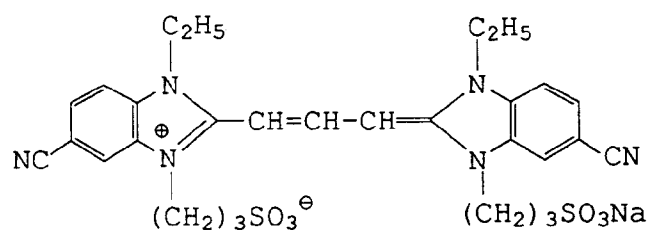
SD-2



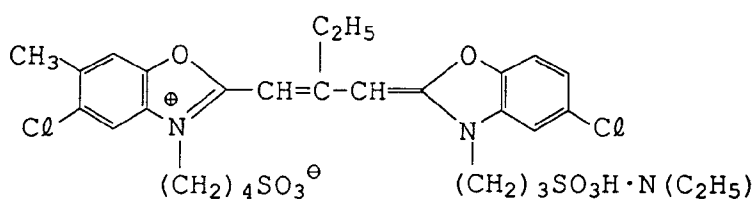
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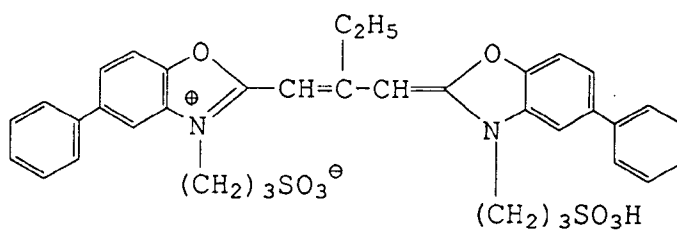
SD-4



SD-5



SD-6

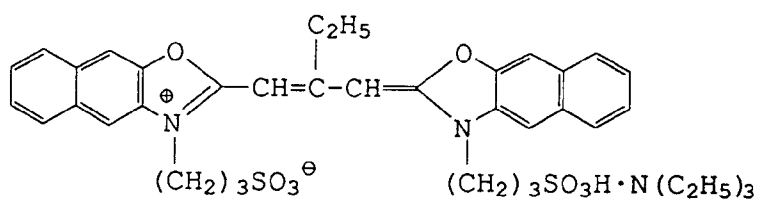


SD-7

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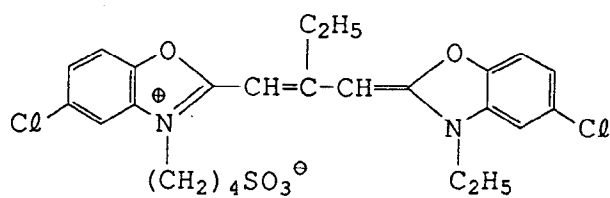
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SD-8

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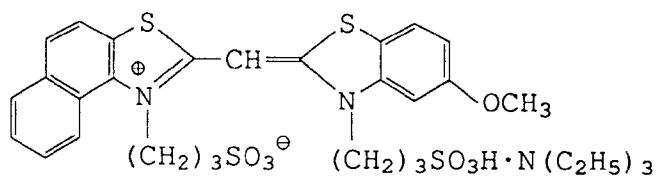


SD-9

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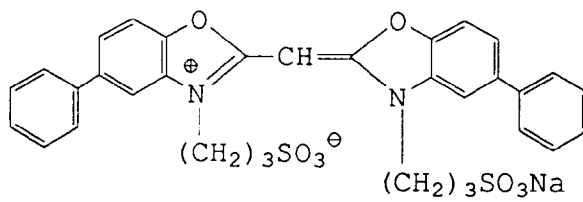


SD-10

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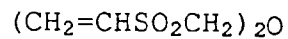
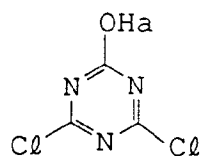
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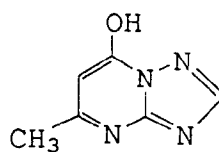


