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Method for processing silver halide color photographic light sensitive materials.

A method for processing a silver halide color photograhic light-sensitive material comprises processing the photographic material with a solution having a fixing ability and, in succession, processing the same directly with a stabilizer without carrying out a washing step, and the method is characterized in that the photographic material contains at least one of two-equivalent couplers; that the processing solution having fixing ability contains ammonium ions in an amount of 50 mol% of the whole cations contained therein; and that the stabilizer does not contains any formaldehyde substantially, but contains a compound represented by the following formula I or II:

formula I

$$R_{21} - O + R_{22} - O \rightarrow X_1$$

formula II

II

$$CH_3$$
 $CH_3$ 
 $CH_$ 

#### **BACKGROUND OF THE INVENTION**

This invention relates to a method for processing a silver halide color photographic light sensitive material and, particularly, to a method for processing a silver halide color photographic light sensitive material, which is capable of providing a light sensitive material excellent in dye image stability and stain prevention and, at the same time, reducing a harmful compound contained in a processing solution or not using any one of the compound and, in addition, performing a rapid processing.

Generally, a silver halide color photographic light sensitive material is exposed imagewise to light and is then processed in the following order, a color developing step, a bleaching step, a fixing step or a processing step having a fixing function such as a bleach-fixing step, and the processing steps such as a stabilizing and washing steps.

In recent years, however, it has been demanded for the processing steps in which an amount of washing water can be saved and the countermeasures against pollution can be taken, for economical reasons of the shortage of water resources and the increase of sewage disposal costs and heat/light expenses and for reansons of pollution prevention, respectively.

Heretofore, the countermeasures thereto include, for example, the methods in which water is counterflowed by providing a washing tank with a multistage structure, such as described in West German Patent No. 2,920,222 and S.R. Goldwasser, 'Water Flow in Immersion-Washing of Motion-picture Film', SMPTE, Vol.64, pp.248 ~ 23, May 1955.

There has been a known processing method in which a pre-washing step is provided just after a fixing bath so as to abate a pollutive component which may be contained in or may adhere to a light sensitive material and may then enter into a washing step, and an amount of washing water is also abated.

The above-mentioned technique is not a processing method in which any washing water is not used at all. Therefore, under the recent situations where the water resources are so short that a washing cost is raised by increasing the costs of crude oil, the problems are getting more serious.

On the other hand, when processing color photographic light-sensitive materials for photographic use typified by those comprising silver iodobromide as the silver halide thereof, a stabilizing bath containing formaldehyde has generally been used in the final processing step following a washing bath.

The formaldehyde applied to the above-mentioned stabilizing bath has the effects of protecting the physical properties of a color light sensitive material including, particularly, an effect of preventing the surface of a photographic light sensitive material from being scratched and an effect of preventing a gradation from being varied by the fact that a photographic light sensitive material is gradually hardened by allowing it to stand. In addition to the above effects, it has also a further known effect of preventing a dyeimage stability from being deteriorated by a coupler remaining unreacted in the color photographic light sensitive material.

Recently, on the other hand, the photofinishing services of color photographic light sensitive materials have been diversified gradually from large-scaled photofinishing laboratories to small-sized photofinishers so-called 'mini-lab' typified by camera and film dealers. Therefore, a processing methods capable of processing light-sensitive material as quickly as possible has been demanded. However, formaldehyde added into a stabilizing bath for the purposes of stabilizing dye images and so forth deteriorates the elution of a thiosulfate brought therein from the preceding bath (that comprises a processing solution having a fixing function), because the formaldehyde adheres to the light sensitive material to be processed. Therefore, when the final processing step is carried out more rapid by making use of a stabilizer containing formaldehyde, it was proved that the effect of stabilizing a dye-image, that is the original object, is rather spoiled.

In the U.S.A., CIIT (Chemical Industry Institute of Toxicity) reported that rats had nasal cancer when they had 15 ppm of formaldehyde. NIOSH (National Institute of Safety and Health) and ACGIH (American Government Committee of Industrial Health) also reported that formaldehyde has a possibility of producing cancer.

Also in Europe, formaldehyde is severely regulated. In West Germany, formaldehyde has been so regulated as to be not more than 0.1 ppm in every housing accommodation for ten years now.

Further in Japan, the harmfulness of formaldehyde has been proved that a mucous membrane is thereby stipulated. Therefore, the following regulations have been put into practice; namely, the toxic substance laws, organic solvent intoxication control under the special regulations of the industrial safety laws, the regulations applied to household goods, the regulations applied to fibers and plywood, and the formaldehyde regulations applied to underwears and baby clothes, which have been recently issued by Japanese Ministry of Health and Welfare since 1975. Accordingly, the techniques capable of reducing or not making use of formaldehyde have so far been waited for.

With the purpose of solving the above-described problems, Japanese Patent Publication Open to Public Inspection - hereinafter referred to as Japanese Patent O.P.I. Publication-Nos. 62-196660/1987, 62-54261/1987 and 63-298344/1988 each disclose the techniques in which a color photographic light sensitive material containing a 2-equivalent coupler is processed with a stabilizer not substantially containing any formaldehyde. However, when making use of the techniques, it was found that the other problems were raised. Namely, a problem that stains are liable to produce due to a sensitizing dye eluted from a light sensitive material to be processed, and another problem that a reticulation is liable to produce. Besides the above-mentioned problems, it was also found to produce a trouble that the above-mentioned dye is transferred to the light sensitive material. Particularly in recent years, a rapid processing requirement has been one of the public needs and a high-speed conveyor system processing is a general tendency. Under the above-mentioned circumstances, the above-described problems have been getting more serious.

### **SUMMARY OF THE INVENTION**

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It is, therefore, an object of the invention to provide an improved method for processing a silver halide color photographic light sensitive material, wherein any stains and reticulations can be prevented from producing even in carrying out a rapid processing.

Another object of the invention is to provide an improved method for processing a silver halide color photographic light sensitive material, wherein a dye transfer can be improved in the stabilizing tank of an automatic processor.

A further object of the invention is to provide a method for processing a silver halide color photographic light sensitive material, wherein any formaldehyde is not used substantially and an excellent social environment can be maintained.

These and other objects will become apparent from the following detailed specifications.

The method for processing a silver halide color photographic light sensitive material, which relates to the invention, is comprised of processing the silver halide color photographic light sensitive material with a processing solution having a fixing ability and, in succession, processing the same directly with a stabilizer without carrying out a washing step, and the method is characterized in that the silver halide color photographic light sensitive material contains at least one kind of 2-equivalent couplers, that the above-mentioned processing solution having the fixing ability contains ammonium ions in a proportion of not more than 50 mol% to the whole cation, and that the above-mentioned stabilizer does not contain any formaldehyde substantially, but contains at least one kind of the compounds represented by the following formula I or II.

Formula I

$$R_{21}-O-(-R_{22}-O-)_{m}X_{1}$$

wherein  $R_{21}$  represents a univalent organic group;  $R_{22}$  represents an ethylene, propylene or isopropylene group; m is an integer of 4 to 50; and  $X_1$  represents a hydrogen atom, -SO<sub>3</sub>M or -PO<sub>3</sub>M in which M represents a hydrogen atom, an alkali metal or ammonium.

Formula II

wherein R<sub>9</sub> represents a hydrogen atom, a hydroxy group, a lower alkyl group, an alkoxy group,

$$-si < R_{11} \atop R_{12}$$

or

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$$-O-Si \stackrel{R_{10}}{\underset{R_{12}}{\overbrace{}}}$$

in which R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> represent each a hydrogen atom or a lower alkyl group (including, preferably, an alkyl group having 1 to 4 carbon atoms, a methyl group, an ethyl group and a propyl group), provided, R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> may be the same with or different from each other; l<sub>1</sub> to l<sub>3</sub> are each an integer of 0 or 1 to 30; p, q<sub>1</sub> and q<sub>2</sub> are each an integer of 0 or 1 to 30; and X<sub>1</sub> and X<sub>2</sub> represent each -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-,

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#### **DETAILED DESCRIPTION OF THE INVENTION**

The processing steps preferably carried out in the processing method in which the processing solution of the invention is to be used include the following processing steps;

- (1) Color developing bleaching fixing stabilizing;
- (2) Color developing bleach-fixing stabilizing;
- (3) Color developing bleaching bleach-fixing stabilizing;
- (4) Color developing fixing bleach-fixing stabilizing;
- (5) Black-and-white developing washing reversing color developing adjusting bleaching fixing stabilizing;

and

(6) Color developing - bleaching - bleach-fixing - fixing - stabilizing

Among these processing steps, the processing steps (1), (2) and (5) may preferably be carried out. When the term, 'a processing bath (or a processing solution) having a fixing ability', is used in the invention, the bath or solution include, for example, a bleach-fixer or a fixer used in the above-given processing steps.

In the invention, the fixer or bleach-fixer contains ammonium ions in a proportion of not more than 50 mol% of the whole cation, desirably not more than 20 mol% thereof and, preferably not more than 10 mol% thereof.

In the fixer or bleach-fixer, a thiocyanate or a thiosulfate may be used as the fixer.

The thiosulfates include, for example, sodium thiosulfate, ammonium thiosulfate and potassium thiosulfate. The thiocyanates include, for example, ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate.

The fixer and bleach-fixer are also allowed to contain a pH buffer comprising various salts such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bycarbonate, acetic acid, sodium acetate and ammonium hydroxide, independently or in combination. The fixer and bleach-fixer are further allowed to contain an alkali halide or ammonium halide such as potassium bromide, sodium bromide, sodium chloride and ammonium bromide. Besides the above, the compounds such as alkyl amines and polyethylene oxides may also suitably be added thereto. When adding an ammonium salt thereto, the ammonium content thereof may be within the scope of the invention.

The fixer or bleach-fixer is also allowed to contain the compounds represented by formula [FA] given in

Japanese Patent O.P.I. Publication No. 64-295258/1989, p.56 and the exemplified compounds thereof. If this is the case, another effect that sludge productions can remarkably be reduced when a small quantity of light sensitive materials are processed with the fixer or bleach-fixer for a long time. The compounds having formula [FA] appeared in the above-given Japanese Patent Publication can be synthesized in the common processes such as those described in U.S. Patent Nos. 3,335,161 and 3,260,718. The compounds having the formula [FA] may be used independently or in combination. When they are added in an amount within the range of 0.1 g to 200 g per liter of a processing solution to be used, a good effect can be obtained.

A sulfite and a sulfurous acid-releasing compound may also be used in the fixer or bleach-fixer. The typically exemplified compounds include, for example, potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. It is further allowed to include therein the compounds given by formula [B-1] or [B-2] appeared in Japanese Patent O.P.I. Publication No. 64-295258/1989, p.60. The above-given sulfites and sulfurous acid-releasing compounds are to contain sulfurous acid ions in an amount of at least 0.05 mols per liter of the fixer or bleach-fixer used, desirably within the range of 0.08 mols/liter to 0.65 mols/liter, preferably 0.10 mols/liter to 0.50 mols/liter and, particularly 0.12 mols/liter to 0.40 mols/liter.

Silver may be recovered from the fixer or bleach-fixer in any known methods. The effectively applicable silver recovery methods include, for example, an electrolyzing method (such as detailed in French Patent No. 2,299,667), a precipitating method (such as detailed in Japanese Patent O.P.I. Publication No. 52-73037/1977 and German Patent No. 2,331,220), an ion-exchange method (such as detailed in Japanese Patent O.P.I. Publication No. 51-17114/1976 and German Patent No. 2,548,237), and a metal-substitution method (such as detailed in British Patent No. 1,353,805). It is particularly preferable to recover silver in an in-line system by making use of an electrolyzing method or an anionic-exchange resin from a tank solution, because a rapid processing aptitude can further be improved. However, silver may be recovered from a waste over-flow solution and then reused.

From the viewpoint of displaying the objective effects of the invention, a fixer or bleach-fixer relating to the invention can be replenished in an amount of not more than 900 ml per m<sup>2</sup> of a light sensitive material to be processed, preferably in an amount within the range of 20 ml to 750 ml per m<sup>2</sup> of the light sensitive material and particularly 50 ml to 620 ml.

When processing a light sensitive material with a fixer or bleach-fixer in the invention, the processing time is preferably not longer than 150 seconds and, particularly, within the range of 5 to 100 seconds.

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The invention can display an excellent effect in such a rapid process as mentioned above. The expression, 'a processing time when a light sensitive material is processed with a fixer or bleach-fixer', means a period of time from the point of time when starting to dip the leading edge of the light sensitive material into the fixer or bleach-fixer to the point of time when the leading edge thereof comes out of the fixer or bleach-fixer.

In the invention, a stabilizing bath is preferably comprised of a plurality of tanks. The flow of a solution connecting between the tanks is preferably a multistaged counter current flowing in the direction relative to the direction of transporting the light sensitive material. In particular, the stabilizing bath is preferably comprised of 2 to 4 units of tanks.

In the invention, the expression, a stabilizer not substantially containing any formaldehyde', means that containing formaldehyde in an amount of not more than  $1.0 \times 10^{-2}$  mols/liter.

In the invention, a replenishment rate into a stabilizer is preferably not more than 800 ml per  $\text{m}^2$  of a light sensitive material to be processed. An excessive reduction of the replenishment causes the discoloration of a dye and the deposition of a salt on the surface of a light sensitive material after it is dried up. Therefore, the replenishment rate is preferably within the range of not less than 100 ml to not more than 620 ml per  $\text{m}^2$ .

The determination of a further concrete amount replenished may be varied according to the tank constitution of a stabilizing bath. The more the number of tanks is increased, the more the amount replenished can be saved.

The pH value of the stabilizing bath relating to the invention is, desirably, within the range of 5.5 to 11.0 and, from the viewpoint of enhancing the effects of the invention, it is, preferably, within the range of 7 to 10.5 and, particularly, 7.5 to 10. The temperature thereof is, desirably, within the range of 15°C to 70°C and, preferably, 20°C to 55°C. The processing time for the stabilizing bath relating to the invention is, desirably, not longer than 120 seconds, preferably, within the range of 3 seconds to 90 seconds and, most preferably, 6 seconds to 60 seconds.

In the invention, it is preferable to provide a squeegee between a processing bath having a fixing function and a stabilizing bath and between the stabilizing baths so that a satisfactorily squeeze a solution.

Thereby a replenishment rate can be saved and a light sensitive material can also be prevented from staining, more effectively.

In the invention, from the viewpoint of the effects of the objects of the invention, the amount carried-over from a processing bath having a fixing function to a stabilizing bath is, desirably not more than 150 ml/m<sup>2</sup>, preferably, within the range of 10 ml/m<sup>2</sup> to 100 ml/m<sup>2</sup> and, particularly, 20 ml/m<sup>2</sup> to 70 ml/m<sup>2</sup>.

Next, the compounds having the afore-given formula I will be further detailed. In formula I,  $R_1$  represents a univalent organic group including, for example, an alkyl group having 4 to 30 carbon atoms and preferably 6 to 20 carbon atoms, (such as each of the groups of hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl) or an aryl group substituted with an alkyl group having 3 to 20 carbon atoms, of which the substituents include, preferably, an alkyl group having 3 to 12 carbon atoms such as each of the groups of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and doceyl. The aryl groups include, for example, a phenyl group, a tolyl group, a xynyl group, a diphenyl group and a naphthyl group and, among them, a phenyl group and a tolyl group are preferable. The alkyl group may be coupled to an aryl group in any one of an ortho, meta and para positions.  $R_2$  represents a substituted or non-substituted ethylene or propylene group. m is an integer of 4 to 50.  $X_1$  represents a hydrogen atom, -SO<sub>3</sub>M or -PO<sub>3</sub>M<sub>2</sub> in which M represents a hydrogen atom, an alkali metal atom (such as an Na, K or Li atom) or NH<sub>4</sub>  $^{\dagger}$ .

The compounds having formula I will be typically exemplified below.

