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(73) Proprietor : **KONICA CORPORATION**
26-2, Nishishinjuku 1-chome,
Shinjuku-ku
Tokyo 160 (JP)

(72) Inventor : **Inoue, Kenichi, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo (JP)
Inventor : **Mitsuhashi, Tsuyoshi, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo (JP)

(74) Representative : **Ellis-Jones, Patrick George Armine**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

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Jouve, 18, rue Saint-Denis, 75001 PARIS

Description

The present invention relates to a photographic developer for a silver halide photographic light-sensitive material capable of forming an image of high sensitivity and high density without silver sludge formation even when processed at low replenishing rates.

Sulfites such as sodium sulfite and potassium sulfite, used as antioxidants for photographic developers, have the ability to dissolve silver halide.

This results in the formation of a large amount of a sulfite-silver complex salt upon light-sensitive material processing, which complex salt elutes in the developer. The eluted silver complex is easily reduced by the developing agent, resulting in the accumulation of precipitated silver known as silver sludge.

In continuous processing using an automatic processing machine, this silver sludge, in suspension in the developer, adheres to the film and the rollers and belts of the automatic processing machine.

This can cause serious failures such as yellow-brown streak stains and flaws on the film during transport.

In recent years, processing solution retention in developing machine tanks has increased as the photographic processing solution replenishing rate has been reduced to meet requirements related to environmental conservation. Thus the amount of silver sludge being accumulated has increased.

Traditionally, there have been proposed a large number of methods for the prevention of silver sludge, including Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 114035/1983, using a thiouracil, Japanese Patent O.P.I. Publication No. 2043/1988, using a mercaptobenzoic acid, Japanese Patent Examined Publication No. 14953/1972, using an aliphatic mercaptocarboxylic acid, Japanese Patent O.P.I. Publication No. 178959/1987, Japanese Patent O.P.I. Publication No. 51844/1991, using a disulfide, Japanese Patent O.P.I. Publication No. 26136/1973, using a sulfur-containing α-amino acid, and various mercaptoazoles, all of which are compounds likely to form a water-soluble silver salt.

US-A-4141734 discloses a process for developing exposed photographic silver halide materials. The aqueous developer preparation used contains a developer compound for the silver halide, a water-soluble solvent for the silver halide and an aliphatic, cycloaliphatic, aromatic or heterocyclic di-or trisulphide, such as L-cystine.

US-A-4254215 discloses a process for the prevention of darkening and the formation of a sediment in photographic developer solutions which contain a silver halide developer, a water-soluble silver halide solvent and, as sulphur compounds, a combination of (a) an organic thiol compound or thione compound capable of tautomerism and (b) a Bunte salt which contains groups conferring solubility in water such as penicillamine or cysteine.

However, many of these compounds have the following drawbacks, and few are satisfactory for practical use.

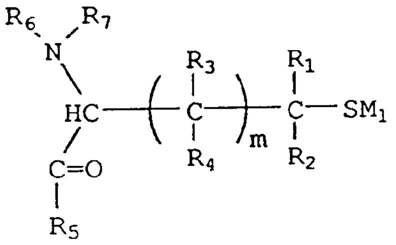
1) Air oxidation degrades the sludge preventing effect of the compounds in the developer.
2) Large amounts must be used to obtain the desired sludge preventing effect.
3) Use in large amounts deteriorates film sensitivity and gamma value.
4) Unpleasant from as are generated.
5) Expensive for processing solutions.

There has been a strong demand for the development of a new method free from these drawbacks.

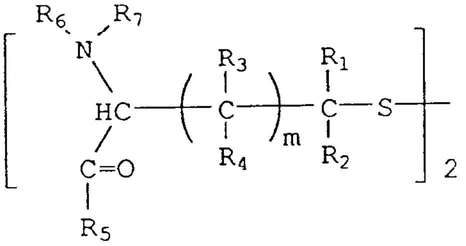
An object of the present invention is to to provide a developer which allows an image of excellent finish quality to be easily obtained without silver sludge formation, photographic developer stain and roller/belt stain even when used at low replenishing rates in the continuous processing of a large amount of light-sensitive material using an automatic processing machine, and which has a sludge-preventing effect without affecting the photographic performance.

According the present invention there is provided a developer for developing a silver halide photographic light-sensitive material which contains a compound represented by the following formula 1 or 2:

Formula 1



Formula 2



wherein R_1 and R_2 each independently represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms provided that R_1 and R_2 do not represent hydrogen atoms at the same time. R_3 and R_4 each independently represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms; R_5 represents a hydroxyl group, an amino group or an alkyl group having 1 to 3 carbon atoms. R_6 and R_7 each independently represent a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, an acyl group having up to 18 carbon atoms or a $-COOM_2$ group, provided that R_6 and R_7 do not represent hydrogen atoms at the same time. M_1 represents a hydrogen atom, an alkali metal atom or an ammonium group, and m represents 0, 1 or 2. M_2 is a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an alkali metal atom, an aryl group or an aralkyl group having not more than 15 carbon atoms.

The present invention is described in detail below. Alkyl groups having 1 to 4 carbon atoms as described above include a methyl group, an ethyl group, a propyl group and a butyl group.

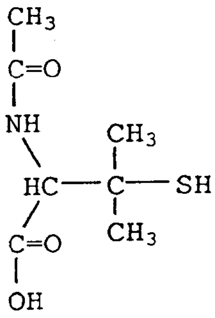
Examples of acyl groups having up to 18 carbon atoms include an acetyl group and a benzoyl group. Examples of aralkyl groups having up to 15 carbon atoms include a benzyl group and a phenethyl group. Aryl groups include a phenyl group and a naphthyl group.

Examples of alkali metal atoms for M_1 include sodium ion and potassium ion.

Although various methods of synthesis can be used to synthesize the above compounds used in the present invention, Strecker's method of amino acid synthesis, known to be an amino acid synthesis method, can be used, wherein amino acid acetylation is achieved by alternate addition of alkali and acetic anhydride in an aqueous solution.

Examples of the compounds used in the present invention, represented by formulas 1 and 2, respectively, are given below, which are not to be construed as limitative.