H-1

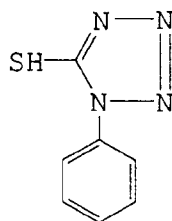
H-2



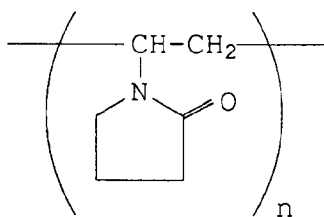
ST-1



AF-1



AF-2



n : polymerization degree

The resulting film samples were exposed practically to light through a camera and the exposed film samples were then subjected to running tests by varying the stabilizer replenished amounts as shown in Tables 4 and 5, under the following conditions.

	Processing step	Processing time	Processing temperature	Amount replenished
5	Color developing	3min.15sec.	38°C	775 ml
	Bleaching	45sec.	38°C	155 ml
	Fixing	1min.30sec.	38°C	500ml
10	Stabilizing	50sec.	38°	See tables 4 & 5
	Drying	1min.	40~70°C	—

15 (The amounts replenished were the values per sq.meter of a subject light sensitive material)

In the above-mentioned processing steps, the stabilizing step was carried out in a dual tank counter-current system in which the replenishment was made to the final stabilizing solution tank and the overflow was so flowed into the tank precedent to the final stabilizing solution tank. Further, a part of the overflow (in a proportion of 275 ml/m²) was flowed from the stabilizing tank following the fixing tank into the fixing tank.

20 The compositions of the processing solutions used in the above-mentioned processing steps were as follows.

Color developer

25	Potassium carbonate	30 g
	Sodium hydrogencarbonate	2.5 g
30	Potassium sulfite	3.0 g
	Sodium bromide	1.2 g
	Potassium iodide	0.6 mg
35	Hydroxylamine sulfate	2.5 g
	Sodium chloride	0.6 g
40	4-amino-3-methyl-N-ethyl-N-(β -hydroxyethyl) aniline sulfate	4.6 g
	Diethylenetriamine pentaacetate	3.0 g
45	Potassium hydroxide	1.2 g
	Add water to make	1 liter
50	Adjust pH with potassium hydroxide or a 20% sulfuric acid solution to be	pH10.01

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Color developer replenisher

5	Potassium carbonate	40 g
	Sodium hydrogencarbonate	3 g
	Potassium sulfite	7 g
10	Sodium bromide	0.5 g
	Hydroxylamine sulfate	3.1 g
15	4-amino-3-methyl-N-ethyl-N-(β -hydroxyethyl) aniline sulfate	6.0 g
	Diethylenetriamine pentaacetate	3.0 g
	Potassium hydroxide	2 g
20	Add water to make	1 liter
	Adjust pH with potassium hydroxide or a 20% sulfuric acid solution to be	pH 10.20

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Bleaching tank solution

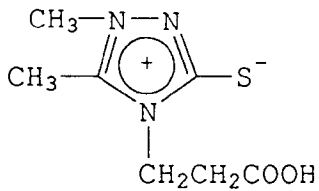
30	Ferric ammonium 1,3-propylenediamine tetraacetate (the ferric ammonium complex salt of Exemplified compound A-1)	0.32 mols
	Disodium ethylenediamine tetraacetate	10 g
35	Ammonium bromide	100 g
	Glacial acetic acid	40 g
	Ammonium nitrate	40 g
40	Add water to make	1 liter
	Adjust pH with aqueous ammonia or glacial acetic acid to be	pH 4.4

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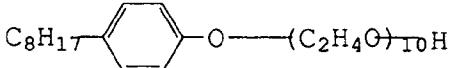
Bleaching replenisher

50	Ferric ammonium 1,3-propylenediamine tetraacetate (the ferric ammonium complex salt of Exemplified compound A-1)	0.32 mols
	Disodium ethylenediamine tetraacetate	2 g