Exemplified compounds

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$$I - I 0 \qquad C_{12}H_{25} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{23}H$$

$$I - I 1 \qquad C_{8}H_{17} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{12}H$$

$$I - I 2 \qquad C_{8}H_{18} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{10}H$$

$$I - I 3 \qquad C_{8}H_{18} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{10}SO_{3}H$$

$$I - I 4 \qquad C_{13}H_{27}O - (-C_{2}H_{4}O \xrightarrow{})_{10}H$$

$$I - I 5 \qquad C_{16}H_{31}O - (-C_{2}H_{4}O \xrightarrow{})_{10}H$$

$$I - I 6 \qquad C_{8}H_{17} \longrightarrow 0 - (-C_{2}H_{8}O \xrightarrow{})_{10}H$$

$$I - I 7 \qquad C_{13}H_{27} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{20}H$$

$$I - I 8 \qquad C_{10}H_{21} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{20}H$$

$$I - I 8 \qquad C_{10}H_{21} \longrightarrow 0 - (-C_{2}H_{4}O \xrightarrow{})_{20}H$$

The compounds having the afore-given formula I can be used in an amount within the range of 0.1 to 40 g and, preferably, 0.3 to 20 g per liter of the stabilizer of the invention

C10H210-(C2H40-)-H

Next, the compounds having the afore-given formula II will be typically exemplified below.

Water-soluble organic siloxane type compounds

I - 19

$$II - I$$

$$CH_{3}$$

$$CH_{3}$$

$$C_{3}H_{8} \leftarrow OC_{2}H_{+} \rightarrow 0H$$

$$II - 2$$

$$CH_{3}$$

$$CH_{3} \rightarrow 0H$$

$$II - 2$$

$$CH_{3}$$

$$CH_{3} \rightarrow 0H$$

$$\Pi - 3$$
 $CH_3$ 
 $(CH_3)_3Si - 0 - (Si - 0)_2 - Si(CH_3)_3$ 
 $C_3H_3 - C_2H_4 - CC_2H_4$ 

 $\Pi - 4$   $(CH_3)_3Si - O - Si - O - Si (CH_3)_3$   $C_3H_6 - OC_2H_{+})_{10} - Si (CH_3)_3$ 

 $C_3H_8 - (OC_2H_{+})_{12}O - Si(CH_3)_3$ 

$$II - 6$$

$$CH_{3}$$

$$(CH_{3})_{3}Si - 0 - Si - 0 - Si (CH_{3})_{3}$$

$$C_{2}H_{4} - (-0C_{2}H_{+})_{7} + H$$

$$II - 7$$

$$CH_{3}$$

$$(CH_{3})_{3}Si - 0 - (Si - 0)_{2} - Si (CH_{3})_{3}$$

$$II - 8$$

$$(CH3)3Si - 0 - (Si - 0)3 Si (CH3)3$$

$$C3H6 - (-0C2H+)0 Si (CH3)3$$

$$II - 9$$

$$CH_{3}$$

$$(CH_{3})_{3}Si - 0 - (Si - 0)_{2} - Si(CH_{3})_{3}$$

$$C_{3}H_{6} - (OC_{2}H_{4})_{10} - Si(C_{2}H_{6})_{3}$$

[1 - 1 2]CH<sub>3</sub> CH<sub>3</sub> | CH<sub>3</sub> | CH<sub>3</sub> | CH<sub>3</sub> - Si - O - Si - (CH<sub>2</sub>)<sub>3</sub> (OCH<sub>2</sub>CH)<sub>2</sub> OH | CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> 

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$$\Pi - 1 \ 4$$

$$CH_{3} \quad CH_{3} \quad CH_{3} \quad CH_{3} \quad CH_{3}$$

$$CH_{3} - Si - 0 - (Si - 0) \xrightarrow{a} (Si - 0) \xrightarrow{b} Si - CH_{3}$$

$$CH_{3} \quad CH_{3} \quad CH_{3} \quad (CH_{2})_{3} \quad CH_{3}$$

$$a + b = 41$$

$$(CH_{2}CH_{2}O \xrightarrow{1} H)$$

$$\begin{array}{c} \text{II} - 18 \\ \text{CH}_{3} \\ \text{(CH}_{3})_{3} \text{SiO} - (-\text{SiO})_{2} - \text{Si(CH}_{3})_{3} \\ \text{I} \\ \text{C}_{3} \text{H}_{6} - (-\text{OC}_{2} \text{H}_{4} - )_{6} - \text{OCH}_{3} \end{array}$$

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When the water-soluble organic siloxane type compound having a polyoxyalkylene group is added in an amount within the range of 0.01 to 20 g per liter of a stabilizer used, the excellent effects including, particularly, any precipitation and scratch prevention effects can be displayed.

When adding the above-mentioned compound in an amount of less than 0.01 g/liter, the effects of the invention cannot be displayed and when adding it in an amount exceeding 20 g/liter, a large amount of the organic siloxane type compounds adhere to the surface of a light sensitive material, so that stains are resultingly increased.

The water-soluble organic siloxane type compounds of the invention means the common water-soluble organic siloxane type compounds such as those described in, for example, Japanese Patent O.P.I. Publication Nos. 47-18333/1972 and 49-62128/1974, Japanese Patent Examined Publication Nos. 55-

51172/1980 and 51-37538/1976, and U.S. Patent No. 3,545,970.

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The above-mentioned water-soluble organic siloxane type compounds can usually be available from Union Carbide Co., Shinetsu Chemical Industry Co. and so forth.

In the invention, it is preferred that a stabilizer contains a chelating agent having a chelate-stability constant of not less than 8 to iron ions. The term, 'a chelate-stabilization constant', means herein a generally known constant described in 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

The chelating agents having a chelate-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-mentioned iron ions mean ferric ions (Fe<sup>3+</sup>).

The typical examples of the chelating agents each having a chelate-stability constant of not less than 8 to ferric ions include the following compounds. It is, however, to be understood that they shall not be limited thereto. They include, for example, ethylenediamine diorthohydroxyphenyl acetic acid, diaminopropane tetraacetic acid, nitrilotriacetic acid, hydroxyethylenediamine triacetic acid, dihydroxyethyl glycine, ethylenediamine diacetic acid, ethylenediamine dipropionic acid, iminodiacetic acid, diethylenetriamine pentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanol tetraacetic acid, transcyclohexanediamine tetraacetic acid, glycoletherdiamine tetraacetic acid, ethylenediaminetetrakismethylene phosphonic acid, nitrilotrimethylene phosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-2-phosphonobutane-1,2,4-tricarboxylic diphosphonoethane-2-carboxylic acid, 1-hydroxy-1phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-diphosphonic acid, sodium pyrophosphoric acid, sodium tetrapolyphosphoric acid, and sodium hexametaphosphoric acid. Among the above-given compounds, diethylenetriamine pentaacetic acid, dinitrilotriacetic acid, nitrilotrimethylene phosphonic acid and 1,hydroxyethylidene-1,1-diphosphonic acid are preferable and, inter alia, 1-hydroxyethylidene-1,1diphosphonic acid is most preferable.

For showing the excellent effects, the above-mentioned chelating agent is to be used in an amount within the range of 0.01 to 50 g per liter of a stabilizer and, preferably, 0.05 to 20 g.

It is preferred to contain a metal salt in a stabilizer used together with the above-mentioned chelating agent in combination. Such a metal salt include, for example, the metal salts of Ba, Ca, Ce, Co, In, La, Mn, Ni, Bi, Pb, Sn, Zn, Ti, Zr, Mg, Al or Sr, which may be supplied as an inorganic salt of a halide, a hydroxide, a sulfate, a carbonate, a phosphate or a acetate or a water-soluble chelating agent. They may be added in an amount within the range of  $1\times10^{-4}$  to  $1\times10^{-1}$  mols per liter of a stabilizer used and, preferably,  $1\times10^{-4}$  to  $2\times10^{-2}$  mols

The stabilizers are each allowed to contain an organic acids (such as citric acid, acetic acid, succinic acid, oxalic acid and benzoic acid) and a pH controller (such as a phosphate, a borate, hydrochloric acid and a sulfate). The above-given compounds may be added in any combination, provided that the pH of the stabilizer can be maintained and the preservation stability of a color photographic image and precipitate-production cannot be spoiled.

In the invention, any antimoulds can be used independently or in combination, provided, the effects of the invention cannot be spoiled.

In the process of the invention, silver may also be recovered from a stabilizer used therein. For this purpose, for example, an electrolytic method (refer to French Patent No. 2,299,667), a precipitation method (refer to Japanese Patent O.P.I. Publication No. 52-73037/1977 and German Patent No. 2,331,220), an ion-exchange method (refer to Japanese Patent O.P.I. Publication No. 51-17114/1976 and German Patent No. 2,548,237) and a metal substitution method (refer to British Patent No. 1,353,805) may effectively be utilized. In the above-mentioned silver recovery, it is particularly preferable that silver is to be recovered in an in-line system from a tank solution in an electrolytic method or by making use of an anion-exchange resin, because the rapid processing aptitude can further be improved. Besides the above, silver may also be recovered from the waste over-flow so as to be reused.

Further, a stabilizer may be subjected to an ion-exchange treatment, an electrodialytic treatment (refer to Japanese Patent O.P.I. Publication No. 61-28949/1986) or a reverse osmotic treatment (refer to Japanese Patent O.P.I. Publication Nos. 60-240153/1985 and 62-254151/1987). In addition to the above, it is preferred to use water which is deionized in advance and is then used in a stabilizer. The reasons of the above-mentioned preference are that the antimoulding property and stability of a stabilizer and the image preservability can be improved. Any one of the means for deionizing treatments may be used, provided that Ca or Mg ions of washing water can be made not higher than 5 ppm after completing the treatment. For example, it is preferred to use the treatments carried out by making use of an ion-exchange resin or a

reverse dialytic film, independently or in combination. The above-mentioned ion-exchange resins and reverse dialytic films are detailed in Journal of Technical Disclosure Nos. 87-1984 and 89-20511.

The salt concentration of a stabilizer is preferably not more than 1000 ppm and particularly not more than 800 ppm.

After completing a stabilizing treatment, no washing step is not required at all. However, it is allowed, if required, to carry out a rinsing or surface cleaning treatment with a small amount of washing water in a substantially short time.

The color developing agents applicable to a color developing step include, for example, an aminophenol type compound and a p-phenylenediamine type compound. In the invention, a p-phenylenediamine type compound having a water-soluble group may preferably be used.

At least one of the above-mentioned water-soluble groups is present on the amino group or benzene nucleus of a p-phenylenediamine type compound. The typical water-soluble groups include, preferably, the following groups;

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    -(CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>OH,
    -(CH<sub>2</sub>)<sub>m</sub>-NHSO<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>3</sub>,
    -(CH<sub>2</sub>)<sub>m</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>3</sub>,
    -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>C<sub>m</sub>H<sub>2m+1</sub>(in which m and n are each an integer of not less than 0),
    -COOH group, and -SO<sub>3</sub>H group.
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The typically exemplified compounds used as the color developing agent preferably applicable to the invention will be given below.

Exemplified color developing agents

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(A-I)C2H5 C2H4NHSO2CH3 5 · 3/2 H2SO4 · H2O CHa NH 2 10

> (A - 2)C2Hs C2H4OH · H2SO4 H NH 2

(A-3)  $C_2H_5$ 25 C2H+OH · H2SO4 30 CH 3  $\rm N\,H_{\,2}$ 

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35 (A - 4)C2H6 C2H4OCH3 40 CHa  $\rm N\,H_{\,2}$ 

C<sub>2</sub>H<sub>5</sub> C<sub>3</sub>H<sub>0</sub>SO<sub>3</sub>H

C<sub>2</sub>H<sub>5</sub> C<sub>3</sub>H<sub>0</sub>SO<sub>3</sub>H

H<sub>2</sub>SO<sub>4</sub>

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(A-6)  $C_{2}H_{\bullet}OH$   $\cdot \frac{1}{2}H_{2}SO_{\bullet}$   $NH_{2}$ 

(A - 7)
HOH, C2 C2H, OH
· H2SO4

NH 2

NH 2

40 (A - 8)

C<sub>+</sub>H<sub>0</sub> C<sub>+</sub>H<sub>0</sub>SO<sub>3</sub>H

N

·  $\frac{1}{2}$  H<sub>2</sub>SO<sub>+</sub>

$$C_{4}H_{6}$$
 $C_{3}H_{6}SO_{3}H$ 

$$\frac{1}{2}H_{2}SO_{4}$$
NH<sub>2</sub>

$$C_2H_5 \qquad (CH_2CH_2O)_2CH_3$$

$$C_2H_5 \qquad (CH_2CH_2O)_2CH_3$$

$$CH_3 \qquad CH_3 \qquad SO_3H$$

$$CH_3 \qquad NH_2$$

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$$C_2H_5$$
  $(CH_2CH_2O)_3CH_3$ 
 $C_2H_5$   $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

C<sub>2</sub>H<sub>5</sub> 
$$(CH2CH2O)2C2H5$$

C<sub>2</sub>H<sub>5</sub>  $(CH2CH2O)2C2H5

C3H5  $(CH3CH2O)3C2H5$ 

C<sub>4</sub>H<sub>5</sub>  $(CH3CH2O)3C2H5

C4H5  $(CH3CH2O)3C3H5$$$ 

$$C_2H_5$$
  $C_2H_4$  NHSO<sub>2</sub>CH<sub>3</sub>
 $C_2H_5$   $C_2H_5$   $C_2H_5$ 
 $C_2H_5$   $C_2H_5$ 
 $C_2H_5$   $C_2H_5$ 

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(A - 16) 
$$C_2H_5$$
  $C_2H_4OH$ 

N

 $C_2H_5$   $C_2H_5$ 
 $C_2H_5$ 
 $C_2H_5$ 
 $C_2H_5$ 

Among the above-exemplified color developing agents, the compounds preferably applicable to the invention include, for example, the exemplified compounds A-1, A-2, A-3, A-4, A-6, A-7 and A-15.

The color developing agents may be added preferably in an amount not less than  $0.5x10^{-2}$  mols per liter of a color developer used, preferably, within the range of  $1.0x10^{-2}$  to  $1.0x10^{-1}$  mols and, most preferably,  $1.5x10^{-2}$  to  $7.0x10^{-2}$  mols.

The above-mentioned color developing agents are usually used in the form of the salts such as a chloride, a sulfate and a p-toluenesulfinate.

The color developers applicable to a color developing step are allowed to contain an alkalizing agent commonly used in developers, such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborate and borax. Further, they are also allowed to contain a variety of additives including, for example, bezyl alcohol, an alkali halide such as potassium bromide and potassium chloride; a development controller such as citradinic acid; and a preservative such as hydroxylamine, a hydroxylamine derivatives (e.g., diethyl hydroxylamine), a hydradine derivative (e.g., hydradinodiacetic acid) and a sulfite.

In addition to the above, they are further allowed to suitably contain a variety of defoaming agents, surface active agents and organic solvents such as methanol, dimethyl formamide and dimethyl sulfoxide.

The pH value of such a color developer as mentioned above is usually not lower than 7 and, preferably, within the range of about 9 to 13.

The color developers are each allowed, if required, to contain an antioxidant including, for example, tetronic acid, tetronimide, 2-anilinoethanol, dihydroxy acetone, aromatic secondary alcohol, hydroxamic acid, pentose or hexose, and pyrogallol-1,3-dimethyl ether.

In the above-mentioned color developers, a variety of chelating agents can be used in combination so as to serve as a metal ion sequestering agent. The above-mentioned chelating agents include, for example, aminopolycarboxylic acids such as ethylenediamine tetraacetic acid and diethylenetriamine pentaacetic acid; organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid; aminopolyphosphonic acids such as aminotri (methylene phosphonic acid) or ethylenediamine tetraphosphoric acid; oxycarboxylic acids such as citric acid and gluconic acid; phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid; and polyphosphoric acids such as tripolyphosphoric acid and hexametaphosphoric acid.