1



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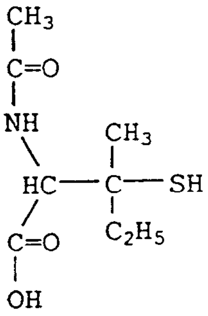

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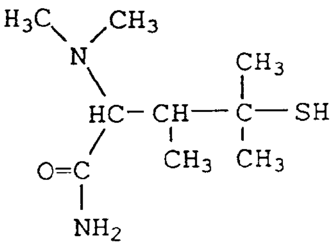

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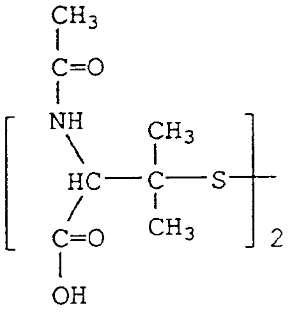

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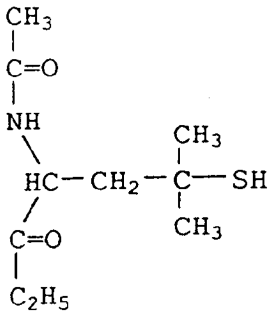

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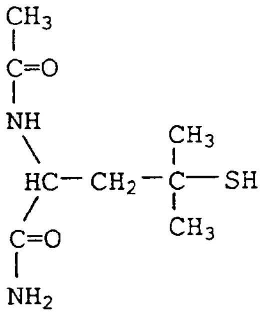

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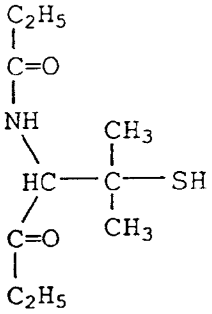

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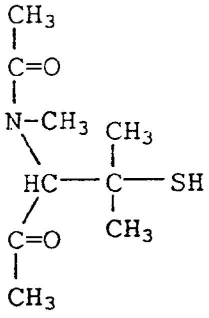

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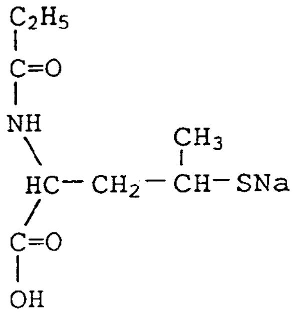


The above compounds used in the present invention may be used singly or in combination. It is also acceptable to use in combination at least one compound of formula 1 and at least one compound of formula 2.

The compounds of formulas 1 and 2 are used in amounts of preferably 1×10^{-5} to 3×10^{-2} mol, more preferably 1×10^{-4} to 1×10^{-2} mol per liter of developer. The replenishing rate for the developer of the present invention is normally 0.05 to 0.65 l, preferably 0.10 to 0.35 l per m^2 of light-sensitive material, though it varies depending on the kinds of light-sensitive material, automatic processing machine, and other factors.

Preferably, the developing through drying processes are completed within 90 seconds when an automatic processing machine capable of developing, fixing and washing or stabilizing is used to process a silver halide light-sensitive material.

In other words, the time from initiation of immersion of the tip of the light-sensitive material in the developer, via the various processes, to discharge of the same tip from the drying zone (what is called "dry to dry time") is preferably not longer than 90 seconds, more preferably not longer than 60 seconds.

Fixing temperature and time are preferably about 20 to 50°C and 6 to 20 seconds, more preferably 30 to 40°C and 6 to 15 seconds.

When the developer of the present invention is used, developing time is normally 5 to 45 seconds, preferably 8 to 30 seconds, and developing temperature is preferably 25 to 50°C, more preferably 30 to 40°C.

Drying may be achieved by hot air blowing at normally 35 to 100°C, preferably 40 to 80°C. Alternatively, a drying zone equipped with a far infrared heating means may be arranged in the automatic processing machine.

The automatic processing machine may be equipped with a mechanism for adding either water or an acidic rinsing solution having no fixing capability to the light-sensitive material, among the above developing, fixing and washing processes such as those described in Japanese Patent O.P.I. Publication No. 264953/199. The automatic processing machine may also have therein equipment for preparing developers and fixers.

The developer of the present invention preferably contains as a developing agent a 1,4-dihydroxybenzene compound or, if necessary, a p-aminophenol compound and/or a pyrazolidone compound.

1,4-dihydroxybenzenes include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dichlorohydroquinone, 2,3-dibromohydroquinone, 2,5-dimethylhydroquinone and hydroquinone monosulfonate, with preference given to hydroquinone. p-aminophenol-based developing agents include N-methyl-p-aminophenol, p-aminophenol, N-(β-hydroxyethyl)-p-aminophenol, N-(4-hydroxyphenyl)glycine, 2-methyl-p-aminophenol and p-benzylaminophenol, with preference given to N-methyl-p-aminophenol.

Examples of pyrazolidone compounds which can be used in the present invention include 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-ethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, 1,5-diphenyl-3-pyrazolidone, 1-p-tolyl-3-pyrazolidone, 1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone, 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone, 1-(2-benzothiazolyl)-3-pyrazolidone and 3-acetoxy-1-phenyl-3-pyrazolidone.

The amount of 1,4-dihydroxybenzene added is preferably 0.01 to 0.7 mol, more preferably 0.1 to 0.5 mol per liter of developer.

The amounts of p-aminophenol compound and pyrazolidone compound added are preferably 0.0005 to 0.2 mol, more preferably 0.001 to 0.1 mol per liter of developer.

Examples of sulfites optionally used in the developer of the present invention include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite and potassium metasulfite. The amount of these sulfites used is preferably 0.1 to 2.0 mol, more preferably 0.1 to 1.0 mol per liter of developer. Also, the upper limit is preferably 3.0 mol per liter of developer for a concentrated developer.

The developer may optionally contain a chelating agent having an iron ion chelating stability constant of over 8. The preferred iron ion mentioned herein is ferric ion (Fe^{3+}).

Chelating agents having an iron ion chelating stability constant of over 8 include organic carboxylic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxyl compounds.

Specifically, such chelating agents include ethylenediamine-di-o-hydroxyphenylacetic acid, triethylenetetramineacetic acid, diaminopropanetetraacetic acid, nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, 1,3-diamino-2-propanoltetraacetic acid, transcyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid, glycol ether amine tetraacetic acid, ethylenediamine-N,N,N′,N′-tetrakismethylenephosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-disulfonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate.