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	Ammonium bromide	120 g
	Ammonium nitrate	50 g
5	Glacial acetic acid	40 g
	Add water to make	1 liter
10	Adjust pH with aqueous ammonia or glacial acetic acid to be	pH 3.4
	Fixing tank solution and fixing replenisher	
15	Ammonium thiocyanate	120 g
20		1.5 mols
25	Ammonium thiosulfate	100 g
	Sodium bisulfite, anhydrous	20 g
	Sodium metabisulfite	4 g
30	Disodium ethylenediamine tetraacetate	1 g
	Add water to make	1 liter
35	Adjust pH with glacial acetic acid or aqueous ammonia to be	pH 6.5

Stabilizing tank solution and stabilizing replenisher

40	Surfactant	0.5 g
		
45	Dearside 702 (manufactured by Dearborn Co.)	1.0 ml
	Additive (I)	See tables 4 & 5
50	Add water to make	1 liter
	Adjust pH with potassium hydroxide or a 20% sulfuric acid solution to be	pH 7.5

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The running treatments were carried out with a small sized running experimental developing machine until a stabilizing replenisher was replenished in an amount double as much as the capacity of the stabilizing tank (that was 0.07R per day, in which R=a total replenisher amount/a tank capacity). After completing the running

treatments, the following conditions were observed; namely, the resulting sulfide precipitates produced in the stabilizing tank, the produced cotton-like suspended matters, the produced tar, the solid matters produced on the tank walls, and the stains, scratches and adhered foreign matters produced on the film samples. With respect to each processed film sample, the magenta density in the maximum density area was measured and, after each film sample was stored for 10 days under the conditions of 70°C and 70%RH, the resulting maximum magenta density was measured so that the dye discoloration ratios were obtained. The results thereof are shown collectively in tables 4 and 5.

The evaluation criteria were set as follows (also for Example 2 and so forth.)

10 [Evaluation criteria]

(1) Production of sulfide precipitates

- Not produced at all;
- 15 △ Not produced on any solution surface, but there may be some instances where some practical problems may be raised, because a suspended matters were confirmed;
- × Confirmed some suspended matters and precipitates; and
- ×× Confirmed suspended matters and precipitates which were fixed to the interface between a solution and a rack.
- 20 The more the numbers of [×] are increased, the more the precipitates were produced.

(2) Cotton-like suspended matter

- Not produced at all;
- 25 △ Slightly produced and there may be some instances where some practical problems may be raised;
- × Confirmed many suspended matters; and
- ×× Confirmed considerably many suspended matters on the bottom portion.
- The more the numbers of [×] are increased, the more the suspended matters were produced.

30 (3) Production of tar

- Not produced at all;
- △ Slightly produced and there may be some instances where some practical problems may be raised; and
- × Confirmed many tar production.

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(4) Stains confirmed after treatments

- Not confirmed at all;
- △ Slightly confirmed, but there may be no problem for the commercial products; and
- 40 × Not applicable to any commercial products.

(5) Scratch and foreign matter adhesion produced after treatments

- Not produced at all;
- 45 △ Slightly produced, but there may be no problem for the commercial products;
- × Not applicable to any commercial products; and
- ×× Not applicable at all to any commercial products.