When a color developer is used for the continuous processing of color negative films, the amount of the developer to be replenished is, desirably, not more than 1.5 liters per 1.0 m<sup>2</sup> of the film subject to the processing, more desirably, within the range of 250 ml to 900 ml and, preferably, 300 ml to 700 ml.

In the invention, the bleaching agents each applicable to a bleaching solution or a bleach-fixing solution include, for example, the ferric complex salts of the organic acids each represented by the following formula A or B and the ferric complex salts of the exemplified compounds each represented by the following formulas A'-1 through A'-16.

#### Formula A

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$$A_1-CH_2$$
  $N-X-N$   $CH_2-A_3$   $CH_2-A_4$ 

wherein  $A_1$  through  $A_4$  represent each -CH<sub>2</sub>OH, -COOM or -PO<sub>3</sub>M<sub>1</sub>M<sub>2</sub>, provided that they may be the same with or the different from each other, in which M, M<sub>1</sub> and M<sub>2</sub> represent each a hydrogen atom, an alkali metal or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms.

#### Formula B

$$A_1-CH_2$$
  
 $A_2-CH_2$   
 $N+B_1-O+_n-B_2-N$   
 $CH_2-A_3$   
 $CH_2-A_4$ 

wherein  $A_1$  through  $A_4$  are each synonymous with those defined in the above-given formula A; n is an integer of 1 to 8; and  $B_1$  and  $B_2$  represent each a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms, provided that they are the same with or the different from each other.

The compounds represented by formula A will now be detailed below.

 $A_1$  through  $A_4$  represent each -CH<sub>2</sub>OH, -COOM or -PO<sub>3</sub>M<sub>1</sub>M<sub>2</sub>, provided that they may be the same with or the different from each other, in which M, M<sub>1</sub> and M<sub>2</sub> represent each a hydrogen atom, an alkali metal such as sodium or potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms, such as a propylene, butylene or pentamethylene group. The substituents thereof include, for example, a hydroxyl group and an alkyl group having 1 to 3 carbon atoms.

The preferable examples of the compounds having the foregoing formula A will be given below.

(A - 1)5  $\begin{array}{c}
\text{HOOC-CH}_2 \\
\text{HOOC-CH}_2
\end{array}$   $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{-N}$   $\begin{array}{c}
\text{CH}_2\text{COOH} \\
\text{CH}_2\text{COOH}
\end{array}$ 10 (A - 2) $\begin{array}{c|c} \text{HOOC-CH}_2 & \text{OH} \\ \text{HOOC-CH}_2 & \text{N-CH}_2 \text{CHCH}_2 \text{-N} \end{array} \qquad \begin{array}{c} \text{CH}_2 \text{COOH} \\ \text{CH}_2 \text{COOH} \end{array}$ 15 (A - 3)20 HOOC-CH<sub>2</sub> N -CH-CH<sub>2</sub>-N  $CH_2$ COOH

HOOC-CH<sub>2</sub> N -CH-CH<sub>2</sub>-N 25 (A-4) $\begin{array}{l} \text{HOOC-CH}_2 \\ \text{HOOC-CH}_2 \end{array} \\ \text{N-CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{COOH} \end{array}$ 30 (A - 5)35  $\begin{array}{c} \text{CH }_{3} \\ \text{HOOC-CH }_{2} \\ \end{array} \\ \begin{array}{c} \text{N-CH }_{2}\text{CHCH }_{2}\text{-N} \\ \end{array} \\ \begin{array}{c} \text{CH }_{2}\text{COOH} \\ \\ \text{CH }_{2}\text{COOH} \end{array}$ 40 (A - 6) $\begin{array}{c|c} \text{HOOC-CH}_2 \\ \text{HOOC-CH}_2 \end{array} \\ \text{N-CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{COOH} \end{array}$ 45

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$$(A - 7)$$

$$H_{2}O_{3}P-CH_{2}$$

$$H_{2}O_{3}P-CH_{2}$$

$$H_{2}O_{3}P-CH_{2}$$

$$A - 8)$$

$$H_{2}O_{3}P-CH_{2}$$

$$H_{3}O-CH_{2}O$$

As the ferric complex salts of the compounds A-1 through A-12, the sodium, patassium or ammonium salts of the above-given ferric complex salts may freely be used. From the viewpoints of the effects of the objects of the invention and the solubility of these complex salts, the ammonium salts of the ferric complex salts can preferably be used.

Among the examples of these compounds, those preferably applicable to the invention include, for example, the compounds A-1, A-3, A-5 and A-9 and, particularly, A-1.

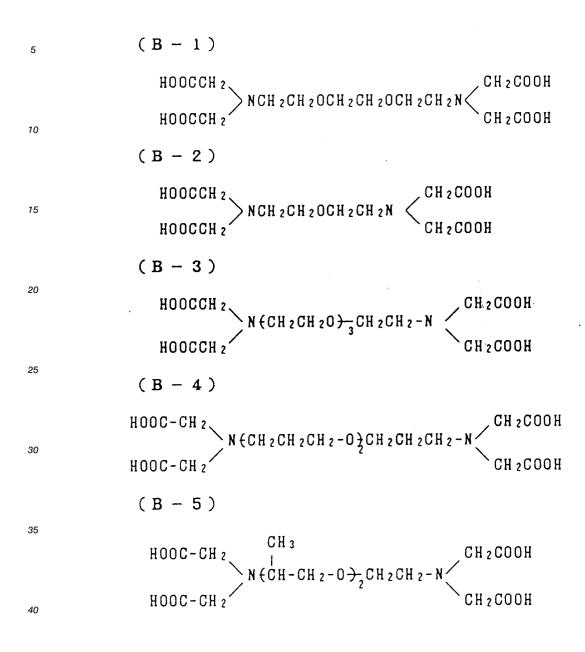
Now, the compounds represented by formula B will be detailed below.

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 $A_1$  through  $A_4$  are each synonymous with those afore-given; n is an integer of 1 to 8; and  $B_1$  and  $B_2$  represent each a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms, such as an ethylene, propylene, butylene or pentamethylene group, provided that they are the same with or the different from each other. The substituents thereof include, for example, a hydroxyl group and a lower alkyl group having 1 to 3 carbon atoms, such as a methyl, ethyl or propyl group.

The preferable examples of the compounds represented by the foregoing formula B will be given below.



$$(B - 6)$$

(B - 7)

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As the ferric complex salts of the above-given compounds B-1 through B-7, the sodium, potassium or ammonium salts of the ferric complex salts of the compounds may freely be used for.

Among the above-given examples of the compounds, those applicable to the invention include, preferably, B-1, B-2 and B-7 and, particularly, B-1.

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

In a bleaching solution or a bleach-fixing solution, the ferric complex salts such as those of ammonium, sodium, potassium or triethanolamine of the following compounds may be exemplified below so as to serve as the preferable bleaching agents other than the compounds having formula A or B. It is, however, understood that the bleaching agents shall not be limited to those above-given.

A'-1: Ethylenediamine tetraacetic acid,

A'-2: Trans-1,2-cyclohexanediamine tetraacetic acid,

A'-3: Dihydroxyethyl glycinic acid,

A'-4: Ethylenediaminetetrakismethylene phosphonic acid,

35 A'-5: Nitrilotrismethylene phosphonic acid,

A'-6: Diethylenetriaminepentakismethylene phosphonic acid,

A'-7: Diethylenetriamine pentaacetic acid,

A'-8: Ethylenediaminediorthohydroxyphenyl acetic acid,

A'-9: Hydroxyethylethylenediamine triacetic acid,

40 A'-10: Ethylenediamine dipropionic acid,

A'-11: Ethylenediamine diacetic acid,

A'-12: Hydroxyethyl iminodiacetic acid,

A'-13: Nitrilotriacetic acid,

A'-14: Nitrilotripropionic acid,

A'-15: Triethylenetetramine hexaacetic acid,

A'-16: Ethylenediamine tetrapropionic acid

In a bleaching solution, a single kind or plural kinds of the ferric complex salts of the compounds A'-1 through A'-16 can be used independently or in combination with the ferric complex salts of the compounds represented by formula A or B.

When making combination use of plural kinds of the ferric complex salts of an organic acid, the ferric complex salts of the compounds represented by formula A or B occupy, desirably not less than 70% of the whole ferric complex salts in terms of mols, more desirably not less than 80%, preferably not less than 90% and, most preferably not less than 95%, from the viewpoint of displaying the effects of the invention more excellently.

The iron (III) complex salts of an organic acid may be used in the form of a complex salt or may produce an iron (III) ion complex salt in a solution by making use of aminopolycarboxylic acids such as a ferric ammonium sulfate, ferric chloride, ferric acetate, ferric ammonium and ferric phosphate, or the salts thereof. When the iron (III) complex salts of an organic acid are used in the form of a complex salt, it is

allowed to use a single kind thereof or two or more kinds thereof in combination. Also, a single kind or two or more kinds of aminopolycarboxylic acids may also be used. Further, in either cases mentioned above, the aminopolycarboxylic acids may be used in an amount too much to produce the iron (III) ion complex salts.

A bleach-fixing solution or a bleaching solution containing the above-mentioned iron (III) ion complexes is also allowed to contain metal ion complexes such as those of cibalt, copper, nickel and zinc, as well as those of iron.

The effect of rapid processability can be displayed when a bleaching solution, a bleach-fixing solution or a fixing solution contains at least one kind of the imidazole and the derivatives thereof described in Japanese Patent O.P.I. Publication No. 64-295258/1989 or the compounds represented by the formulas I through IX and the exemplified compounds thereof each described in the same Patent O.P.I. Publication.

Besides the above-described accelerators, it is also allowed to use similarly the exemplified compounds described in Japanese Patent O.P.I. Publication No. 62-123459/1987, pp.51 to 115, the exemplified compounds described in Japanese Patent O.P.I. Publication No. 63-17445/1988, pp.22 to 25, and the compounds described in Japanese Patent O.P.I. Publication Nos. 53-95630/1978 and 53-28426/1978.

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

When adding the accelerator, it may be added and dissolved as it is. It is, however, usual to add it after dissolving it in water, alkali or an organic acid in advance. Besides the above, it may be added after dissolving it in an organic solvent such as methanol, ethanol or acetone, if required.

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

The bleaching solution is to have a pH of, desirably, not higher than 6.0 and, preferably, within the range of not lower than 1.0 to not higher than 5.5. The bleach-fixing solution is to have a pH within the range of, desirably, 5.0 to 9.0 and, preferably, 6.0 to 8.5.

The pH values of the bleaching solution or the bleach-fixing solution are the same with the pH values of a processing tank solution when processing a silver halide light sensitive material. The pH values thereof can clearly be distinguished from the pH values of the so-called replenishers.

The bleaching solution or the bleach-fixing solution are commonly used after adding a halide such as ammonium bromide, potassium bromide or sodium bromide thereinto. The bleaching solution or the bleach-fixing solution are also allowed to contain a variety of fluorescent brightening agents, defoamers or surface active agents.

The bleaching solution or the bleach-fixing solution may be replenished in an amount of, desirably, not more than 500 ml per  $\text{m}^2$  of a silver halide color photographic light sensitive material to be processed, preferably, within the range of 20 ml to 400 ml and, most preferably, 40 ml to 350 ml. The smaller the amount replenished is, the more the effects of the invention can become remakable.

In the invention, the air or oxygen may be blown into a processing bath or a processing replenisher reservoir tank, or a suitable oxidizer such as hydrogen peroxide, a bromate and a persulfate may be added thereinto, if required for enhancing the activity of a bleaching solution or a bleach-fixing solution.

In the processing method of the invention, it is preferred for the embodiments of the invention to give a forcible agitation to a stabilizer, a bleach-fixing solution or a fixing solution, because of not only the excellent displays of the objective effects of the invention, but also the viewpoint of the rapid processing aptitude. The expression, 'a forcible agitation', herein means that a forcible agitation is given by adding an agitating means, but not that a solution is diffusively stirred in an ordinary manner. As for the forcibly agitating means, the means described in Japanese Patent O.P.I. Publication Nos. 64-222259/1989 and 1-206343/1989 may be utilized.

In the invention, when a cross-over time required from a color developing tank to a bleach-fixing tank is preferably within 10 seconds and particularly within 7 seconds, the other effect than the effects of the invention can be displayed to a bleaching fog.

In the silver halide color photographic light sensitive materials of the invention, the silver halide emulsions described in Research Disclosure No. 308119 (hereinafter referred simply to as RD 308119) can be used for the silver halide emulsions thereof. The following table indicates where the descriptions are.

	[Item]	[Page No. in RD 308119]
	Iodide compositions	p.993, I-A
5	Preparation procedures	p.993, I-A & p.994, E
	Crystal habits: Regular crystal	p.993, I-A
10	Twinned crystal	p.993, I-A
	Epitaxial crystal	p.993, I-A
15	Halogen compositions: In uniform Not in uniform	p.993, I-B orm p.993, I-B
	Halogen conversion	p.994, I-C
	Halogen substitution	p.994, I-C
20	Metal dopants	p.994, I-D
	Monodispersion	p.995, I-F
25	Solvent addition	p.995, I-F
	Latent image forming position: On surface Inside	p.995, I-G p.995, I-G
30 35	Applicable light sensitive material Negative type Positive type (including internal fogged grains)	al: p.995, I-H p.995, I-H
	Mixed emulsion used	p.995, I-J
	Desalinization	p.995, II-A

In the invention, the silver halide emulsions each physically and chemically ripened and spectrally sensitized are to be used. The additives used in preparing the emulsions are described in Research Disclosure Nos. 17643, 18716 and 308119 (hereinafter referred simply to as RD 17643, RD 18716 and RD 308119).

The following table indicates where the descriptions are.

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	[Item]	[Page No. in RD 308119;	RD 17643;	RD 18716]
	Chemical sensitizer	p.996, III-A	p.23	p.648
	Spectral sensitizer	p.996, IV-A-A,B,C, D,E,H,I,J	pp.23-24	pp. <b>648-649</b>
	Super color sensitizer	p.996, IV-A-E,J	pp.23-24	pp.648-649
	Antifoggant	p.998, VI	pp.24-25	p.649
	Stabilizer	p.998, VI	pp.24-25	p.649

The known photographic additives each applicable to the invention are also described in the abovegiven Research Disclosures. The following table indicates where they are described.

	[Item] [Pa	ge No. in RD 308119;	RD 17643;	RD 18716]
5	Color stain inhibitor	p.1002, VII-I	p.25	p.650
	Dye-image stabilizer	p.1001, VII-J	p.25	
10	Brightening agent	p.998, V	p.24	
	UV absorbent	p.1003, VIII-C XIII-C	pp.25-26	
15	Light absorbent	p.1003, VIII	pp.25-26	
20	Light scattering agent	p.1003, VIII		
	Filtering dye	p.1003, VIII	pp.25-26	
25	Binder	p.1003, IX	p.26	p.651
	Antistatic agent	p.1006, XIII	p.27	p.650
30	Layer hardener	p.1004, X	p.26	p.651
	Plasticizer	p.1006, XII	p.27	p.650
	Lubricant	p.1006, XII	p.27	p.650
35	Activator Coating aid	p.1005, XI	pp. <b>2</b> 6-27	p.650
	Matting agent	p.1007, X VI		
40	Developing agent (contained in ligh sensitive materia	p.1011, XX-B t ls)		

Next, the 2-equivalent couplers each applicable to the invention will now be detailed below. As for the 2-equivalent couplers, the couplers represented by the following formula 2eq-1 may preferably be used.

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# Formula 2eq-1

Cp \* | | | X

wherein Cp represents a coupler residual group; \* represents the coupling position of a coupler; and X represents a group released when a dye is produced upon coupling to the oxidized products of an aromatic

primary amine color developing agent.

In the coupler residual groups represented by Cp, the typical yellow coupler residual groups are described in, for example, U.S. Patent Nos. 2,298,443, 2,407,210, 2,875,057, 3,048,194, 3,265,506 and 3,447,928; and (Farbkupplerine Literaturubersiecht Agfa Mitteilung (Band II)), pp.126-156, 1961. Among them, acylacetanilides such as benzoyl acetanilide and pivaloyl acetanilide are preferred.