The developer of the present invention may optionally contain a hardener which enhances the film physical properties by reacting with the gelatin in the light-sensitive material during the developing process. Examples of hardeners include glutaraldehyde, α-methylglutaraldehyde, β-methylglutaraldehyde, maleic dialdehyde, succinic dialdehyde, methoxysuccinic dialdehyde, methylsuccinic dialdehyde, α-methoxy-β-ethoxyglutaraldehyde, α-n-butoxyglutaraldehyde, α, α-dimethoxysuccinic dialdehyde, β-isopropylsuccinic dialdehyde, α,α-diethylsuccinic dialdehyde, butylmaleic dialdehyde and bisulfite adducts thereof.

In addition to these components, the developer may further contain developing inhibitors such as sodium bromide and potassium iodide, organic solvents such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol and methanol, mercapto compounds such as 1-phenyl-5-mercaptotetrazole and sodium 2-mercaptobenzimidazole-5-sulfonate, and antifoggants such as 5-methylbenzotriazole and other benzotriazole compounds. Other additives such as toning agents, surfactants, defoaming agents may also be added as necessary.

The pH of the developer is preferably 9.0 to 12, more preferably 9.0 to 11.5. Examples of the alkali or buffer used for pH adjustment include pH regulators such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, boric acid, sodium tertiary phosphate and potassium tertiary phosphate.

A fixer used for fixing the light sensitive material developed by the developer of the invention may contain a fixing agent such as sodium thiosulfate or ammonium thiosulfate, with preference given to ammonium thiosulfate from the viewpoint of fixing speed. These fixing agents are usually used in amounts of about 0.1 to 6 mol/liter.

The fixer may also optionally contain a water-soluble aluminum salt as a hardener, such as aluminum chloride, aluminum sulfate or potassium alum.

The fixer may optionally incorporate malic acid, tartaric acid, citric acid, gluconic acid and derivatives thereof, singly or in combination. These compounds are effective when contained at not less than 0.001 mol per liter of fixer, with a greater effect obtained at 0.005 to 0.03 mol per liter of fixer.

Fixer pH is normally not lower than 3.8, preferably 4.2 to 7.0. In view of hardening in the fixer and the emission of sulfurous acid gas odor the pH is more preferably 4.3 to 4.8.

Silver halide photographic light-sensitive material emulsions to which the developer of the present invention is applicable include medical radiographic materials, photographic materials for printing plate making and direct positive photographic materials.

The silver halide photographic light-sensitive material to which the developer of the present invention is applied may comprise a silver halide such as silver iodobromide, silver iodochloride or silver iodochlorobromide, with preference given to silver iodobromide from the viewpoint of high sensitivity.

Suitable emulsions for the silver halide photographic light-sensitive material include monodispersed grains of high inner iodine content such as those disclosed in Japanese Patent O.P.I. Publication Nos. 177535/1984, 802237/1986, 132943/1986 and 49751/1988. Crystalline form may be, for example, cubic, tetradecahedral or octahedral, and intermediate (111) and (100) planes may be present in any ratio.

The emulsion may be of tabular grains having an aspect ratio of not less than 2. Such tabular grains have advantages such as improvements in spectral sensitizing efficiency, image granularity and sharpness, and are disclosed in British Patent No. 2,112,157, US Patent Nos. 4,439,520, 4,433,048, 4,414,310 and 4,434,226, and Japanese Patent O.P.I. Publication Nos. 113927/1983, 127921/1983, 138342/1988, 284272/1988 and 305343/1988. The emulsion can be prepared as described in these publications.

Additives and other substances used in the silver halide photographic light-sensitive material include those described in Research Disclosure Nos. 17643 (December, 1978), 18716 (November, 1979) and 308119 (December, 1989) (hereinafter referred to as RD17643, RD18716 and RD308119, respectively). The following table shows where they are described.

Item	RD17643		RD18716		RD308119	
	Page	Category	Page	Category	Page	Category
Chemical sensitizer	23	III	648, upper right	-	996	III
Sensitizing dye	23	IV	648-649	-	996-998	IV
Desensitizing dye	23	IV	-	-	998	B
Dye	25-26	VIII	649-650	-	1003	VIII
Developing accelerator	29	XXI	648, upper right	-	-	-
Antifoggant /Stabilizer	24	IV	649, upper right	-	1006-1007	VI
Brightening agent	24	V	-	-	998	V
Hardener	26	X	651, left	-	1004-1005	X
Surfactant	26-27	XI	650, right	-	1005-1006	XI
Antistatic agent	27	XII	650, right	-	1006-1007	XIII
Plasticizer	27	XII	650, right	-	1006	XII
Lubricant	27	XII	-	-	-	-
Matting agent	28	XVI	650, right	-	1008-1009	XVI
Binder	26	XXII	-	-	1003-1004	IX
Support	28	XVII	-	-	1009	XVII

EXAMPLES

Example 1

Preparation of emulsions A, B and C

1) Preparation of seed emulsion

While maintaining a temperature of 60°C, a pAg of 8 and a pH of 2.0, monodispersed cubic grains of silver iodobromide having an average grain size of 0.3 μm and a silver iodide content of 2 mol% were prepared by the double jet method.

The resulting reaction mixture was desalinized at 40°C, using an aqueous solution of Demol-N (produced by Kao Atlas) and an aqueous solution of magnesium sulfate, after which it was re-dispersed in an aqueous gelatin solution, to yield a seed emulsion.

2) Grain growth from seed emulsion

Using the above seed emulsion, grains were grown as follows: First, the seed emulsion was dispersed in an aqueous gelatin solution being kept at 40°C, and aqueous ammonia and acetic acid were added to obtain a pH of 9.7. An aqueous solution of ammoniacal silver nitrate and an aqueous solution of potassium bromide and potassium iodide were then added to the dispersion by the double jet method, while maintaining a pAg of 7.3 and a pH of 9.7, to yield a layer containing 35 mol% silver iodide. Next, another aqueous solution of ammoniacal silver nitrate and an aqueous solution of potassium bromide were added by the double jet method.

Until 95% of the desired grain size was reached, the pAg was kept at 9.0, with the pH varied continuously over the range of 9.0 to 8.0. The pAg was then changed to 11.0, and while keeping the pH at 8.0, grains were grown up to the desired grain size. Subsequently, acetic acid was added to obtain a pH of 6.0, after which 400 mg of the anhydride of 5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)oxacarbocyanine sodium salt was added per mol of silver halide. This mixture was then desalinized with the above aqueous solution of Demol-N and an aqueous solution of magnesium sulfate, and then re-dispersed in a gelatin solution.