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Table 4

Experi- ment No.	Additives (I)		Replenisher amount added (ml)	Discoloring ratio (%)	Remarks
	Compound No.	Amount added (g/l)			
10	1- 1	—	775	39.6	Comparison
	1- 2	Formaldehyde	775	5.0	Comparison
	1- 3	Formaldehyde	750	5.0	Comparison
	1- 4	Formaldehyde	670	4.9	Comparison
15	1- 5	Formaldehyde	500	4.9	Comparison
	1- 6	Formaldehyde	460	5.0	Comparison
	1- 7	Formaldehyde	300	5.3	Comparison
	1- 8	Formaldehyde	160	6.0	Comparison
20	1- 9	(F- 3)	775	5.3	Comparison
	1-10	(F- 3)	750	5.0	Comparison
	1-11	(F- 3)	670	4.3	Invention
	1-12	(F- 3)	500	4.0	Invention
25	1-13	(F- 3)	460	4.2	Invention
	1-14	(F- 3)	300	4.4	Invention
	1-15	(F- 3)	160	4.8	Invention
	1-16	(F- 2)	400	4.7	Invention
30	1-17	(F- 4)	400	5.0	Invention
	1-18	(F- 6)	400	5.1	Invention
	1-19	(F-23)	400	4.9	Invention
	1-20	(F-24)	400	4.8	Invention
35	1-21	(F-52)	400	5.0	Invention
	1-22	(F-61)	400	5.2	Invention

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Table 5

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Experi- ment No.	Sulfide precipi- tate	Cotton- like suspended matter	Tar produc- tion	Fixed adhesion	Stain after treatment	Scratch/f oreign matter adhesion after treatment	Remarks
1-1	×	×	×	×	×	×	Comp.
1-2	×	△	○	×	△	×	Comp.
1-3	×	△	○	×	△	×	Comp.
1-4	×	△	○	×	△	×	Comp.
1-5	×	△ ~ ×	△	×	×	×	Comp.
1-6	×	×	△	×	×	×	Comp.
1-7	×	×	△	×	×	×	Comp.
1-8	×	×	△ ~ ×	×	×	×	Comp.
1-9	○	○	○	△	△	△	Comp.
1-10	○	○	○	△ ~ ○	△	△	Comp.
1-11	○	○	○	○	○	○	Inv.
1-12	○	○	○	○	○	○	Inv.
1-13	○	○	○	○	○	○	Inv.
1-14	○	○	○	○	○	○	Inv.
1-15	△ ~ ○	△	○	○	△ ~ ○	○	Inv.
1-16	○	○	○	○	○	○	Inv.
1-17	○	○	○	△ ~ ○	○	○	Inv.
1-18	○	○	○	○	○	△ ~ ○	Inv.
1-19	○	○	○	○	△ ~ ○	△ ~ ○	Inv.
1-20	△ ~ ○	○	○	○	○	○	Inv.
1-21	△ ~ ○	○	○	○	○	○	Inv.
1-22	○	○	○	○	○	△ ~ ○	Inv.

Comp.: Comparison

Inv.: Invention

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It was found from the contents of Tables 4 and 5 that the effects of the objects of the invention can be excellently displayed when making use of the compounds of the invention (which are the compounds represented by Formula [F]) and replenishing the stabilizing solution in an amount of not more than 670 ml/m².

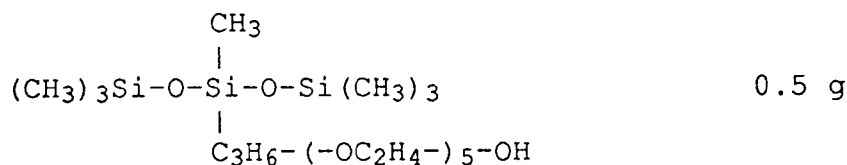
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When the replenishing solution is replenished in an amount of more than 670 ml/m², not only the full effects can scarcely be displayed, but also the waste solutions are increased, so that it is not preferred from the social environmental viewpoint and it is also not preferred from the viewpoint of the cost because of the increase in the amount of the stabilizing solution used.

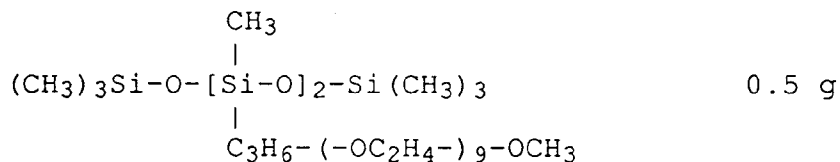
EXAMPLE 2

By making use of the samples prepared in Example 1, the following compounds (which were the water-soluble organic siloxane type compounds) were added to the stabilizing solutions used in Experiment Nos. 1 through 19, respectively.