The typical magenta coupler residual groups are described in, for example, U.S. Patent Nos. 2,369,486, 2,343,703, 2,311,082, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,519,429, 3,725,067 and 4,540,654; Japanese Patent O.P.I. Publication No. 59-162548/1984; and the above-given Agfa Mitteilung (Band II), pp.126-156, 1961. Among them, pyrazolones or pyrazoloazoles such as pyrazoloimidazole and pyrazolotriazole are preferred.

The typical cyan coupler residual groups are described in U.S. Patent Nos. 2,367,531, 2,423,730, 2,474,293, 2,772,162, 2,895,826, 3,002,836, 3,034,892 and 3,041,236; and the above-given Agfa Mitteilung (Band II), pp.156-175, 1961. Among them, phenols or naphthols are preferred.

The releasable groups represented by X include, for example, a halogen atom, an alkoxy group, an aryloxy group, a heterocyclic-oxy group, an acyloxy group, an alkylthio group, an arylthio group, a heterocyclic-thio group, a

-N X<sub>1</sub>

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in which  $X_1$  represents a group consisting of the atoms necessary to form a 5- or 6-membered ring together with at least one of the atoms selected from the group consisting of the nitrogen atom contained in the formula, carbon atom, oxygen atom, nitrogen atom and sulfur atom, a monovalent group such as an acylamino group and a sulfonamido group, and a divalent group such as an alkylene group; provided, a dimer is formed by X in the case of a divalent group.

The typical examples thereof will be given below.

Halogen atoms: chlorine atom, bromine atom and fluorine atom;

30 Alkoxy groups:

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$$-OCH_2 - OCH_2CH_2SO_2CH_3$$
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Aryloxy groups:

$$-0 \longrightarrow -0 \longrightarrow COOH, -0 \longrightarrow NO_{2},$$

$$-0 \longrightarrow SO_{2} \longrightarrow OCH_{2} \longrightarrow$$

$$-0 \longrightarrow SO_{2} \longrightarrow OH,$$

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$$-0 \longrightarrow NHCOCH_{2}CH_{2}COOH, -0 \longrightarrow OCH_{3},$$

 $-0 \longrightarrow C_8 H_{17}(t), \qquad -0 \longrightarrow NO_2,$   $CH_2 NHCOCH_3$ 

30 Heterocyclic-oxy groups:

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Acyloxy groups:

Alkylthio groups:

$$-SCH_3$$
 ,  $-SC_2H_5$  ,  $-SC_8H_{17}$  ,  $-SC_{12}H_{25}$  ,

$$-SCH_{2} \longrightarrow -SCH_{2}CH_{2}N(C_{2}H_{5})_{2}.$$

$$- SCH_{2}COOC_{2}H_{5} , - SCH_{2}CH_{2}OC_{2}H_{5} ,$$

Arylthio groups:

$$-S \longrightarrow -S \longrightarrow -S \longrightarrow F \longrightarrow F$$

Hetrocyclic-thio groups:

 $-\dot{N}$   $\dot{X}_1$ :

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A pyrazolyl group, an imidazolyl group, a triazolyl group, a tetrazolyl group,

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55 Acylamino groups:

- NHCOCF<sub>3</sub>

- NHCO 
$$\stackrel{\mathsf{F}}{}$$

- NHCO  $\stackrel{\mathsf{F}}{}$ 

- NHCOCH<sub>2</sub>O  $\stackrel{\mathsf{F}}{}$ 

- NHCOCH<sub>2</sub>O  $\stackrel{\mathsf{F}}{}$ 

OH

Sulfonamido groups:

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 $- \, \text{NHSO}_{\,2} \, \text{CH}_{\,3} \quad , \qquad - \, \text{NHSO}_{\,2} \, \underbrace{- \, \text{NHSO}_{\,2} \, \cdots \, \text{CH}_{\,3}}_{\text{CC}_{\,4} \, \text{H}_{\,9}}$ 

Alkylene groups:

As the 2-equivalent yellow couplers, those represented by the following formulas 2eq-2 and 2eq-3 are preferably used.

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Formula 2eq-2

$$(CH_3)_3CCOCHCONH$$
 $(R_1)_k$ 

Formula 2eq-3

$$(R_2)_{a}$$
 COCHCONH  $(R_1)_{a}$ 

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In the above-given formulas,  $R_1$  and  $R_2$  represent each a hydrogen atom or a substituent; k and  $\ell$  are each an integer of 1 to 5, provided, when k and  $\ell$  are each not less than 2,  $R_1$  and  $R_2$  may be the same with or different from each other; and X is synonymous with X denoted in formula 2eq-1.

The substituents represented by R<sub>1</sub> and R<sub>2</sub> include, for example, a halogen atom or each of an alkyl group, a cycloalkyl group, an aryl group and a heterocyclic group capable of coupling directly or through a divalent atom or group.

The above-mentioned divalent atoms or groups include, for example, an oxygen atom, a nitrogen atom, a sulfur atom and the groups of carbonyl amino, aminocarbonyl, sulfonylamino, aminosulfonyl, amino, carbonyl, carbonyloxy, oxycarbonyl, ureylene, thioureylene, thiocarbonylamino, sulfonyl and sulfonyloxy.

As the examples of the substituents represented by  $R_1$  and  $R_2$ , the above-given alkyl, cycloalkyl, aryl and heterocyclic groups include those each having a substituent. Such a substituents include, for example, a halogen atom and the groups of nitro, cyano, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, carboxy, sulfo, sulfamoyl, carbamoyl, acylamino, ureido, urethane, sulfonamido, heterocyclic, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, anilino, hydroxy, imido and acyl.

In the 2-equivalent yellow couplers, X include those exemplified in formula 2eq-1 and, among them, an aryloxy group and

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(in which  $X_1$  is synonymous with the foregoing  $X_1$ ) are preferable.

In formula 2eq-2, there includes the case where a polymer not less than dimer is formed by  $R_1$  or X and, in formula 2eq-3, there includes the case where a polymer not less than dimer is formed by  $R_1$ ,  $R_2$  or X.

The preferable 2-equivalent magenta couplers include, for example, those represented by the following formulas 2eq-4, 2eq-5, 2eq-6 and 2eq-7.

Formula 2eq-4

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Formula 2eq-5

$$R_3$$
-NH  $X$ 
 $N$ 
 $O$ 
 $(R_2)_{Q}$ 

Formula 2eq-6

Formula 2eq-7

$$\begin{array}{c|c} X & H \\ N & N \\ N & N \end{array}$$

In the above-given formulas 2eq-4 through 2eq-7,  $R_3$  represents a substituent; and  $R_1$ ,  $R_2$ , X and  $\ell$  are each synonymous with  $R_1$ ,  $R_2$ , X and  $\ell$  denoted in 2eq-2 and 2eq-3, respectively, provided that, when  $\ell$  is not less than 2,  $R_2$ s may be the same with or different from each other.

The examples of  $R_1$  and  $R_2$  include those exemplified for  $R_1$  and  $R_2$  denoted in formula 2eq-3.  $R_3$  include, for example, each of the groups of alkyl, cycloalkyl, aryl and heterocyclic, provided, they include those each having a substituent. Such substituents include, for example, those exemplified for the substituents which are each substituted to the groups given as the examples for  $R_1$  and  $R_2$  denoted in formula 2eq-2.

In the 2-equivalent magenta couplers, the examples of X include those exemplified in formula 2eq-1 and, among them, a halogen atom, an alkylthio group, an arylthio group, an aryloxy group, an acyloxy group,

$$-$$
N $x_1$ 

(in which  $X_1$  is synonymous with the foregoing  $X_1$ ), and an alkylene group are each preferable.

In formulas 2eq-4 and 2eq-5, there include the case where a polymer not less than a dimer is formed by  $R_2$ ,  $R_3$  or X and, in formulas 2eq-6 and 2eq-7, there include the case where a polymer not less than a dimer is formed by  $R_1$ ,  $R_2$  or X

The preferable 2-equivalent cyan couplers include those represented by the following formulas 2eq-8, 2eq-9 and 2eq-10.

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# Formula 2eq-8

OH NHCOR<sub>3</sub>

# Formula 2eq-9

 $(R_2)_n$   $R_4$ CONH X

# Formula 2eq-10

 $(R_2)_p$  CONHR

In the above-given formulas,  $R_2$  and  $R_3$  are each synonymous with those denoted in 2eq-4;  $R_4$  represents a substituent; m is an integer of 1 to 3; n is an integer of 1 or 2; and p is an integer of 1 to 5, provided, when m, n and p are each not less than 2,  $R_2$ s may be the same with or different from each other.

 $R_2$  and  $R_3$  include, for example, those exemplified in formula 2eq-4, and  $R_4$  includes, for example those exemplified for  $R_3$  denoted in formula 2eq-4.

In the 2-equivalent cyan couplers, the examples of X include, those exemplified in formula 2eq-1 and, among them, a halogen atom, an alkoxy group, an aryloxy group and a sulfonamido group are particularly preferable.

In formulas 2eq-8 and 2eq-10, there include the case where a polymer not less than a dimer is formed by  $R_2$ ,  $R_3$  or X and, in formula 2eq-9, there includes the case where a polymer not less than a dimer is formed by  $R_2$ ,  $R_3$ ,  $R_4$  or X.

The typical examples of the 2-equivalent couplers each applicable to the invention will now be given below. It is, however, to be understood that the 2-equivalent couplers of the invention shall not be limited thereto.

### 2-equivalent yellow couplers

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Y - 1

$$CH_3 - C - COCHCONH - C_5H_{11}(t)$$

Y - 3

$$Y - 4$$

$$CH_3 - C - COCHCONH - C_5H_{11}(t)$$

Y - 5

$$Y - 6$$

$$CH_{3}O \longrightarrow COCHCONH \longrightarrow COOC_{12}H_{25}$$

$$CH_{2} \longrightarrow CH_{2} \longrightarrow COCHCONH \longrightarrow COOC_{12}H_{25}$$

$$CH_3 - C - COCHCONH - CH_3 O NHSO_2C_{16}H_{33}$$

ОН

Y - 8

CH<sub>3</sub> 
$$CH_3$$
  $CC$ 

CH<sub>3</sub>  $CC$ 

CH<sub>3</sub>  $CC$ 

CH<sub>3</sub>  $CC$ 

NHSO<sub>2</sub>C<sub>1.8</sub>H<sub>3.3</sub>

Y - 10

$$CH_3 - C - COCHCONH - C_5H_{11}(t)$$

$$CH_3 - C_7 + C_$$

Y - 11

Y - 12

Y - 13

CH<sub>3</sub>O COCHCONH CC<sub>6</sub>H<sub>11</sub>(t)

ONHCOCHO C<sub>5</sub>H<sub>11</sub>(t)

CH<sub>2</sub>O C<sub>2</sub>H<sub>5</sub>

Y - 14

15

25 CH<sub>3</sub> C CQ COCHCONH COOC, 2 H<sub>2</sub> 5

CH<sub>3</sub> C COCHCONH COOC, 2 H<sub>2</sub> 5

CH<sub>2</sub> COC<sub>2</sub> H<sub>5</sub>

Y - 15

 $CH_{3} - C - COCHCONH - C_{5}H_{11}(t)$   $CH_{3} - C - COCHCONH - C_{5}H_{11}(t)$ 

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Y - 16

CH<sub>3</sub> CH<sub>3</sub> CC
$$C$$
 COCHCONH NHCO(CH<sub>2</sub>)<sub>3</sub>O C<sub>5</sub>H<sub>1,1</sub>(t)

NHCO(CH<sub>2</sub>)<sub>3</sub>O C<sub>5</sub>H<sub>1,1</sub>(t)

Y - 17

Y - 18

CH<sub>3</sub>

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$COOCH_3$$

$$C_5H_{11}(t)$$

$$C_5H_{11}(t)$$

$$COOCH_3$$

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Y - 19

$$CH_3 - C - COCHCONH - C_5H_{11}(t)$$

$$CH_3 - C - COCHCONH - C_5H_{11}(t)$$

$$CH_3 - COCC_8H_{13}$$

$$NHCO(CH_2)_3O - C_5H_{11}(t)$$

$$Y - 20$$

$$Y - 21$$

Y - 22

5
$$C_5H_{11}(t) \longrightarrow COCHCONH$$

$$C_2H_5 \longrightarrow CH_2$$

Y - 23  $CH_3$   $CH_3$   $COOC_{12}H_{25}$   $CH_2 - N$   $OC_{2}H_{5}$ 

$$Y - 24$$

$$CH_{2} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_{2} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_{2} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$C$$

50

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(by weight)

Y - 26

Y - 27

CH<sub>3</sub> CC 
$$C_{5}H_{11}(t)$$

CH<sub>3</sub>  $C_{5}H_{11}(t)$ 

CH<sub>3</sub>  $C_{5}H_{11}(t)$ 

NHCO(CH<sub>2</sub>)<sub>3</sub>O  $C_{5}H_{11}(t)$ 

$$Y - 28$$

Y - 29

$$CQ$$

$$(t)C_{\bullet}H_{\bullet}COCHCONH$$

$$NHSO_{2}C_{1}_{2}H_{2}_{5}(f_{1})$$

$$COOC_{3}H_{7}(iso)$$

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \\ \text{CH}_2 \\ \end{array}$$

$$\begin{array}{c} \text{CQ} \\ \text{NHCO(CH}_2)_3 \\ \text{O} \\ \text{C}_5 \\ \text{H}_1, (t) \\ \text{C}_5 \\ \text{H}_1, (t) \\ \end{array}$$

$$Y - 32$$

$$Y - 33$$

CH<sub>3</sub> CH<sub>3</sub> OCH<sub>3</sub>

CH<sub>3</sub> C C COCHCONH NHCOC<sub>13</sub>H<sub>27</sub>

Y - 34

CH<sub>3</sub>O COCHCONH COOC<sub>12</sub>H<sub>25</sub>

Y - 35

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CH<sub>3</sub>O — COCHCONH — COOCH<sub>2</sub>CHCH<sub>2</sub>CHC<sub>3</sub>H<sub>7</sub>

C<sub>2</sub>H<sub>5</sub> C<sub>2</sub>H<sub>5</sub>

SO<sub>2</sub> — OH

Y - 36

CH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCO(CH<sub>2</sub>)<sub>5</sub>COO

SO<sub>2</sub>

(CH<sub>3</sub>)<sub>3</sub>CCOCHCONH—CQ

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Y - 37

$$Y - 38$$

$$\begin{array}{c|c} CH_3 & CC \\ CH_3 & C - COCHCONH \\ CH_3 & O \\ \hline \\ O & CH_3 \\ \hline \\ CH_3 & CH_3 \\ \end{array}$$

$$Y - 39$$

2-equivalent magenta couplers

$$M-1$$

$$C_{10}H_{21}$$

$$OCH_{2}COO(CH_{2})_{3}$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$M-2$$

$$C_5H_{11}(t)$$

$$OC_4H_8$$

$$C_5H_{11}(t)$$

$$OC_8H_{17}(t)$$

$$C_8H_{17}(t)$$

$$C_8H_{17}(t)$$

$$M - 3$$

$$C_5 H_{11}(t) \longrightarrow CONH \longrightarrow N$$

$$OCHCONH$$

$$C_2 H_5 \longrightarrow CQ$$

Cl

M-4

$$\begin{array}{c|c} C\ell \\ C_{1} \bullet H_{35} & O \\ O & C\ell \\ \end{array}$$

$$M-5$$

$$M - 6$$

$$C\ell$$

$$NH - S$$

$$C_{13}H_{27}CONH$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

M - 7

5

5
$$HO \longrightarrow SO_2 \longrightarrow OCHCONH$$

$$CQ$$

$$CQ$$

$$CQ$$

$$CQ$$

$$CQ$$

$$CQ$$

M - 8

$$\begin{array}{c} C_5H_{11}(t) \\ C_5H_{11} - CONH \\ C_4CONH \\ C_6CCC \\ C_6CCC$$