Monodispersed silver iodobromide emulsions A, B and C, comprising tetradecahedral grains with round tips having an average silver iodide content of 2.0 mol%, were thus prepared, having average grain sizes of 0.40, 0.65 and 1.00 μm and variation coefficients of grain size distribution $(\sigma/\bar{r})$ of 0.17, 0.16 and 0.16, respectively, in which σ is the standard deviation of grain size distribution and $\bar{r}$ is the average grain size.

Preparation of emulsion D

1) Preparation of seed emulsion

A hexagonal tabular seed emulsion was prepared as follows:

Solution A

Ossein gelatin	60.2 g
Distilled water	20 l
Sodium salt of polyisopropylene-polyethyleneoxydisuccinate (10% aqueous ethanol solution)	5.6 ml
KBr	26.8 g
10% H_2SO_4	144 ml

Solution B

2.5 N aqueous $AgNO_3$ solution	3500 ml

Solution C

KBr	1029 g
KI	29.3 g

Water was added to 3500 ml.

Solution D

1.75 N aqueous KBr solution: amount required to obtain the silver potential shown below

64.1 ml of each of solutions B and C was added to solution A at 35°C by the double jet method over a period of 2 minutes, using the mixer stirrer described in Japanese Patent Examined Publication Nos. 58288/1983 and 58289/1983, whereby nuclei were formed.

After stopping the addition of solutions B and C, the temperature of solution A was increased to 60°C over a period of 60 minutes, and solutions B and C were again added by the double jet method at a flow rate of 68.5 ml/min over a period of 50 minutes, while keeping the silver potential (determined using a silver ion selective electrode in combination with a saturated silver-silver chloride electrode as a reference electrode) at +6 mV using solution D.

After completion of the addition, 3% KOH solution was added to obtain a pH of 6, followed by immediate desalinization and washing. The resulting emulsion was designated as seed emulsion Em 0. Electron microscopy revealed that this emulsion comprised hexagonal tabular silver halide grains not less than 90% by projected area of which had a ratio of the largest edge length to the shortest edge length of 1.0 to 2.0 and which tabular grains had an average thickness of 0.07 μm and an average diameter of 0.5 μm as an equivalent circle diameter.

Using the following four solutions, a tabular silver iodobromide emulsion D containing 1.53 mol% AgI was prepared.

Solution A

Ossein gelatin	29.4 g
Seed emulsion Em 0	Equivalent to 1.6 mol of AgI
Sodium salt of polyisopropylene-polyethyleneoxy-disuccinate (10% aqueous ethanol solution)	2.5 ml

Distilled water was added to 1400 ml.

Solution B

3.5 N aqueous $AgNO_3$ solution	2360 ml

Solution C

KBr	963 g
KI	27.4 g

Distilled water was added to 2360 ml.

Solution D

1.75 N aqueous KBr solution: amount to abtain the silver potential shown below

Grains were grown at 60°C by adding all of solutions B and C to solution A at a flow rate of 21.26 ml/min over a period of 111 minutes, using the mixer stirrer described in Japanese Patent Examined Publication Nos. 58288/1983 and 58289/1983 as above.

Throughout this operation, the silver potential was kept at +25 mV using solution D. After completion of the addition, the following spectral sensitizing dyes A and B were added in amounts of 300 mg and 15 mg, respectively, per mol of silver halide.

After the excess salts were removed by precipitation and desalinization with the same aqueous solutions of Demol-N and of magnesium sulfate as above, an aqueous solution of 92.2 g of ossein gelatin was added, and the mixture was stirred and re-dispersed.

A tabular silver iodobromide emulsion D having an average silver iodide content of 1.5 mol%, a projected area diameter of 0.96 μm, a coefficient of variation of 0.25 and an aspect ratio of 4.0 was thus prepared.

Sensitizing dye A:	Anhydride of 5,5′-dichloro-9-ethyl-3,3′di-(3-sulfopropyl)oxacarboxycyanine sodium salt
Sensitizing dye B:	Anhydride of 5,5′-di-(butoxycarbonyl)-1,1′-diethyl-3,3′-di-(4-sulfobutyl)benzimidazolocarbocyanine sodium salt

Sample preparation

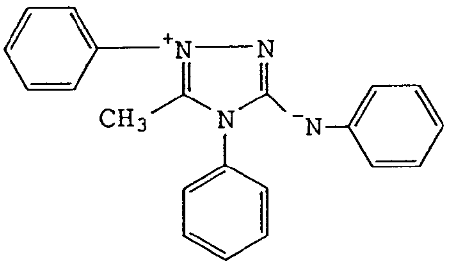
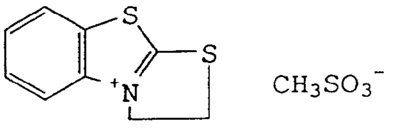
To each of the thus-obtained emulsions A, B, C and D, a 200:1 (w/w) mixture of the above sensitizing dyes A and B was added at 975 mg, 600 mg, 390 mg and 500 mg per mol of silver halide, respectively.

Ten minutes later, appropriate amounts of chloroauric acid, sodium thiosulfate and ammonium thiocyanate were added for optimum chemical sensitization. Fifteen minutes before completion of ripening, 200 mg of potassium iodide was added per mol of silver halide. Subsequently, 3×10^{-2} mol of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added per mol of silver halide, and this mixture was dispersed in an aqueous solution of 70 g of gelatin.

Of the four ripened emulsions, A, B and C were mixed in a weight ratio of 15:65:20, to yield emulsion I, while emulsion D, designated as emulsion II, was used by itself.

To each emulsion, the following additives were added. The amounts of addition are shown per mol of silver halide.