Exemplified compound (1)



Exemplified compound (3)



The running experiments were tried in the same manner as in Example 1, except that the samples and the compounds were used as mentioned above.

The resulting magenta discoloring ratios were the same. However, the sulfide precipitates, cotton-like suspended matters and the stains, scratches and foreign matter adhesion found after treatments were each proved to be O, so that the invention could be more improved.

When replacing the above-mentioned exemplified compounds (1) and (3) by the water-soluble organic siloxane type compounds (7), (13), (15), (16) and (17) each given in this patent specifications, almost the same effects as in Exemplified compounds (1) and (3) could be displayed.

EXAMPLE 3

By making use of the samples prepared in Example 1, the running treatment experiments were tried on Experiment No. 1-8 by setting the areas, which come into contact with the air per liter of the stabilizing solution used, to be 3cm², 5cm², 8cm², 20cm², 50cm² and 100cm², respectively. Each of the evaluations obtained from the above-mentioned areas except 100cm² was quite the same as in Experiment No. 1-12.

In the case of 100cm², the results were the same, except that the sulfide precipitates were valuated to be Δ , (wherein the contact areas of popularly applicable automatic processing machines are generally within the range of 10 to 20cm²/liter)

As is obvious from the above-mentioned results, the invention could be proved to be excellent in the solution preservability even if the aperture area should be widened.

EXAMPLE 4

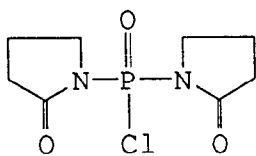
The experiments were tried in the same manner as in Experiment No. 1-14 of Example 1, except that layer hardener (H-2) used in the film samples tried in Experiment No. 1-14 of Example 1 was replaced by the layer hardeners shown in the following Table 6. The results thereof are shown collectively in Table 6.

However, the tar production and the fixed adhesion were not particularly varied even when using any one of the layer hardeners, so that the two evaluations were omitted from Table 6.

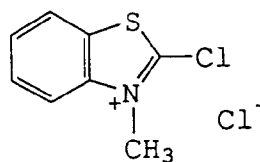
Table 6

Experiment No.	Layer hardener	Discolored ratio (%)	Sulfide precipitates	Cotton-like suspension	Stains after treated	Scratch, foreign matter adhesion after treated
4-1	Exemp. (VS-2)	4.0	○	○	○	○
4-2	Exemp. (VS-4)	4.2	○	○	○	○ ~ Δ
4-3	Exemp. (VS-6)	4.0	○	○ ~ Δ	○	○
4-4	Exemp. (VS-9)	4.0	○	○	○	○ ~ Δ
4-5	Exemp. (VS-10)	4.5	○	○	○ ~ Δ	○
4-6	Exemp. (VS-12)	4.6	○	○ ~ Δ	○	○
4-7	Exemp. (VS-22)	4.1	○	○ ~ Δ	○	○ ~ Δ
4-8	Exemp. (VS-33)	4.2	○	○	○	○ ~ Δ
4-9	Exemp. (VS-54)	4.4	○	○ ~ Δ	○	○
4-10	RH-1 given below	6.5	Δ	○	Δ	○ ~ Δ
4-11	RH-2 given below	8.1	○	Δ	Δ	○ ~ Δ
4-12	RH-3 given below	6.7	Δ	○ ~ Δ	○	Δ
4-13	RH-4 given below	5.6	○	Δ	Δ	○ ~ Δ
4-14	RH-5 given below	9.0	○ ~ Δ	Δ	Δ	○ ~ Δ