M - 9

35 OC.H. NHCOC(CH<sub>3</sub>)<sub>3</sub> 40 (t)C<sub>8</sub>H<sub>17</sub> ·CQ 45

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M - 10

 $C_5H_{11}(t)$  CONH CU CU CU CU

ĊQ

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M - 11

15

40

50

$$\begin{array}{c|c} & & & & \\ \hline \\ (t)C_5H_{11} & & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \hline \\ \end{array} \\ \begin{array}{c|c} & & \\ \end{array} \\ \begin{array}{c|c} & & \\ \\ \end{array} \\ \begin{array}{c|c} &$$

45

ĊQ

M - 12

CH<sub>3</sub>

CH<sub>3</sub>

CH<sub>3</sub>

CH<sub>3</sub>

NHCOC<sub>1</sub> 3 H<sub>2</sub> 7

CL

CL

CL

M - 13

15

20

$$C_{5}H_{11}(t)$$

$$CONH$$

$$N$$

$$C_{2}CONH$$

$$C_{2}CONH$$

$$C_{2}CONH$$

$$C_{2}CONH$$

$$C_{3}CONH$$

M - 14

50

M - 15

M - 16

M - 17

M - 18

M - 19

M - 20

$$M-22$$

$$C_{12}H_{26}O \longrightarrow SO_{2}NH \longrightarrow (CH_{2})_{3} \longrightarrow N$$

$$N \longrightarrow N$$

$$M - 23$$

M - 24

CH<sub>2</sub> 
$$\stackrel{CQ}{\longrightarrow}$$
  $\stackrel{H}{\longrightarrow}$   $\stackrel{N}{\longrightarrow}$   $\stackrel{N}{\longrightarrow}$   $\stackrel{N}{\longrightarrow}$   $\stackrel{C}{\longrightarrow}$   $\stackrel{N}{\longrightarrow}$   $\stackrel{N}{\longrightarrow}$ 

$$M - 25$$

$$M - 26$$

M - 27

$$M - 28$$

$$M - 29$$

M - 30

x : y : z = 50 : 25 : 25 (by weight)

25 '

20

M - 31

$$\begin{array}{c|c} & \begin{array}{c|c} & \begin{array}{c|c} & \\ & \\ & \end{array} \end{array} \end{array} \begin{array}{c|c} CH_2 - CH \\ \hline \\ CONH \end{array} \begin{array}{c|c} & \\ & \\ & \\ \end{array} \begin{array}{c|c} & \\ \end{array} \begin{array}{c|c} & \\ \end{array} \begin{array}{c|c} & \\ & \\ \end{array} \begin{array}{c|c} & \\ \end{array} \begin{array}{c|c} & \\ & \\ \end{array} \begin{array}{c|c} &$$

x : y = 50 : 50 (by weight)

55

45

$$M - 32$$

$$\begin{array}{c|c} CH_2 - CH & \\ \hline \\ CONH & N & CQ \\ \end{array}$$

$$\begin{array}{c|c} CH_2 - CH & \\ \hline \\ COOC_4H_9 \\ \end{array}$$

$$x : y = 50 : 50$$
 (by weight)

M - 33

$$M - 34$$

$$M - 35$$

M - 36

$$\begin{array}{c|c} C\ell & H \\ CH_3 & N \\ \hline & N \\ \hline & N \\ \hline & N \\ \hline & C_{10}H_{21} \\ \hline & C\ell \\ \hline \\ & C_{10}H_{21} \\ \hline \end{array}$$

$$C_{\bullet}H_{\bullet}O$$
 $C_{\bullet}H_{\bullet}O$ 
 $C_{\bullet$ 

$$M - 38$$

$$(t)C_5H_{11} \longrightarrow OCHCONH \longrightarrow (CH_2)_3 \longrightarrow N \longrightarrow N$$

$$C_8H_{13} \longrightarrow OCHCONH \longrightarrow (CH_2)_3 \longrightarrow N \longrightarrow N$$

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CHCH_2SO_2$ 
 $OC_0H_{17}$ 
 $OC_0H_{17}$ 

2-equivalent cyan couplers

$$C-1$$
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 
 $C_5H_1(t)$ 

C - 4

C - 5

10

50

C - 6

C - 7

C - 10

30

55

NHSO<sub>2</sub>CH<sub>3</sub>

$$C - 12$$

$$OH$$

$$Conh(CH2)4O \longrightarrow C5H11(t)$$

$$O$$

$$NCOCH3$$

$$C2H5$$

$$COOC4H9$$

$$C = 13$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C - 14$$

$$C_5 H_{11}(t)$$

$$C_5 H_{11}(t)$$

$$C_5 H_{11}(t)$$

$$C_5 H_{11}(t)$$

$$C_5 H_{11}(t)$$

C - 16OH инсосно-C<sub>4</sub>H<sub>8</sub> C<sub>5</sub>H<sub>11</sub>(t) CaHs

$$C-17$$

$$C_1H_9SO_2NH \longrightarrow OCHCONH$$

$$C_12H_25$$

$$C$$

C - 18

$$(t)C_5H_{11} \longrightarrow OCHCONH$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

$$C\ell$$

55

50

5

15

20

25

30

C - 23

C - 24

15

30

35

C<sub>5</sub>H<sub>1,1</sub>(t)

C<sub>5</sub>H<sub>1,1</sub>(t)

OCHCONH

CN

CAH<sub>9</sub>

OCH<sub>2</sub>COOCH<sub>3</sub>

C - 25

C<sub>5</sub>H<sub>1</sub>,(t)  $C_5H_1$ OCHCONH  $C\ell$ 

C<sub>4</sub>H<sub>8</sub> O C<sub>5</sub>H<sub>1,1</sub>(t)

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C - 26

 $(t)C_5H_{1,1} \longrightarrow OCHCONH \longrightarrow F$   $(t)C_5H_{1,1} \longrightarrow OCHCONH \longrightarrow OCH_2CH_2OH$ 

C - 27

C - 28

C - 29

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C = 30$$

$$C - 31$$

$$(t)C_{5}H_{1} = OCHCONH$$

$$C_{4}H_{8}$$

$$OH$$

$$OH$$

$$NHCOC_{3}F_{7}$$

C<sub>4</sub>H<sub>e</sub>(t)

$$C - 32$$

$$CH_{2} - CH$$

$$CONH - O(CH_{2})_{3}NHCO - OCHCOOH$$

$$CH_{3}$$

$$X$$

$$Y$$

x : y = 40 : 60 (by weight)

x : y = 50 : 50 (by weight)

(副祖监)

C - 33  $CH_{2} - CH$  CONH CONH  $CH_{2} - CH$   $COOC_{\bullet}H_{9}$   $CH_{2} - CH$   $COOC_{\bullet}H_{9}$   $CH_{2} - CH$   $COOC_{\bullet}H_{9}$ 

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$$C - 34$$

$$C\ell \longrightarrow NHCOCHO \longrightarrow C_5H_{11}(t)$$

$$C_2H_5 \longrightarrow C\ell$$

$$C - 35$$
 $C\ell$ 
 $C_2H_5$ 
 $C\ell$ 
 $C\ell$ 
 $C\ell$ 
 $C\ell$ 
 $C\ell$ 

$$C - 36$$

$$C\ell \longrightarrow NHCOCHO \longrightarrow C_5H_{11}(t)$$

$$C_2H_5 \longrightarrow C_5H_{11}(t)$$

$$C - 37$$
 $C\ell$ 
 $CH_3$ 
 $CH_3$ 
 $CC\ell$ 
 $C_5H_{11}(t)$ 
 $C = C_5H_{11}(t)$ 

C - 38

$$C\ell \longrightarrow NHCOCHO \longrightarrow C_5H_{1,1}(t)$$

$$CH_3 \longrightarrow C_4H_9 \longrightarrow C_5H_{1,1}(t)$$

$$C - 39$$

5
$$(t)C_5H_{11} \longrightarrow OCHCONH$$

$$CH(CH_3)_2 CQ$$

$$C_5H_{11}(t)$$

15

25

35

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In the invention, the yellow couplers may be added in an amount within the range of, desirably, 5x10<sup>-5</sup> to  $2x10^{-3}$  mols/m<sup>2</sup>, more desirably,  $1x10^{-4}$  to  $2x10^{-3}$  mols/m<sup>2</sup> and, preferably,  $2x10^{-4}$  to  $2x10^{-3}$  mols/m<sup>2</sup>. The magenta couplers may be added in an amount within the range of, desirably, 2x10<sup>-5</sup> to 1x10<sup>-3</sup> mols/m<sup>2</sup>, more desirably,  $5x10^{-5}$  to  $1x10^{-3}$  mols/m<sup>2</sup> and, preferably,  $1x10^{-4}$  to  $1x10^{-3}$  mols/m<sup>2</sup>. The cyan couplers may be added in an amount within the range of, desirably,  $5x10^{-5}$  to  $2x10^{-3}$  mols/m<sup>2</sup>, more desirably,  $1x10^{-4}$  to  $2x10^{-3}$  mols/m<sup>2</sup> and, preferably,  $2x10^{-4}$  to  $2x10^{-3}$  mols/m<sup>2</sup>.

The light sensitive silver halide emulsion layers of the invention contains each a 2-equivalent coupler, and they are also allowed to contain each a 4-equivalent coupler in combination. In this case, it is desirable when the 2-equivalent coupler content is within the range of 50 to 100 mol% of the whole coupler content and the 4-equivalent couplers occupy the rest. It is more desirable when the 2-equivalent coupler content is within the range of 70 to 100 mol% of the whole coupler content. It is preferable when the 2-equivalent coupler content is 100 mol% of the whole coupler content, that is to say, the whole coupler consist of 2equivalent couplers.

The term, 'a 4-equivalent coupler', herein means a coupler having no substituent in the coupling position. The yellow couplers include, preferably, an acylacetanilide of the pivalylacetanilode type or the benzoylacetanilide type. The magenta couplers include, for example, an indazolone, a cyanoacetyl, a 5pyrazolone, and a pyrazoloazole of the pyrazoloimidazole type. Among them, a 5-pyrazolone and a pyrazoloazole are preferable. The cyan couplers include, preferably, a phenol and a naphthol.

The 4-equivalent couplers applicable in combination include, for example, those in which the couplingpositioned X denoted in the foregoing formulas 2eq-2 to 2eq-10 represents a hydrogen atom. The examples of R<sub>1</sub> through R<sub>4</sub> include those exemplified in formulas 2eq-2 through 2eq-10. In each of the foregoing formulas, there include the cases where a polymer having not less than dimer is formed by R<sub>1</sub> through R<sub>4</sub>.

In the invention, a variety of the other couplers then the above-mentioned couplers may be used in combination. The concrete examples thereof are described in, for example, the foregoing Research Disclosures. The following table indicates where they are described.

	[Item]	Pages in [RD 30819]	[RD 17643] [RD 18716]
	DIR coupler	p.1001, VII-F	VII-F
5	BAR coupler	p.1002, VII-F	
10	The other useful fragments releasing coupler	p.1001, VII-F g	
	Alkali-soluble coupler	p.1001, VII-E	

The additives applicable to the invention may be added in the dispersion method such as those 15 described in RD 108119, XIV.

In the invention, it is permitted to use the supports described in the foregoing RD 17643, p.28; RD 18716, pp.647-648; and RD 308119, XIX.

A light sensitive material may be provided thereto with the auxiliary layers such as a filtering layer and an intermediate layer, such as those described in, for example, the foregoing RD 308119.

The light sensitive materials of the invention can have a variety of layer arrangements such, as a regular layered arrangement, a reversed layer arrangement and a unit layer arrangement each described in, for example, the foregoing RD 308119, VII-K.

In the invention, the effects of the invention can more excellently be displayed when a vinylsulfone type layer hardener is used in a light sensitive material.

The vinylsulfone type layer hardenrs herein mean the compounds each having a vinyl group coupled to a sulfonyl group or a group capable of forming a vinyl group coupled thereto. Among them, those having at least two groups each capable of forming a vinyl group coupled to a sulfonyl group or a vinyl group. For example, the compounds represented by the following formula VS-1 may preferably be used in the invention.

Formula VS-1

 $L-(SO_2-X)_m$ 

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wherein L represents a m-valent coupling group; X represents  $-CH = CH_2$  or  $-CH_2CH_2Y$  in which Y represents a group capable of being released in the form of an HY by a base and, for example, Y represents a halogen atom, a sulfonyloxy group, a sulfoxy including the salts thereof, and a tertiary amine residual group.;

m is an integer of 2 to 10, provided, when m is not less than 2, -SO2-Xs may be the same with or the different from each other.

An m-valent coupling group L is a m-valent group formed by a single coupling or plural combination couplings of, for example, an aliphatic hydrocarbon group such as an alkylene, alkylidene or an alkylidine group or the group formed by coupling the above-mentioned groups to each other, an aromatic hydrocarbon group such as an arylene group or the group formed by coupling them to each other, -O-, -NR'- in which R' represents a hydrogen atom or, preferably, an alkyl group having 1 to 15 carbon atoms, -S-,

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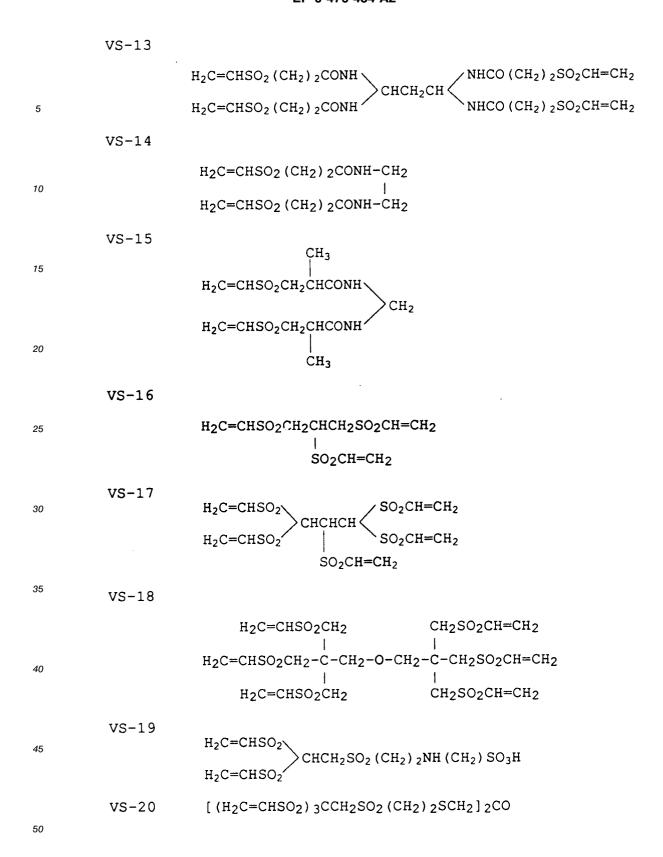
-CO, -SO-, -SO<sub>2</sub>-, or -SO<sub>3</sub>-. When an m-valent coupling group L contains not less than two -NR'-s, it is allowed to form a ring upon coupling R's to each other. Such a coupling group L include those each having a substituent such as a hydroxy, alkoxy, carbamoyl, sulfamoyl, alkyl or aryl group.