1,1-dimethylol-1-bromo-1-nitromethane	70 mg
t-butylcatechol	400 mg
Polyvinylpyrrolidone (molecular weight 10,000)	1.0 g

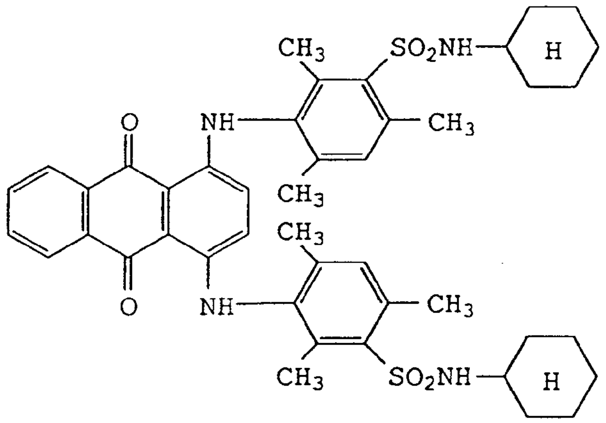
Styrene-maleic anhydride copolymer	2.5 g
Trimethylolpropane	10 g
Nitrophenyl-triphenylphosphonium chloride	50 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	15 mg
1-phenyl-5-mercaptotetrazole	10 mg
$C_4H_9OCH_2CH(OH)CH_2N(CH_2COOH)_2$	1 g
	60 mg
	35 mg
Dye dispersion (see below)	1.2 g

Preparation of dye dispersion

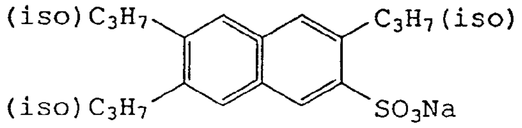
Ten Kilograms of the following dye was dissolved in a mixed solvent of 28 l of tricresyl phosphate and 85 l of ethyl acetate at 55°C. This solution is called the oily solution.

Separately, 270 l of a 9.3% aqueous solution of gelatin containing 1.35 kg of an anionic surfactant AS was prepared. This solution is called the aqueous solution. Next, the oily solution and the aqueous solution were placed in a dispersing vessel and dispersed while keeping the liquid temperature at 40°C. To the resulting dispersion were added appropriate amounts of phenol and 1,1-dimethylol-bromo-1-nitromethane, and water was added to 240 kg.

Dye

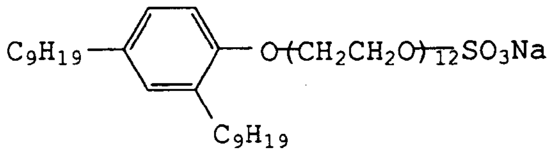
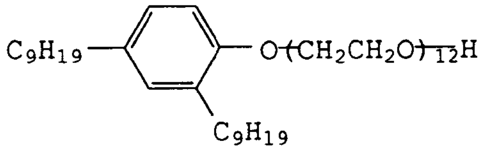
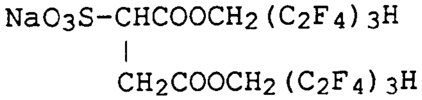


AS



The composition of the protective layer is as follows: The amounts of addition are shown per liter of coating solution.

Inert lime-processed gelatin	68 g
Acid-processed gelatin	2 g
Sodium isoamyl-n-decylsulfosuccinate	0.3 g
Polymethyl methacrylate (matting agent of area-average grain size of 3.5 μm)	1.1 g
Silicon dioxide grains (matting agent of area-average grain size of 1.2 μm)	0.5 g
Ludox AM (colloidal silica, produced by Du Pont)	30 g

40% aqueous solution of glyoxal (hardener)	1.5 ml
Bis(vinylsulfonylmethyl) ether (hardener)	500 mg
	1.0 mg
	0.4 mg
 $NaO_3S\text{-}\underset{\displaystyle CH_2COOCH_2(C_2F_4)_3H}{\underset{\vert}{CH}}COOCH_2(C_2F_4)_3H$	0.5 mg
$C_{12}H_{25}CONH(CH_2CH_2O)_5H$	2.0 g

The resulting coating solution was coated and dried uniformly on a blue-colored subbed polyethylene terephthalate film base 180 μm thick.

Using two slide hopper coaters, both the emulsion layer and the protective layer were coated simultaneously at a coating speed of 90 m per minute, to yield samples, wherein coating rates were 1.7 g/m^2 as of silver for the emulsion layer and 0.99 g/m^2 as of gelatin for the protective layer.

In Table 1, developing sample 1 was obtained from emulsion I, and developing sample 2 obtained from emulsion II.

The compositions of the developer and fixer used in the present invention are as follows:

Developer

Part A (for 12 liter of finished solution)

Potassium hydroxide	450 g
Potassium sulfite (50% solution)	2280 g
Diethylenetetraaminepentaacetic acid	120 g
Sodium hydrogen carbonate	132 g
5-methylbenzotriazole	1.2 g
1-phenyl-5-mercaptotetrazole	0.2 g
Hydroquinone	340 g

Water was added to 5000 ml.

Part B (for 12 liter of finished solution)

Glacial acetic acid	170 g
Triethylene glycol	185 g
1-phenyl-3-pyrazolidone	22 g
5-nitroindazole	0.4 g

Starter

Glacial acetic acid	120 g
Potassium bromide	225 g

Water was added to 1000 ml.

Fixer

Part A (for 18 liter of finished solution)

Ammonium thiosulfate (70 w/v%)	6000 g
Sodium sulfite	110 g
Sodium acetate trihydrate	450 g
Sodium citrate	50 g
Gluconic acid	70 g
1-(N,N-dimethylamino)-ethyl-5-mercaptotetrazole	18 g

Part B

Aluminum sulfate	800 g

To prepare the developer, parts A and B were added at the same time to about 5 liters of water, and while stirring and dissolving the mixture, water was added to 12 liters, and glacial acetic acid was added to obtain a pH of 10.40, to yield a developer replenisher.

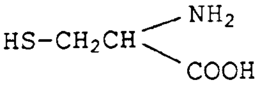
To this developer replenisher, the above starter was added at 20 ml/l, followed by pH adjustment to 10.26 before use.

To prepare the fixer, parts A and B were added at the same time to about 5 liters of water, and while stirring and dissolving the mixture, water was added to 18 liters, and sulfuric acid or NaOH were added to obtain a pH of 4.4, to yield a fixer replenisher.

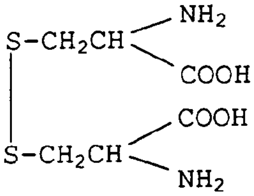
Based on the above developer compounds used in the present invention and comparative compounds were added as listed in Table 1 below to prepare developers, which were used for actual developing.

The following Comparative Compounds 1 - 12 were used as comparative compounds.