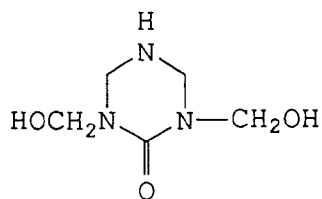
RH-1



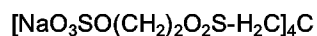
RH-2



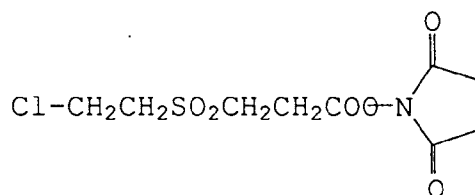
RH-3



RH-4



RH-5



From Table 6, it was proved that the effects of the objects of the invention can excellently be displayed when making combination use of the vinyl sulfone type layer hardeners in the processes of the invention.

EXAMPLE 5

The experimental samples were each prepared in the same manner as in Experiment No. 1-13, except that 10 mg/m² each of the additives shown in the following Table 7 was added to the film samples prepared in Experiment No. 1-13 of Example 1, respectively. The results thereof are collectively shown in Table 7.

Table 7

Experi- ment No.	Additives (10 mg/m ²)	Discoloring ratio (%)	Sulfide precipitate
5-1	Not added	4.2	○
5-2	Phenol	4.9	○
5-3	Dehydroacetic acid	5.2	○
5-4	Chlorodiphenyl	5.2	△
5-5	Imidazole	6.5	○ ~ △
5-6	p-amino-benzene sulfamide	4.9	○ ~ △
5-7	Thiazolyl benzimidazole	7.0	○
5-8	(B-1-1)	3.0	○
5-9	(B-1-16)	3.2	○
5-10	(B-1-18)	3.0	○
5-11	(B-2-1)	2.9	○
5-12	(B-2-2)	3.1	○
5-13	(B-2-7)	3.5	○
5-14	(B-2-10)	3.0	○
5-15	(B-3-1)	3.1	○
5-16	(B-3-6)	3.4	○

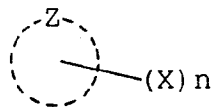
From the contents of Table 7, it was proved that the effects of the invention could be excellently resulted when making combination use of the compounds represented by the foregoing Formulas [B-1] through [B-3] in the processes of the invention.

The process for a silver halide color photographic light sensitive material, which is capable of not only providing stable processing characteristics even when a low replenishment is made to a stabilizing solution and disusing any conventional formaldehyde, but also preventing the productions of any sulfide precipitates in a stabilizing bath, any cotton-like suspended matters, any tar and any fixed adhesion to the walls of the stabilizing tank and, further, capable of positively preventing the productions of any tar, scratches and foreign matter adhesion after completing drying step.

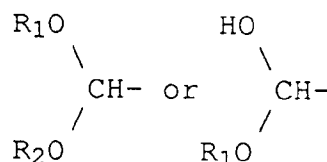
Claims

1. A processing method for a silver halide color photographic light-sensitive material comprising a step selected from the group consisting of:
 - (a) color developing, bleaching-fixing, stabilizing;
 - (b) color developing, bleaching, fixing, stabilizing;
 - (c) color developing, bleaching, bleaching-fixing, stabilizing;
 - (d) color developing, bleach-fixing, fixing, stabilizing;
 - (e) color developing, bleach-fixing, bleach-fixing-stabilizing;
 in which a processing is carried with a developing solution, a bleaching solution, a bleach solution having a fixing ability, a processing solution having a fixing ability, a bleach-stabilizing solution having a fixing ability and a stabilizing solution;
 wherein the stabilizing solution contains a compound represented by formula F:

formula F



wherein Z represents a group consisting of atoms necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring; X represents an aldehyde group,



wherein R_1 and R_2 represent each a lower alkyl group, and n is an integer of 1 to 4;
and a replenished amount of the stabilizing solution per sq meter of the material is not more than 670 ml.