The typical examples of X include, preferably,  $-CH = CH_2$  or

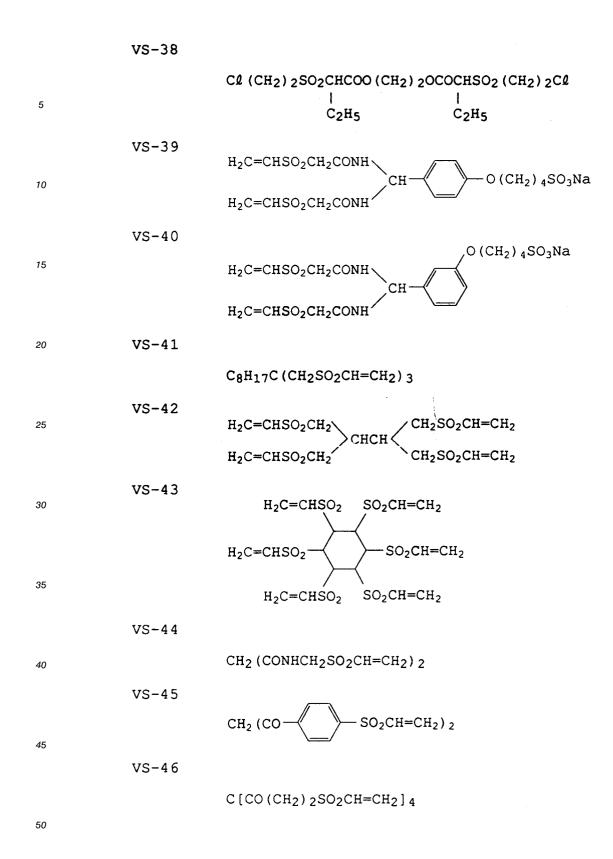
-CH2CH2Cl.

The typically concrete examples of the vinylsulfone type layer hardeners will be given below.

	VS-1	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
	VS-2	H <sub>2</sub> C=CHSO <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
5	VS-3	H <sub>2</sub> C=CHSO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
	VS-4	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
10	VS-5	H <sub>2</sub> C=CHSO <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> O (CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
10	VS-6	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CHCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>   OH	
		OH	
15	VS-7	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CHCH <sub>2</sub> CHCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub> 	
	<b>v</b> s-8	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CONHCH <sub>2</sub> NHCOCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
20	VS-9	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CONH (CH <sub>2</sub> ) <sub>2</sub> NHCOCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
	VS-10	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CONHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCOCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
25	VS-11	H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CON NCOCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
30	VS-12	COCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	
		N	
35		H <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> CO N COCH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	



VS-21  $(H_2C=CHSO_2CH_2)_3CCH_2SO_2(CH_2)_2CH_2O^{-1}$ 5 VS-22 (H2C=CHSO2CH2) 4C 10 VS-23 H2C=CHSO2CH2N NSO<sub>2</sub>CH=CH<sub>2</sub> VS-24 15 (H<sub>2</sub>C=CHSO<sub>2</sub>CH<sub>2</sub>) <sub>3</sub>CC<sub>2</sub>H<sub>5</sub> VS-25 SO<sub>2</sub>CH=CH<sub>2</sub> 20 CH2=CHSO2 SO<sub>2</sub>CH=CH<sub>2</sub> 25 VS-26 SO<sub>2</sub>CH=CH<sub>2</sub> CH<sub>3</sub>· CH<sub>3</sub> 30 CH<sub>2</sub>=CHSO<sub>2</sub> SO<sub>2</sub>CH=CH<sub>2</sub> CH<sub>3</sub> 35 VS-27 CH<sub>2</sub>SO<sub>2</sub>CH=CH<sub>2</sub> 40 CH2=CHSO2CH2 CH<sub>2</sub>SO<sub>2</sub>CH=CH<sub>2</sub> VS-28 SO<sub>2</sub>CH=CH<sub>2</sub> 45 50



The vinylsulfone type layer hardeners applicable to the invention include, for example, aromatic type compounds such as those described in German Patent No. 1,100,842; alkyl compounds each coupled with a hetero atom, such as those described in Japanese Patent Examined Publication Nos. 44-29622/1969, 47-

25373/1972 and 47-24259/1972; sulfonamide ester type compounds such as those described in Japanese Patent Examined Publication No. 47-8736/1972; 1,3,5-tris [ $\beta$ -(vinylsulfonyl)-propionyl]-hexahydro-S-triazine such as those described in Japanese Patent O.P.I. Publication No. 49-24435/1974; alkyl type compounds such as those described in Japanese Patent O.P.I. Publication No.s 51-44164/1976; and the compounds described in Japanese Patent O.P.I. Publication No. 59-18944/1984.

These vinylsulfon type layer hardeners are used in a proportion within the range of 0.005 to 20% by weight and, preferably, 0.02 to 10% by weight to a binder such as gelatin to be used, after they are dissolved in water or an organic solvent.

They are added into a photographic layer in a batch system or in an in-line addition system.

The photographic layers to which these layer hardeners are to be added shall not specially be limited, but the hardeners may be added into, for example, the uppermost layer or the lowermost layer solely, or the whole photographic layer.

In the invention, it is also preferred to contain at least one kind of the compounds represented by the following formulas B-1 through B-3 in a silver halide color photographic light sensitive material.

### Formula B-1

$$R^2$$
 $R^3$ 

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wherein  $R^1$  represents an alkyl group, a cycloalkyl group, an aryl group, a hydroxyl group, an alkoxycarbonyl group, an amino group, a carboxylic acid group including the salts thereof, or a sulfonic acid group including the salts thereof;  $R^2$  and  $R^3$  represent each a hydrogen atom, a halogen atom, an amino group, a nitro group, a hydroxyl group, an alkoxycarbonyl 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 or an ammonium group.

#### Formula B-2

#### Formula B-3

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wherein R<sup>4</sup> represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a halogenoalkyl group, -R<sup>12</sup>-OR<sup>13</sup> or -CONHR<sup>14</sup> (in which R<sup>12</sup> represents an alkylene group and, R<sup>13</sup> and R<sup>14</sup> represent each a hydrogen atom, an alkyl group or an arylalkyl group) or an arylalkyl group; R<sup>5</sup> and R<sup>6</sup> represent each a hydrogen atom, a halogen atom, a halogenoalkyl group or an alkyl group; R<sup>7</sup> represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a halogenoalkyl group, arylalkyl group, -R<sup>15</sup>-OR<sup>16</sup> or -CONHR<sup>17</sup> (in which R<sup>15</sup> represents an alkylene group and, R<sup>16</sup> and R<sup>17</sup> represent each a hydrogen atom or an alkyl group); and R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> 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

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B-1-5

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B-1-11

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B-1-2

B-1-4

B-1-6

B-1-8

B-1-10

B-1-12

The compounds represented by the above-given formula B-1 include some kinds of the known antiseptics such as tangerines which are available on the market readily for the skilled in the art.

Among the above-exemplified compounds, the preferable include B-1-1, B-1-2, B-1-3, B-1-4 and B-1-5.

The compounds having formula B-1 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, preferably, 0.12 to 10 g and, particularly, 0.15 to 5 g.

The typical examples of the compounds having formulas B-2 and B-3 will be given below. It is, however, to be understood that the compound 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
50	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
55	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
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

Concerning the exemplified compounds, the synthesizing processes thereof and the examples thereof to be applied to the other fields 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 compounds are available on the market under the trade names, for example, Topcide 300 manufactured by Permachem Asia Co., Topcide 600 by the same company, Finecide J-700 manufactured by Tokyo Fine-Chemical Co., and Proxel GXL manufactured by I.C.I.

The compounds having formulas B-1 through B-3 may be used in an amount within the range of 0.1 mg to 500 mg per m<sup>2</sup> of a light sensitive material used and, preferably, 0.5 mg to 100 mg. The compounds having formulas B-1 through B-3 may also be used independently or in combination.

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

#### Examples

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Some of 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

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A mutilayered color photographic light sensitive material sample No. 1 was prepared by forming the layers having the following compositions on a triacetyl cellulose film support, respectively, in the order from the support side.

the amounts of the materials added into the silver halide photographic light sensitive material are indicated in terms of grams per sq.meter of the light sensitive material, unless otherwise expressly stated, and the amounts of silver halides and colloidal silver are indicated in terms of the silver contents. However, the amounts of the sensitizing dyes used therein are indicated by the number of mols per mol of the silver halides contained in the same layer.

5 Light sensitive material sample 1

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Layer 1 : An antihalation layer		
Black colloidal silver	0.18	
UV absorbent, UV-1	0.23	
High boiling solvent, Oil-1	0.18	
Gelatin	1.2	
0.010		

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Layer 2 : The fi	rst interlayer
Gelatin	1.1

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Layer 3 : A low-speed red-sensitive emulsion layer			
Silver iodobromide emulsion (with an average grain size: 0.4µm; Agl content: 2.0 mol%) Sensitizing dye, SD-1 Sensitizing dye, SD-2 Sensitizing dye, SD-3 Cyan coupler, CCp-1 Colored cyan coupler, CC-1 DIR compound, D-1	1.0  1.8×10 <sup>-5</sup> mols/mol of silver 2.8×10 <sup>-4</sup> mols/mol of silver 3.0×10 <sup>-4</sup> mols/mol of silver 1.13×10 <sup>-3</sup> mols/m <sup>2</sup> 0.07 0.03		
DIR compound, D-3 High boiling solvent, Oil-1 Gelatin	0.02 0.60 1.1		

Layer 4 : A medium-speed red-sensitive emulsion layer			
Silver iodobromide emulsion (with an average grain size: 0.7µm; AgI content: 8.0 mol%)	0.85		
Sensitizing dye, SD-1	2.1x10 <sup>-5</sup> mols/mol of silver		
Sensitizing dye, SD-2	1.9x10 <sup>-4</sup> mols/mol of silver		
Sensitizing dye, SD-3	1.9x10 <sup>-4</sup> mols/mol of silver		
Cyan coupler, CCp-1	4.53x10 <sup>-4</sup> mols/m <sup>2</sup>		
Colored cyan coupler, CC-1	0.03		
DIR compound, D-1	0.01		
High boiling solvent, Oil-1	0.26		
Gelatin	0.6		

Layer 5 : A medium-speed red-sensitive emulsion layer			
Silver iodobromide emulsion (with an average	1.5		
grain size: 0.8µm; AgI content: 8.0 mol%)			
Sensitizing dye, SD-1	1.9x10 <sup>-5</sup> mols/mol of silver		
Sensitizing dye, SD-2	1.7x10 <sup>-4</sup> mols/mol of silver		
Sensitizing dye, SD-3	1.7x10 <sup>-4</sup> mols/mol of silver		
Cyan coupler, CCp-1	8.30x10 <sup>-5</sup> mols/m <sup>2</sup>		
Cyan coupler, CCp-2	2.90x10 <sup>-4</sup> mols/m <sup>2</sup>		
Colored cyan coupler, CC-1	0.02		
DIR compound, D-1	0.025		
High boiling solvent, Oil-1	0.26		
Gelatin	1.2		

Layer 6 : The second interlayer

Gelatin 0.6

Layer 7 : A low-speed green-sensitive emulsion layer			
Silver iodobromide emulsion (with an average	1.1		
grain size: 0.4µm; AgI content: 2.0 mol%)			
Sensitizing dye, SD-4	6.8x10 <sup>-5</sup> mols/mol of silver		
Sensitizing dye, SD-5	6.2x10 <sup>-4</sup> mols/mol of silver		
Magenta coupler, MCp-1	7.49x10 <sup>-4</sup> mols/m <sup>2</sup>		
Magenta coupler, MCp-2	2.90x10 <sup>-4</sup> mols/m <sup>2</sup>		
Colored magenta coupler, CM-1	0.08		
DIR compound, D-2	0.017		
DIR compound, D-3	0.01		
High boiling solvent, Oil-2	0.81		
Gelatin	1.6		

Layer 8 : A medium-speed green-sensitive emulsion layer Silver iodobromide emulsion (with an average grain size: 0.7µm; Agl content: 8.0 mol%) Sensitizing dye, SD-6 1.9x10<sup>-4</sup> mols/mol of silver Sensitizing dye, SD-7 1.2x10<sup>-4</sup> mols/mol of silver Sensitizing dye, SD-8 1.5x10<sup>-5</sup> mols/mol of silver Magenta coupler, MCp-1  $9.7x10^{-5} \text{ mols/m}^2$  $6.0x10^{-5} \text{ mols/m}^2$ Magenta coupler, MCp-2 Colored magenta coupler, CM-1 0.04 DIR compound, D-2 0.018 High boiling solvent, Oil-2 0.30 Gelatin 0.9

Layer 9 : A high-speed green-sensitive emulsion layer			
Silver iodobromide emulsion (with an average grain size: 1.0µm; AgI content: 8.0 mol%) Sensitizing dye, SD-6 Sensitizing dye, SD-7 Sensitizing dye, SD-8 Magenta coupler, MCp-1 Magenta coupler, MCp-3 Colored magenta coupler, CM-1 High boiling solvent, Oil-2 Gelatin	1.5 1.2x10 <sup>-4</sup> mols/mol of silver 1.0x10 <sup>-4</sup> mols/mol of silver 3.4x10 <sup>-6</sup> mols/mol of silver 1.25x10 <sup>-4</sup> mols/m <sup>2</sup> 1.0x10 <sup>-4</sup> mols/m <sup>2</sup> 0.04 0.31 1.1		

Layer 10 : A yellow filtering layer		
Yellow colloidal silver	0.08	
Color staining inhibitor, SC-1	0.12	
High boiling solvent, Oil-2	0.13	
Gelatin	0.7	
Formalin scavenger, HS-1	0.09	
Formalin scavenger, HS-2	0.07	

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	Layer 11 : A low-speed blue-se	nsitive emulsion layer
5	Silver iodobromide emulsion grain-size: 0.4 $\mu$ m, AgI cont	
10	Silver iodobromide emulsion grain-size: 0.7 $\mu$ m, AgI cont	(with an average
.0	Sensitizing dye, SD-9	$5.2 \times 10^{-4}$ mols/mol of silver
	Sensitizing dye, SD-10	$1.9 \times 10^{-5}$ mols/mol of silver
15	Yellow coupler, YCp-1	$1.55 \times 10^{-3} \text{ mols/m}^2$
	Yellow coupler, YCp-2	$6.88 \times 10^{-4} \text{ mols/m}^2$
20	DIR compound, D-1	0.02
20	High boiling solvent, Oil-2	0.24
	Gelatin	1.2
25	Formalin scavenger, HS-1	0.10

Layer 12 : A high-speed blue-sensitive emulsion layer					
Silver iodobromide emulsion (with an average grain-size: 1.0µm, Agl content: 8.0 mol%) Sensitizing dye, SD-9 Sensitizing dye, SD-10 Yellow coupler, YCp-1 Yellow coupler, YCp-2 High boiling solvent, Oil-2 Gelatin Formalin scavenger, HS-1	1.1  1.8x10 <sup>-4</sup> mols/mol of silver 7.9x10 <sup>-5</sup> mols/mol of silver 3.59x10 <sup>-4</sup> mols/m <sup>2</sup> 1.43x10 <sup>-4</sup> mols/m <sup>2</sup> 0.011 1.30 0.05				
Formalin scavenger, HS-2	0.12				

	Layer 13 : The first protective layer	
45	Finely-grained silver iodobromide emulsion (with an average grain-size: 0.08µm, Agl content: 1 mol%)	0.5
	UV absorbent, UV-1	0.07
	UV absorbent, UV-2	0.10
50	High boiling solvent, Oil-1	0.07
50	High boiling solvent, Oil-3	0.07
	Formalin scavenger, HS-1	0.13
	Formalin scavenger, HS-2	0.37
	Gelatin	1.3

Layer 14 : The second protective layer	
Alkali-soluble matting agent (with an average particle size: 2 µm) Polymethyl methacrylate (with an average particle size: 3 µm) Lubricant, WAX-1 Gelatin	0.13 0.02 0.04 0.6

Besides the above-given compositions, coating aid Su-1, dispersion aid Su-2, a viscosity controller, layer hardeners H-1 and H-2, stabilizer ST-1, antifoggant AF-1 and two kinds of AF-2 having Mw:10,000 and Mw:1,100,000 were added.

The emulsions each used in the above-prepared sample were a monodispersive emulsion having a low silver iodide content on the surface of the emulsion grains and were subjected to the optimum gold sulfur sensitization in an ordinary sensitizing method. The average grain size thereof is indicated by a grain size obtained by converting the grains into cubes.