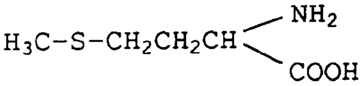
Comparative Compound 1: L-cysteine (free base)



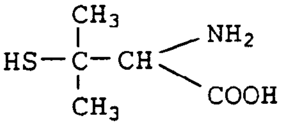
Comparative Compound 2: Cystine



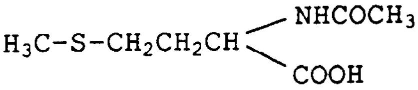
Comparative Compound 3: L-methionine



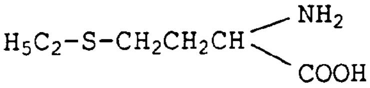
Comparative Compound 4: DL-penicillamine



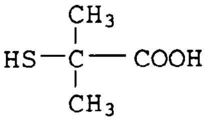
Comparative Compound 5: Acetylmethionine



Comparative Compound 6: DL-ethionine

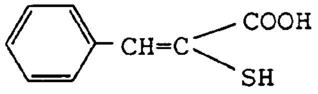


Comparative Compound 7: Mercaptoisobutyric acid

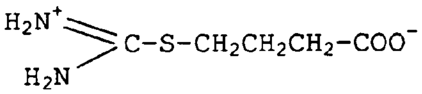


$$HS-C(CH_3)_2-COOH$$

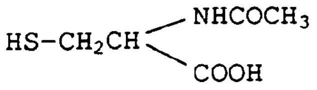
Comparative Compound 8: β-phenyl-α-mercaptoacrylic acid



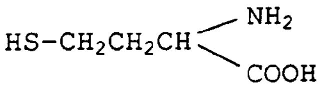
Comparative Compound 9: γ-isothioureidobutyric acid



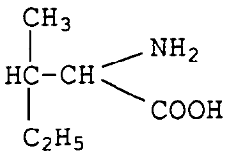
Comparative Compound 10: N-acetyl-L-cysteine



Comparative Compound 11: Homocysteine



Comparative Compound 12: Isoleucine



Developing was conducted using the roller transport automatic processing machines described below.

Automatic processing machine No.	Model (produced by Konica Corporation)	Processing conditions
1	SRX-1001	Dry to Dry, 45 sec.
2	SRX-502	Dry to Dry, 45 sec.
3	SRX-251	Dry to Dry, 65 sec.

Processing temperatures were 35°C for developing, 33°C for fixation, 20°C for washing and 50°C for drying.

The samples were evaluated as follows:

1. Sensitometry

The sample, inserted between two sheets of fluorescent sensitizing paper KO-250, manufactured by Konica Corp., was subjected to exposure through an aluminum wedge of at a tube voltage of 80 kV, a tube amperage of 100 mA and an irradiation time of 50 msec, after which it was processed using the above automatic processing machines. With respect to the processed sample, the reciprocal of the exposure amount required to obtain a density of base density + fog density + 1.0 was calculated as a percent sensitivity relative to the sensitivity of sample No. 1 processed with the above developer and fixer of basic composition using automatic processing machine No. 2 (experiment No. 15).

The density in the unexposed portion of the exposed sample was determined using Konica PDA-65 densitometer, and the base density was subtracted therefrom to obtain the fog density, and the maximum density was expressed as Dm. 2. Silver sludge evaluation

Next, developing samples, subjected to X-ray exposure to a density of 1.0 over the entire surface of the sample, were processed at a fixer replenishing rate of 300 cc/m^2 at 70 sheets per day for 30 consecutive days, using the above-described automatic processing machine Nos. 1, 2 and 3, wherein the developer replenishing rate and developing sample were changed as shown in Table 1.

The developing samples used were the above sample Nos. 1 and 2.

Upon processing, visual evaluation was made for possible stains on the developing rack, rollers and wall, and on the processed sample, using the following four grades:

A: Almost no silver sludge seen, with no stain on the rollers or wall.
B: Developer turbidity seen, with slight stain on the processing tank wall.
C: Silver sludge seen, with developing rack stain difficult to wash down.
D: Much silver sludge seen on the developer tank, causing image stain as a result of its adhesion to the film being processed.

3. Evaluation of residual silver

The above sample No. 2 was processed unexposed and evaluated for residual silver as follows:

One drop of a 2.6×10^{-3} mol/l aqueous solution of sodium sulfide, as the residual silver evaluating solution, was dropped on a surface of the above residual silver evaluating film. Three minutes later, the solution was thoroughly wiped away, and the film was kept standing at normal temperature and normal humidity for 15 hours.

Then, using a PDA-65 densitometer (produced by Konica Corporation), blue light transmission densities were determined for the portion where the residual silver evaluating solution was dropped and the other portion. The difference of the densities was used as the index of residual silver. The residual silver concentration in the processed film increases as this difference increases.

The results are given in Tables 1 through 3 below.

Table 1

Experiment No.	Automatic processing machine No.	Anti-silver sludge agent		Sensitometry		Residual silver	Developing sample	Developer replenishing rate (cc/m^2)	Silver sludge preventing effect
		Compound added	Amount of addition (mol/l)	Relative sensitivity	Dm				
1 (inventive)	2	No.1	0.0005	100	3.43	0.01	1	650	A
2 (inventive)	2	No.1	0.0005	100	3.45	0.00	1	325	A
3 (inventive)	2	No.1	0.0005	100	3.40	0.02	1	200	A
4 (inventive)	2	No.1	0.0005	100	3.50	0.01	2	650	A
5 (inventive)	2	No.1	0.0005	100	3.46	0.01	2	325	A
6 (inventive)	2	No.1	0.0005	100	3.49	0.00	2	200	A
7 (inventive)	2	No.1	0.00025	100	3.48	0.00	2	200	A
8 (inventive)	2	No.2	0.0005	100	3.48	0.00	2	650	A
9 (inventive)	2	No.2	0.0005	100	3.45	0.02	2	325	A
10 (inventive)	2	No.2	0.0005	100	3.46	0.02	2	200	A
11 (inventive)	2	No.6	0.0005	100	3.45	0.00	2	325	A
12 (inventive)	3	No.1	0.0005	100	3.46	0.00	2	200	A
13 (inventive)	3	No.1	0.0005	100	3.45	0.01	2	325	A
14 (inventive)	1	No.1	0.0005	100	3.46	0.00	2	200	A
15 (inventive)	2	No.1 No.4	0.00025 0.00025	100	3.42	0.01	2	200	A