2. The method of claim 1 wherein the stabilizing solution contains the compound represented by formula F 0.05 to 20 gr per liter.
3. The method of claim 2 wherein the content of the compound is 0.1 to 15 gr per liter.
4. The method of claim 2 wherein the content is 0.5 to 10 gr per liter.
5. The method of claim 1 wherein the replenished amount of the stabilizing solution is 100 ml to 500 ml per sq meter of the material.
6. The method of claim 5 wherein the replenished amount of the stabilizing solution is 160 ml to 460 ml per sq meter of the material.
7. The method of claim 1 wherein a pH value of the stabilizing solution is not lower than 6.0.
8. The method of claim 7 wherein the pH value is not lower than 7.0.
9. The method of claim 8 wherein the pH value is 7.5 to 9.0.
10. The method of claim 1 wherein the stabilizing solution contains a chelating agent having a chelating stability constant of not less than 8 to to an iron ion.
11. The method of claim 10 wherein the chelating agent is selected from the group consisting of an organic carboxylic acid chelating agent, an organic phosphoric acid chelating agent, an inorganic phosphoric acid chelating agent and a polyhydroxy compound wherein the iron ion is a ferric ion.
12. The method of claim 11 wherein the chelating agent is used in an amount of 0.01 to 50 g per liter of the stabilizing solution.
13. The method of claim 12 wherein the amount is 0.05 to 20 g.
14. The method of claim 1 wherein the stabilizing solution contains a metal salt in combination of the chelating agent.
15. The method of claim 14 wherein a metal of the metal salt is selected from the group consisting of Ba, Ca, Ce, Co, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al and Sr.
16. The method of claim 1 wherein the stabilizing solution contains a water-soluble organic siloxane type compound.

17. The method of claim 16 wherein a volume of the siloxane type compound used is 0.01 to 20 g per liter of the stabilizing solution.

18. The method of claim 1 wherein the step is (a), (b) or (c).

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19. The method of claim 18 wherein the step is (b) and the solution having the fixing ability is a fixing solution.

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20. A processing method for a silver halide color photographic light-sensitive material comprising steps of: color developing, bleaching, fixing and stabilizing wherein the step of stabilizing comprises a stabilizing solution containing 0.5 to 10 g per liter of 3-hydroxy benzaldehyde, 0.05 to 20 g per liter of a chelating agent having a chelating stability constant of not less than 8 to ferric ion, and 4×10^{-4} to 2×10^{-2} mols/liter of Ba, Ca, Ce, Co, In, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al or Sr salt of halide, hydroxide, sulfate, carbonate, phosphate, acetate, or the chelating agent;

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and a replenished amount of the stabilizing solution per sq meter of the material is 160 ml to 460 ml.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6619

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)
A	EP-A-0 217 643 (KONISHIROKU PHOTO INDUSTRY CO.) * page 28, line 1 - line 46; claims 1,9,10 * * page 22, line 5 - line 11 * * page 6, line 55 - page 8, line 45 * ---	1-20	G03C7/30 G03C7/44
A	DE-A-3 517 396 (KONISHIROKU PHOTO INDUSTRY CO.) * page 8, paragraph 4 - page 11, paragraph 3 * ---	10-15	
A	EP-A-0 186 504 (KONISHIROKU PHOTO INDUSTRY CO.) * page 9, compound I-32 * * page 70, line 23 - page 71, line 23 * ---	1-15	
A	FR-A-2 174 251 (FUJI PHOTO FILM COMPANY) * claims 3,4 * * page 17, table * ---	1-4	
A	FR-A-2 154 699 (FUJI PHOTO FILM COMPANY) * claims 2,3 * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-2 440 954 (A. J. JENNINGS) * the whole document * -----	1	G03C
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 23 NOVEMBER 1992	Examiner STOCK H.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>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</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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