C C p - 1

$$C_5H_{11}(t)$$

OH

NHCONH

CN

CN

CAHB

$$C C p - 2$$

$$OH$$

$$CONH(CH_2)_4 - O - C_5H_{11}(t)$$

$$C_5H_{11}(t)$$

$$M C p - 2$$

$$0$$

$$N + COCH_2O$$

$$C_5 H_{11}(t)$$

$$C_6 H_{11}(t)$$

$$\begin{array}{c|c}
M & C & p - 3 \\
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Y C p - 1

CH<sub>3</sub>0

COCH<sub>2</sub>CONH

COOC<sub>1,2</sub>H<sub>2,5</sub>

Y Cp - 2

(CH<sub>3</sub>)<sub>3</sub>CCOCH<sub>2</sub>CONH

C<sub>4</sub>H<sub>8</sub>

C C - 1 OH

CONH(CH<sub>2</sub>)<sub>4</sub> - 0 - C<sub>5</sub>H<sub>11</sub>(t)
$$C_5H_{11}(t)$$
OH NHCOCH<sub>3</sub>

$$NaO_3S$$

$$SO_3Na$$

CM-1

5 
$$CH_3O$$
 $N=N$ 
 $N+CO$ 
 $C_5H_{11}(t)$ 
 $C_6H_{11}(t)$ 
 $C_6H_{11}(t)$ 
 $C_6H_{11}(t)$ 
 $C_6H_{11}(t)$ 

D-1

OH

CONH

OCIAH26

CH2S

N

CH3

$$\begin{array}{c} D-3 \\ \\ OC_{1} \cdot H_{2} \cdot \theta \\ \\ CH_{2}S - N - N \\ \\ N - N \end{array}$$

$$0 = P \longrightarrow 0$$

O i l - 2

UV-1

5 0H 0H C<sub>+</sub>H<sub>9</sub>(t)

U V - 2

CH<sub>3</sub> CH - CH CONHC<sub>12</sub>H<sub>25</sub>

C<sub>2</sub>H<sub>6</sub>

25 WAX-1

weight average molecular weight Mw=3,000

C3H7(iso) C3H7(iso)

Su-1 Su-2

NaO<sub>3</sub>S - CHCOOC<sub>8</sub>H<sub>17</sub>

CH<sub>2</sub>COOC<sub>8</sub>H<sub>17</sub>

C<sub>3</sub>H<sub>7</sub>(iso) SO<sub>3</sub>Na

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S D - 2

$$C_{2}H_{5}$$

$$CH = C - CH$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{3}H_{5}$$

$$C_{4}H_{5}$$

$$C_{4}H_{5}$$

$$C_{5}H_{5}$$

$$C_{6}H_{2}H_{3}H_{5}$$

$$C_{7}H_{2}H_{5}$$

$$C_{8}H_{5}$$

$$C_{8}H_{7}$$

$$C_{8$$

SD-3
$$C\ell = C - CH = C - CH$$

$$C\ell = C - CH = C - CH$$

$$C\ell = C - CH = C - CH$$

$$C\ell = C - CH = C - CH$$

SD-4 
$$C_2H_5$$
  $C_2H_5$   $C_2H_$ 

SD-5

CH<sub>3</sub>

$$CH_3$$

$$CH = C - CH$$

$$CU$$

$$CH_2)_{+}SO_3$$

$$CH_5$$

$$CH_5$$

$$CH_7$$

$$C$$

SD-6
$$C_2H_5$$

$$CH=C-CH$$

$$CH_2)_3SO_3\Theta$$

$$CH_2)_3SO_3H$$

SD-7

$$C_2H_5$$

$$CH = C - CH$$

$$(CH_2)_3SO_3\Theta$$

$$(CH_2)_3SO_3H \cdot N(C_2H_5)_3$$

$$SD-8$$

$$C\ell \longrightarrow CH = C-CH \longrightarrow C\ell$$

$$C\ell \longrightarrow CH_{5}$$

$$C\ell \longrightarrow CH_{5}$$

$$C\ell \longrightarrow CH_{5}$$

$$C\ell \longrightarrow CH_{5}$$

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$$CH = \begin{array}{c} S \\ OCH_3 \\ (CH_2)_3 SO_3 \\ \end{array}$$
  $(CH_2)_3 SO_3 H \cdot N(C_2H_5)_3$ 

SD-9

SD-10
$$(CH_2)_3SO_3 \stackrel{\Theta}{\longrightarrow} (CH_2)_3SO_3Na$$

H-1ONa

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10

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H-2 $(CH_2 = CHSO_2CH_2)_2O$ 

S T - 1

ĆH₃ 30 A F - 1 35

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A F 
$$-2$$

CH  $-CH_2$ 

N

N

N

n : A polymerization degree

Next, Film samples Nos. 2 through 8 were each prepared by making use of the 2-equivalent couplers relating to the invention, as shown in Table 1.

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	Remarks		Inventive	sample	Inventive	sample	Inventive	sample	Inventive	sample	Inventive	sample	Inventive	sample	Inventive	,
	날	*pa	-	Sal	1.80/ In	_		_	1.		1.80/ In		1.80/ In	_	1.80/ In	
Lawer 12	Amount	added*	2.51		L	0.71		0.71	_		L	0.71				
T			Y-5		Y-2/	¥-5	Y-2/	¥-5	X-2/	¥-5	x-2/	Y-5	Y-2/	¥-5	Y-2/	ì
Laver 11	Amount	added*	11.2		7.75/	3.44	7.75/	3.44	7.75/	3.44	7.75/	3.44	7.75/	3.44	7.75/	
Lav			x-2		Y-2/	¥-5	Y-2/	Y-5	Y-2/	Y-5	Y-2/	Y-5	Y-2/	Y-5	Y-2/	
Laver 9	Amount	added*	0.30		0.90		0.90		0.90		0.83/	0.07	0.90		0.90	
Iav			<b>M</b> −3		₩ <b>-</b> 3		<b>M</b> −18		M-25		M-18/	MCp-3	M-18		M-18	
Layer 8	Amount	added*	0.71		0.71		0.71		0.71		0.71		0.65/	0.06	0.71	
Jay			<del>Σ</del>		Ϋ́		M-18		M-25		M-18		M-18/	MD9-3	¥-18	
Layer 7	Amount	added*	5.16		5.16		5.16		5.16		5.16		5.16		4.75/	:
Lay			M-3		ğ- Έ-		M-18		M-25		M-18		M-18		M-18/	
Layer 5	Amount	added*	1.93			1.52	0.81/	1.52	0.81/	1.52	0.81/	1.52	0.81/	1.52	0.81/ M-18/	
Laye			8-U	-	% 7-d8 7-	9 0	&p-1∕	9-J	8p-1/	8-J	8p-1/	8 <del>-</del> 0	000-1√	9-J	8 <del>p-</del> 1/	(
Layer 4	Amount	added*	2.27		4.53		4.53		4.53		4.53		4.53		4.53	-
Lay		_	C-24		8		8		8 -d		8		<del>6</del>		8	
Layer 3	Amount	added*	5.66		11.32		11.32		11.32		11.32		11.32		11.32	
			C-24		8		<u>1</u>		8		8		8		<del>[</del>	
Sample	Š.		(5)		ල		<del>(4)</del>		(2)		(9)		6		(8)	

Table 1

\* Unit of the amounts added :  $[x10^{-4} mols/m^2]$ 

The samples prepared in the above-described procedures were exposed to white light through a wedge and were then processed continuously under the following conditions.

	Processing step	Processing time	Processing temperature	Replenish- ment rate
5	Color developing	3min.15sec.	38±0.3°C	536 ml
	Bleaching	45sec.	38±2.0°C	150 ml
	Fixing	1min.30sec.	38±2.0°C	600 ml
10	Stabilizing	60sec.	38±5.0°C	600 ml
	Drying	50sec.	65±5.0°C	-

(Replenishment rate is in terms of sq.meter of a light sensitive material used.)

The color developer, bleaching solution, fixing solution, stabilizing solution and their replenishers each used therein were as follows.

## Color developer

25	Water	800	ml	-
25	Potassium carbonate	30	g	
	Sodium hydrogencarbonate	2.	. 5	g
30	Potassium sulfite	3.	. 0	g
	Sodium bromide	1.	. 3	g
35	Potassium iodide	1.	2	mg
30	Hydroxylamine sulfate	2.	. 5	g
	Sodium chloride	0.	8	g
40	4-amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxylethyl) aniline sulfate	4.	. 5	g
	Diethylenetriamine pentaacetate	3.	. 0	g

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	Potassium hydroxide	1.2 g
	Add water to make	1 liter
5	Adjust pH with potassium hydroxide or a 20% sulfuric acid solution to be pH10.06	
	Color developer replenisher	
10	Water	800 ml
	Potassium carbonate	35 g
	Sodium hydrogencarbonate	3 g
15	Potassium sulfite	5 g
	Sodiu bromide	0.4 g
20	Hydroxylamine sulfate	3.1 g
	4-amino-3-methyl-N-ethyl-N- $(\beta$ -hydroxylethyl) aniline sulfate	6.3 g
25	Potassium hydroxide	2 g
	Diethylenetriamine pentaacetate	3.0 g
	Add water to make	1 liter
30	Adjust pH with potassium hydroxide or a 20% sulfuric acid solution to be pH 10.1	8

Bleaching solution	Bleaching solution						
Water	700 ml						
Iron (III) ammonium 1,3-diaminopropane tetraacetate	125 g						
Ethylenediamine tetraacetic acid	2 g						
Sodium nitrate	40 g						
Ammonium bromide	150 g						
Glacial acetic acid	40 g						
Add water to make	1 liter						
Adjust pH with aqueous ammonia or glacial acetic acid to be	pH 4.4						

Bleaching solution replenisher	
Water	700 ml
Iron (III) ammonium 1,3-diaminopropane tetraacetate	175 g
Ethylenediamine tetraacetic acid	2 g
Sodium nitrate	50 g
Ammonium bromide	200 g
Glacial acetic acid	56 g
Adjust pH with aqueous ammonia or glacial acetic acid to be	pH 4.0
Add water to make	1 liter

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15	Fixer solution and the replenisher thereof	\ :
	Water	800 ml
20	Thiosulfate (ammonium thiosulfate and sodium thiosulfate)	1.5 mols
	Sodium sulfite	15 g
	Ethylenediamine tetraacetic acid	2 g
25	Adjust pH with aqueous ammonia, an aqueous caustic potash solution or acetic acid to be	pH 7.2
30	Adjust ammonium ions to have the mol% to the whole cation as given in the following Table 2	
	Add water to make	1 liter
35	Stabilizer solution and the replenisher ther	eof
	Water	900 ml
40	Additives (See Table 2)	See Table 2
45	Add water to make	1 liter

The automatic processor used in the continuous processing steps was that having a transport speed of 20m/min. The tanks for the stabilizing bath were arranged in a three-tank counter-current system. Each of the tanks was provided with a thermostating-circulating filter and a replenishing inlet as well as with the same functions as those provided to the ordinary types of automatic processors for processing color negative films, which are generally available on the market. When the term, 'one round', is defined as that an amount of a replenisher to a stabilizing bath reaches the same amount with the capacity of a stabilizing tank, the continuous processing was carried out up to three rounds in the combination shown in Table 2.

Adjust pH with aqueous ammonia or

a 50% sulfuric acid solution to be pH 8.5

After completing the continuous processing, the resulting film samples were observed of the reticulation production and the dye transfers to the film samples were then observed. The yellow transmission density

variations,  $\Delta D min(B)$ , were observed in the unexposed portions at each time when the continuous processing was started and then completed (up to 3 rounds), respectively. Next, after storing the processed film samples for six weeks under the conditions at a temperature of 60 °C and a humidity of 80%RH, the comparisons of the density variations,  $\Delta D_{1.0}(G)$ , obtained before storing them with those obtained after storing them were made at a magenta density D = 1.0. The results thereof are collectively shown in Table 2.

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Experi- ment No.	Film sample No.	Armonium content (mol%) of the whole cation in a stabilizer	Additives in a stabilizer (q/l)	Reticula- tions produced	Dye stain (transfer) produced	ΔDmin (B)	ΔD <sub>1.0</sub> (G)	Remarks
1-1	(1)		(I-12) (3g/Ø)	A	υ	+0.03	-0.25	Comparison
1-2	(2)	10	$(1-12)$ $(3g/\ell)$	A	A	+0.01	90.0-	Invention
1-3	(3)	10	$(1-12)$ $(3g/\ell)$	ď	A	+0.01	-0.05	Invention
1-4	(4)	10	$(I-12)$ $(3g/\ell)$	K	Ø	0	-0.05	Invention
1-5	(5)	10	$(I-12)$ $(3g/\ell)$	Ą	Æ	0	90.0-	Invention
1-6	(9)	10	$(I-12)$ $(3g/\ell)$	ď	æ	+0.01	-0.10	Invention
1-1	(7)	10	$(1-12)$ $(3g/\ell)$	K	æ	+0.01	-0.09	Invention
1-8	(8)	10	$(1-12)$ $(3g/\ell)$	Æ	æ	+0.01	-0.09	Invention
1-9	(2)	70	(1-12) $(3g/2)$	ပ	υ	+0.04	-0.04	Comparison
1-10	(2)	09	(1-12) $(3g/l)$	υ	Ф	+0.03	-0.04	Comparison
1-11	(2)	50	$(1-12)$ $(3g/\ell)$	<b>£</b>	B - A	+0.02	-0.05	Invention
1-12	(2)	40	$(I-12)$ $(3g/\ell)$	æ,	Æ	+0.02	-0.05	Invention
1-13	(2)	30	$(1-12)$ $(3g/\ell)$	Д	Ø	+0.02	-0.05	Invention
1-14	(2)	20	$(I-12)$ $(3g/\ell)$	B B A	æ	+0.01	90.0-	Invention
1-15	(2)	10	$(I-12)$ $(3g/\ell)$	Ą	Ą	+0.01	90.0-	Invention
1-16	(2)	ഹ	$(1-12)$ $(3g/\ell)$	Æ	Æ	0	-0.07	Invention
1-17	(2)	0	$(I-12)$ $(3g/\ell)$	K	Æ	0	-0.07	Invention
1-18	(2)	10	Unadded	U	υ	+0.01	-0.09	Comparison
1-19	(2)	10	Ethylene glycol (3g/1)	Ф	C - B	+0.03	-0.08	Comparison
1–20	(2)	10	Diethylene glycol (3g/1)	ф	Ø	+0.04	-0.07	Comparison
1-21	(2)	10	TEAC (39/0)	B - A	Д	+0.03	-0.18	Comparison
1-22	(2)	10	DTMAC $(3g/l)$	Ф	C - B	+0.03	-0.15	Comparison

5		Remarks	Comparison	Comparison	Invention	Invention	Invention	Invention	Invention	Invention	Invention											
10		ΔD <sub>1.0</sub> (G)	60.0-	-0.10	-0.04	-0.03	-0.04	90.0-	-0.05	-0.04	-0.04	-0.05	90.0-	-0.03	-0.04	90.0-	90.0-	-0.04	-0.07	-0.07	-0.05	-0.04
15		ΔDmin(B)	+0.02	+0.03	+0.01	+0.01	0	+0.01	+0.02	+0.01	+0.01	0	+0.01	+0.01	+0.01	+0.01	0	+0.01	0	0	+0.01	0
20		Dye stain (transfer) produced	ф	щ	B - A	Æ	ď	ď	В - А	A	Ą	Æ	Ø	В - А	æ	Æ	Ą	K	Æ	Æ	K	æ
25	-5	Reticula- tions produced	æ	C - B	K	K	K	ď	ď	ď	Ø	Æ	Ą	æ	æ	<b>&amp;</b>	ď	K	Æ	Ą	K	Æ
	Table 2-2	res in a izer	(3/gE)	(36/8)	(3/6)	(3g/g)	(3g/g)	(3g/1)	(3g/1)	(0.39/1)	(0.39/1)	(0.39/1)	(0.39/1)	(0.39/1)	(0.39/1)	(36/8)	(0.39/1)	(0.39/0)	(0.39/0)	(3g/1)	(3g/1)	(3g/l) / (3g/l)
30		Additives stabilizer (q/l)	IMTS	DBSS	(I-1)	(I-5)	(1-e)	(I-12)	(I-14)	(I-3)	(I-4)	(I-8)	(I-12)	(I-15)	(I-16)	(I-5)	(I-17)	(I-3)	(I-12)	(I-12)	(I-1)	(I-12) (II-3)
35		content (mol%) ble cation in zer																				
40		Ammonium cont of the whole a stabilizer	10	10	10	10	10	10	10	10	10	10	10	10	10	5	5	10	0	0	m	3
45		Film sample No.	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(4)	(5)	(3)	(9)	(7)	(8)	(4)
50		Experi- ment No.	1-23	1-24	1-25	1–26	1-27	1-28	1–29	1–30	1-31	1-32	1–33	1-34	1–35	1-36	1–37	1–38	1–39	1-40	1-41	1–42

In the evaluation of the reticulations produced shown in the above table, A means no reticulation observed; B means some reticulations observed; and C means apparent reticulations so observed as to be defective. In the evaluation of the dye stains (transfers), A means no dye stain observed at all; B means some stains observed; and C means apparent stains so observed as to be problematic.