Table 2

Experiment No.	Automatic processing machine No.	Anti-silver sludge agent		Sensitometry		Residual silver	Developing sample	Developer replenishing rate (cc/m^2)	Silver sludge preventing effect
		Compound added	Amount of addition (mol/1)	Relative sensitivity	Dm				
16 (comparative)	2	Not added	0	100	3.46	0.10	1	650	C
17 (comparative)	2	Not added	0	100	3.45	0.08	1	325	D
18 (comparative)	2	Not added	0	100	3.45	0.09	1	200	D
19 (comparative)	2	Not added	0	100	3.48	0.14	2	650	C
20 (comparative)	2	Not added	0	100	3.46	0.09	2	325	D
21 (comparative)	2	Not added	0	100	3.46	0.10	2	200	D
22 (comparative)	2	Comparative* 1	0.0005	90	2.90	0.11	2	650	B
23 (comparative)	2	Comparative 1	0.0005	90	2.91	0.10	2	325	D
24 (comparative)	2	Comparative 2	0.0005	90	3.01	0.09	2	650	B
25 (comparative)	2	Comparative 2	0.0005	90	3.05	0.10	2	325	D
26 (comparative)	2	Comparative 3	0.0005	83	3.03	0.11	2	650	B
27 (comparative)	2	Comparative 3	0.0005	83	2.95	0.11	2	325	D
28 (comparative)	2	Comparative 4	0.0005	86	2.93	0.10	2	650	B
29 (comparative)	2	Comparative 4	0.0005	86	2.93	0.09	2	325	D
30 (comparative)	2	Comparative 5	0.0005	81	3.12	0.10	2	650	B

Comparative*: Comparative compound

Table 3

Experiment No.	Automatic processing machine No.	Anti-silver sludge agent		Sensitometry		Residual silver	Developing sample	Developer replenishing rate (cc/m^2)	Silver sludge preventing effect
		Compound added	Amount of addition (mol/l)	Relative sensitivity	Dm				
31 (comparative)	2	Comparative 5	0.0005	81	3.12	0.10	2	325	D
32 (comparative)	2	Comparative 6	0.0005	82	3.02	0.15	2	650	B
33 (comparative)	2	Comparative 6	0.0005	82	3.02	0.20	2	325	D
34 (comparative)	2	Comparative 7	0.0005	80	2.89	0.13	2	650	B
35 (comparative)	2	Comparative 7	0.0005	80	2.89	0.10	2	325	D
36 (comparative)	2	Comparative 8	0.0005	90	2.91	0.08	2	650	B
37 (comparative)	2	Comparative 8	0.0005	90	2.93	0.12	2	325	D
38 (comparative)	2	Comparative 9	0.0005	95	3.15	0.13	2	650	B
39 (comparative)	2	Comparative 9	0.0005	95	3.15	0.14	2	325	D
40 (comparative)	2	Comparative 10	0.0005	88	2.87	0.11	2	650	B
41 (comparative)	2	Comparative 10	0.0005	88	2.86	0.10	2	325	D
42 (comparative)	2	Comparative 11	0.0005	81	2.94	0.09	2	650	B
43 (comparative)	2	Comparative 11	0.0005	81	2.94	0.10	2	325	D
44 (comparative)	2	Comparative 12	0.0005	80	2.88	0.12	2	650	B
45 (comparative)	2	Comparative 12	0.0005	80	2.88	0.10	2	325	D

As seen in these tables, according to the present invention, silver sludge is substantially prevented without photographic performance deterioration even at reduced developer replenishing rates.

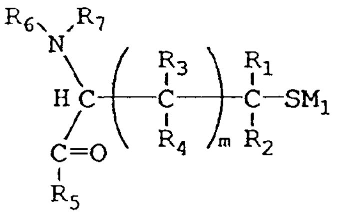
Specifically, Table 1 shows that the addition of the compound used in the present invention to the developer did not lower the sensitivity or Dm (maximum density), while the addition of a comparative compound significantly lowered the sensitivity, though it had a slight preventative effect on silver sludge at high replenishing rates.

Results of experiment Nos. 1 through 10 demonstrate that developers containing a compound used in the present invention remain excellently effective without deterioration of the silver sludge preventing effect even when the replenishing rate is reduced to 200 ml/m^2. Also, the results of experiment Nos. 12 and 14 demonstrate that there is no difference in silver sludge preventing effect among different automatic processing machines.

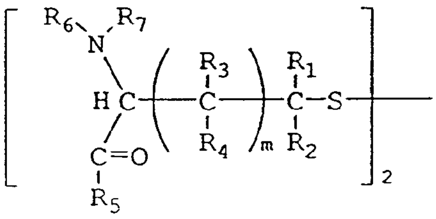
An unexpected finding is that the present invention offers improved fixing performance with no residual silver.

Claims

1. A developer suitable for developing a silver halide photographic light-sensitive material comprising a compound represented by Formula 1 or Formula 2;



(1)



(2)

wherein R_1 and R_2 each independently represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms provided that both of R_1 and R_2 do not represent hydrogen atoms; R_3 and R_4 each independently represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms; R_5 represents a hydroxy group, an amino group or an alkyl group having 1 to 3 carbon atoms; R_6 and R_7 each independently represent a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, an acyl group having 1 to 18 carbon atoms or a -COOM$_2$ group, provided that both of R_6 and R_7 do not represent hydrogen atoms; M_1 is a hydrogen atom, an alkali metal atom or an ammonium group; m represents an integer 0, 1 or 2; M_2 is a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an alkali metal atom, an aryl group or an aralkyl group having not more than 15 carbon atoms.

2. The developer of claim 1 which contains said compound represented by formula 1 or 2 in an amount of 1×10^{-5} to 3×10^{-2} mol per liter.

3. The developer of claim 2, which contains said compound represented by formula 1 or 2 in an amount of 1×10^{-4} to 3×10^{-2} mol per liter.

4. The developer of any one of the previous claims, which contains a 1,4-dihydroxybenzene compound.

5. The developer of claim 4, which contains said 1,4-dihydroxybenzene compound is an amount of 0.01 mol to 0.7 mol per liter.

6. The developer of claim 5, which contains said 1,4-dihydroxybenzene compound in an amount of 0.1 mol

to 0.5 mol per liter.

7. The developer of any one of the preceding claims, which contains a p-aminophenol compound or a pyrazolidone compound.

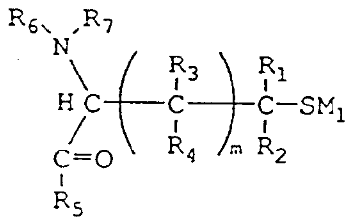
8. The developer of claim 7, which contains said p-aminophenol compound or said pyrazolidone compound in an amount of 0.0005 mol to 0.2 mol per liter.

9. The developer of claim 8, which contains said p-aminophenol compound or said pyrazolidone compound in an amount of 0.001 mol to 0.1 mol per liter.