Further in the table; TEAC stands for triethyl ammonium chloride; DTMAC, dodecyl trimethyl ammo-

nium chloride; LMTS, sodium lauroylmethyl taurinate; and DBSS, sodium dodecylbenzene sulfinate.

It can be proved from the contents of the above-given table 2 that every objective effect of the invention can excellently be displayed when using a 2-equivalent coupler in a light sensitive material, containing, in a fixing solution, ammonium ions in a proportion of not more than 50 mol% of the whole cation content of the fixing solution and containing, in a stabilizing solution, at least one kind of the compounds represented by the afore-given formula I or II. However, when any one of the above-mentioned requirements is lacking, nothing can satisfy every objective effect of the invention and, therefore, nothing can be put to practical use.

#### Example 2

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The running experiments were tried in the same manner as in Example 1, except that each of the bleaching and bleach-fixing solutions used in Example 1 was replaced by each of the following bleaching and bleach-fixing solutions.

15	Bleaching solution and the replenisher there	eof
	Ferric ammonium ethylenediamine tetraacetate	100 g
20	Ferric ammonium 1,3-propylene-diamine tetraacetate	50 g
	Ammonium bromide	100 g
25	Ammonium nitrate	45 g
	Bleach accelerator	0.005 mols
30	$\begin{bmatrix} CH_3 \\ CH_3 \end{bmatrix} N-CH_2CH_2-S + 2 + 2 + C + 2 + C + C + C + C + C + C$	
	Aqueous ammonia (a 27% solution)	12 ml
35	Acetic acid	5 α
	Add water to make	1 liter
40	Adjust pH with aqueous ammonia or acetic acid to be	рн 6.0

Bleach-fixing solution and the replenisher thereof	
Ferric ammonium ethylenediamine tetraacetate	50 g
Ethylenediamine tetraacetic acid	3 g
Sodium sulfite	12 g
Thiosulfate (ammonium thiosulfate and potassium thiosulfate)	1.5 mols
Potassium thiocyanate	70 g
Add water to make	1 liter
Adjust pH with aqueous ammonia, an aqueous caustic potash solution and acetic acid to be	pH 7.2

The following processing steps were carried out.

	Processing step	Processing time	Processing <u>temperature</u>	Replenish- ment rate
5	Color developing	2min.30sec.	40°C	610 ml
	Bleaching	1min.	38°C	480 ml
	Bleach-fixing	3min.	38°C	500 ml
10	Stabilizing	1min.	38°C	700 ml
	Drying	1min.	40~70°C	-

(Replenishment rate are shown as per m<sup>2</sup> of a light sensitive material to be processed.)

The stabilizing step was carried out in a 3-tank counter-current system in which the replenishments were made to the final tank of the stabilizing bath and the over-flow was flown into the tank precedent to the final tank. All the over-flows of the bleaching solution were flown into the bleach-fixing solution in the tank subsequent to the over-flown tank. The others including the film samples were subjected to the same experiments as in Example 1. The results thereof were almost the same as in Example 1.

### Example 3

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The experiments were tried in the same manner as in Experiment No. 1-2 tried in Example 1, except that the hardener H-2 contained in the film samples used in Experiment No. 1-2 tried in Example 1 was replaced by the hardeners each shown in Table 3.

The results thereof are collectively shown in Table 3.

Table 3

5	Experi- ment No.	Hardener	Reticula- tion produced	Dye stain produced	$\Delta$ Dmin(B)	ΔD <sub>1.0</sub> (G)
	3-1	Exemplified (VS-2)	Α	A	0	-0.05
10	3-2	Exemplified (VS-4)	A	Α	+0.01	-0.06
15	3-3	Exemplified (VS-6)	Α	A	+0.01	-0.05
	3-4	Exemplified (VS-9)	Α	A	+0.02	-0.04
20	3-5	Exemplified (VS-10)	A	A	0	-0.06
	3-6	Exemplified (VS-12)	A	A	0	-0.06
25	3-7	Exemplified (VS-22)	A	A	+0.01	-0.05
30	3-8	Exemplified (VS-33)	Α	A	+0.01	-0.06
	3-9	Exemplified (VS-54)	Α	A	+0.01	-0.05
35	3-10	RH-1 w/formula given below	B - A	В	+0.02	-0.08
	3-11	RH-2 w/formula given below	Α	В	+0.02	-0.09
40	3-12	RH-3 w/formula given below	В - А	A	+0.02	-0.07
<b>4</b> 5	3-13	RH-4 w/formula given below	Α	B - A	+0.03	-0.08
	3-14	RH-5 w/formula given below	В	B - A	+0.02	-0.09

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RH-1

RH-2

S Cl

10 RH-3

RH-4

 $[NaO_3SO(CH_2)_2O_2S-H_2C]_4C$ 

RH-5

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Cl-CH2CH2SO2CH2CH2COO-N

It can be proved from the contents of the above-given table 3 that, when making combination use of a vinylsulfon type layer hardener in the processing methods of the invention, the objective effects of the invention can excellently be displayed.

Example 4

The experiments were tried in the same manner as in Experiment No. 1-13 in Example 1, except that the compounds indicated in the following table 4 were added to contain in the color negative film samples used in Experiment No. 1-13 of Example 1.

The results thereof are shown in Table 4.

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Table 4

_	Experiment No.	Additives (10mg/m²)	Reticulation produced	Dye stain produced	ΔDmin(B)	ΔD <sub>1.0</sub> (G)
5	4-1	Unadded	В	Α	+ 0.02	-0.05
	4-2	Phenol	B - A	B - A	+ 0.02	-0.06
	4-3	Dihydroacetic acid	В	В	+ 0.03	-0.05
	4-4	Thiazolyl benzimidazole	В	В	+ 0.02	-0.06
10	4-5	Chlorodiphenyl	B - A	В	+ 0.03	-0.06
	4-6	Cresol	B - A	В	+0.03	-0.05
	4-7	p-amino-benzene sulfamide	B - A	Α	+ 0.03	-0.06
	4-8	(B-1-1)	Α	Α	+ 0.01	-0.04
	4-9	(B-1-16)	Α	Α	+0.02	-0.03
15	4-10	(B-1-8)	Α	Α	+ 0.01	-0.04
	4-11	(B-2-18)	Α	Α	+ 0.01	-0.04
	4-12	(B-2-1)	Α	Α	+ 0.01	-0.03
	4-13	(B-2-2)	Α	Α	0	-0.03
	4-14	(B-2-7)	Α	Α	+ 0.01	-0.03
20	4-15	(B-3-10)	Α	Α	+ 0.01	-0.03
	4-16	(B-3-1)	Α	Α	0	-0.04
	4-17	(B-3-3)	Α	Α	+ 0.01	-0.04
	4-18	(B-3-6)	Α	Α	+ 0.01	-0.03
	4-19	(B-2-2)/(B-3-1)	Α	Α	0	-0.03
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It can be proved from the contents of Table 4 that, when making combination use of the compounds represented by the foregoing formulas B-1 through B-3 in a light sensitive material to be processed in the processing methods of the invention, the effects of the invention can excellently be displayed.

# 30 Example 5

The experiments were tried in the same manner as in Experiment No. 1-2 of Example 1, except that the couplers contained in the film samples used in Experiment No. 1-2 of Example 1 were replaced by the couplers indicated in Table 5.

The results thereof are shown in Table 6.

Table 5

40	Sample No.	Layer 3	Layer 4	Layer 5	Layer 7	Layer 8	Layer 9	Layer 11	Layer 12
	(9)	C-2	C-2	C-2	M-3	M-3	M-3	Y-2	Y-5
	(10)	C-2	C-6	C-6	M-3	M-3	M-3	Y-2	Y-5
	(11)	C-2	C-6	C-15	M-3	M-3	M-3	Y-2	Y-5
45	(12)	C-19	C-20	C-20	M-3	M-3	M-3	Y-2	Y-5
45	(13)	C-19	C-34	C-34	M-3	M-3	M-3	Y-2	Y-5
	(14)	C-20	C-35	C-35	M-3	M-3	M-3	Y-2	Y-5
	(15)	C-24	C-24	C-8	M-1	M-6	M-6	Y-2	Y-5
	(16)	C-24	C-24	C-8	M-30	M-30	M-30	Y-2	Y-5
50	(17)	C-24	C-24	C-8	M-33	M-33	M-33	Y-2	Y-5
50	(18)	C-24	C-24	C-8	M-23	M-29	M-34	Y-2	Y-5
	(19)	C-24	C-24	C-8	M-35	M-35	M-35	Y-2	Y-5
	(20)	C-24	C-24	C-8	M-3	M-3	M-3	Y-6	Y-13
	(21)	C-24	C-24	C-8	M-3	M-3	M-3	Y-6	Y-14
55	(22)	C-24	C-24	C-8	M-3	M-3	M-3	Y-6	Y-29
55	(23)	C-24	C-24	C-8	M-3	M-3	M-3	Y-11	Y-13
	(24)	C-24	C-24	C-8	M-3	M-3	M-3	Y-21	Y-29

Table 6

5	Experiment No.	Film sample No.	Reticulation produced	Dye stain produced	ΔDmin(B)	ΔD <sub>1.0</sub> (G)
	5-1	(9)	Α	Α	+ 0.01	-0.06
	5-2	(10)	Α	Α	+ 0.01	-0.05
	5-3	(11)	Α	Α	+0.02	-0.05
	5-4	(12)	Α	Α	+ 0.01	-0.04
10	5-5	(13)	Α	Α	+ 0.01	-0.05
	5-6	(14)	Α	Α	+0.02	-0.06
	5-7	(15)	Α	Α	+0.02	-0.07
	5-8	(16)	Α	Α	+ 0.01	-0.05
	5-9	(17)	Α	Α	0	-0.04
15	5-10	(18)	Α	Α	0	-0.04
	5-11	(19)	Α	Α	0	-0.05
	5-12	(20)	Α	Α	+0.02	-0.06
	5-13	(21)	Α	Α	+0.01	-0.05
	5-14	(22)	Α	Α	+0.02	-0.06
20	5-15	(23)	Α	Α	+0.02	-0.07
	5-16	(24)	Α	Α	+ 0.01	-0.05

It can be proved from the contents of the above-given Table 6 that, when making combination use of the processing methods and the couplers relating to the invention, every effect of the invention can excellently be displayed as in Example 1.

#### **Claims**

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**1.** A method for processing a silver halide color photographic light-sensitive material comprising steps of developing said photographic material with a color developer,

processing, after said developing step, said photographic material with a solution having fixing ability, and

processing, in succession, said photographic material with a stabilizer without carrying out a washing step, wherein

said photographic material contains at least one of two-equivalent couplers;

said solution having fixing ability contains ammonium ions in an amout of not more than 50 mol% of the whole cations contained therein; and

said stabilizer contains formaldehyde in an amount of not more than  $1.0 \times 10^{-2}$  mols per liter and a compound represented by the following formula I or II:

#### formula I

$$R_{21} - O + R_{22} - O \rightarrow n - X_1$$

wherein  $R_{21}$  represents a univalent organic group;  $R_{22}$  represents ethylene, propylene or isopropylene; m is an integer of 4 to 50; and  $X_1$  represents hydrogen,  $-SO_3M$  or  $-PO_3M$  in which M represents hydrogen, an alkali metal atom or ammonium,

formula II

$$\begin{array}{c|ccccc} CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ \hline CH_{3} - Si - O & (Si - O)_{\ell 1} & (Si - O)_{\ell 2} & (Si - O)_{\ell 3} & CH_{3} \\ \hline CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ \hline (CH_{2})_{0} & (O - X_{1})_{\alpha 1} & (O - X_{2})_{\alpha 2} R_{9} \end{array}$$

wherein R<sub>9</sub> represents hydrogen, hydroxy, alkyl, alkoxy,

 $-si \stackrel{R_{10}}{\underset{R_{12}}{\overbrace{}}}$ 

or

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$$\text{-O-Si} \underset{R_{12}}{\overset{R_{10}}{\overleftarrow{R_{11}}}}$$

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in which  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  each represent hydrogen or alkyl, provided,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  may be the same with or different from each other;  $\ell_1$ ,  $\ell_2$  and  $\ell_3$  are each an integer of 0 to 30; p,  $q_1$  and  $q_2$  are each an integer of 0 to 30; and  $X_1$  and  $X_2$  each represent-CH<sub>2</sub>CH<sub>2</sub>-,

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or -CH2CH2CH2-.

2. A method of claim 1, wherein said solution having fixing ability is a fixer or a bleach-fixer.

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- 3. A method of claim 1, wherein said solution having fixing ability contains ammonium ions in an amount of not more than 20 mol% of whole cations.
- **4.** A method of claim 3, wherein said ammonium ions are contained in an amount of not more than 10 mol% of the whole cations.
  - 5. A method of claim 1, wherein said solution having fixing ability is replenished in an amount of not more than 900 ml per m² of said photographic material to be processed.
- 40 6. A method of claim 1, wherein said stabilizer has a pH value of 5.5 to 11.0.
  - 7. A method of claim 1, wherein said stabilizer has a temperature of 15 °C to 70 °C.
- **8.** A method of claim 1, wherein said photographic material contains at least one of two-equivalent couplers represented by the following formula 2eq-2 through 2eq-10:

formula 
$$2eq-2$$

$$(CH_3)_3CCOCHCONH$$

$$(R_1)_k$$

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# formula 2eq-3

$$(R_z)_0 \longrightarrow COCHCONH \longrightarrow (R_i)_k$$

wherein  $R_1$  and  $R_2$  represent each a hydrogen or a substituent; k and  $\ell$  are each an integer of 1 to 5, provided that when k and  $\ell$  are each not less than 2,  $R_1$  and  $R_2$  may be the same with or different from each other; and X represent a group capable of being released upon reaction with the oxidized product of an aromatic primary amine color developing agent,

## formula 2eq-4

$$R_3 - CONII \longrightarrow X$$

$$(R_2)_Q$$

# formula 2eq-5

$$R_3 - NII \longrightarrow X$$

$$(R_2)_Q$$

## formula 2eq-6

## formula eq-7

$$R_2$$
 $N$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 

wherein  $R_3$  represents a substituent; and  $R_1$ ,  $R_2$ , X and  $\ell$  are each synonymous with  $R_1$ ,  $R_2$ , X and  $\ell$  denoted in 2eq-2 and 2eq-3, respectively, provided that, when  $\ell$  is not less than 2,  $R_2$ s may be the same with or different from each other,

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# formula 2eq-8

OH NHCOR,

# formula 2eq-9

R.CONH X

# formula 2eq-10

(R<sub>2</sub>)<sub>p</sub> CONHR<sub>3</sub>

wherein  $R_2$  and  $R_3$  are each synonymous with those denoted in 2eq-4;  $R_4$  represents a substituent; m is an integer of 1 to 3; n is an integer of 1 or 2; p is an integer of 1 to 5, provided that, when m, n and p are each not less than 2,  $R_2$ s may be the same with or different from each other.

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