10. The developer according to claim 1 comprising a compound represented by Formula 1 or Formula 2 in an amount of from 1 x 10^{-4} to 3 x 10^{-2} mol per liter, a 1,4-dihydroxybenzene compound in an amount of from 0.1 mol to 0.5 mol per liter, and a p-aminophenol compound or a pyrazolidone compound in an amount of from 0.001 mol to 0.1 mol per liter.

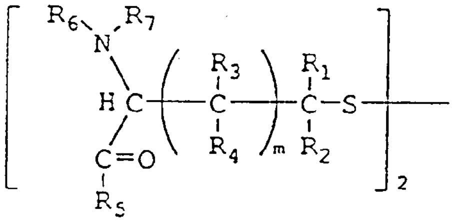
Patentansprüche

1. Zum Entwickeln eines lichtempfindlichen photographischen Silberhalogenid-Aufzeichnungsmaterials geeigneter Entwickler mit einer Verbindung der Formel 1 oder der Formel 2:



$$(R_6R_7N)(R_5C{=}O)HC-\left(CR_3R_4\right)_m-CR_1R_2-SM_1$$

(1)



$$\left[(R_6R_7N)(R_5C{=}O)HC-\left(CR_3R_4\right)_m-CR_1R_2-S\right]_2$$

(2)

worin bedeuten:

R_1 und R_2 jeweils unabhängig voneinander ein Wasserstoffatom oder eie Alkylgruppe mit 1 bis 3 Kohlenstoffatom(en), wobei nicht beide Reste R_1 und R_2 für Wasserstoffatome stehen dürfen;

R_3 und R_4 jeweils unabhängig voneinander ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 3 Kohlentoffatom(en);

R_5 eine Hydroxygruppe, eine Aminogruppe oder eine Alkylgruppe mit 1 bis 3 Kohlenstoffatom(en);

R_6 und R_7 jeweils unabhängig voneinander ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 5 Kohlenstoffatom(en), eine Acylgruppe mit 1 bis 18 Kohlenstoffatom(en) oder eine -$COOM_2$-Gruppe, wobei nicht beide Reste R_6 und R_7 für Wasserstoffatome stehen dürfen; M_1 ein Wasserstoffatom, ein Alkalimetallatom oder eine Ammoniumgruppe;

m eine ganze Zahl, nämlich 0, 1 oder 2;

M_2 ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatom(en), ein Alkalimetallatom, eine Arylgruppe oder eine Aralkylgruppe mit nicht mehr als 15 Kohlenstoffatomen.

2. Entwickler nach Anspruch 1, welcher die betreffende Verbindung der Formel 1 oder 2 in einer Menge von 1 x 10^{-5} bis 3 x 10^{-2} Mol/l enthält.

3. Entwickler nach Anspruch 2, welcher die betreffende Verbindung der Formel 1 oder 2 in einer Menge von

1 x 10^{-4} bis 3 x 10^{-2} Mol/l enthält.

4. Entwickler nach einem der vorhergehenden Ansprüche, der eine 1,4-Dihydroxybenzolverbindung enthält.

5. Entwickler nach Anspruch 4, der die betreffende 1,4-Dihydroxybenzolverbindung in einer Menge von 0,01 Mol bis 0,7 Mol/l enthält.

6. Entwickler nach Anspruch 5, der die betreffende 1,4-Dihydroxybenzolverbindung in einer Menge von 0,1 Mol bis 0,5 Mol/l enthält.

7. Entwickler nach einem der vorhergehenden Ansprüche, der eine p-Aminophenol- oder eine Pyrazolidonverbindung enthält.

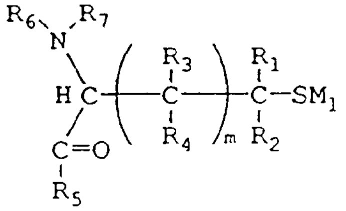
8. Entwickler nach Anspruch 7, der die betreffende p-Aminophenol- oder die betreffende Pyrazolidonverbindung in einer Menge von 0,0005 Mol bis 0,2 Mol/l enthält.

9. Entwickler nach Anspruch 8, der die betreffende p-Aminophenol- oder die betreffende Pyrzolidonverbindung in einer Menge von 0,001 Mol bis 0,1 Mol/l enthält.

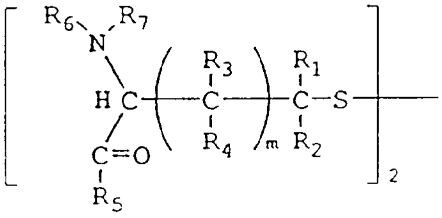
10. Entwickler nach Anspruch 1, umfassend eine Verbindung der Formel 1 oder der Formel 2 in einer Menge von 1 x 10^{-4} bis 3 x 10^{-2} Mol/l, eine 1,4-Dihydroxybenzolverbindung in einer Menge von 0,1 Mol bis 0,5 Mol/l und eine p-Aminophenol- oder eine Pyrazolidonverbindung in einer Menge von 0,001 Mol bis 0,1 Mol/l.

Revendications

1. Agent de développement destiné à développer un matériau photographique photosensible à base d'halogénure d'argent, comprenant un composé représenté par la formule 1 ou la formule 2 :



$$(R_6R_7N)(R_5C{=}O)HC{-}\left(CR_3R_4\right)_m{-}CR_1R_2{-}SM_1 \qquad (1)$$



$$\left[(R_6R_7N)(R_5C{=}O)HC{-}\left(CR_3R_4\right)_m{-}CR_1R_2{-}S{-}\right]_2 \qquad (2)$$

où R_1 et R_2 représentent, chacun indépendamment, un atome d'hydrogène ou un groupe alkyle ayant de 1 à 3 atomes de carbone, étant entendu que R_1 et R_2 ne représentent pas à la fois des atomes d'hydrogène ; R_3 et R_4 représentent, chacun indépendamment, un atome d'hydrogène ou un groupe alkyle ayant de 1 à 3 atomes de carbone; R_5 représente un groupe hydroxy, un groupe amino ou un groupe alkyle ayant 1 à 3 atomes de carbone ; R_6 et R_7 représentent, chacun indépendamment, un atome d'hydrogène, un groupe alkyle ayant 1 à 5 atomes de carbone, un groupe acyle ayant 1 à 18 atomes de carbone ou un groupe -$COOM_2$, étant entendu que R_6 et R_7 ne représentent pas à la fois des atomes d'hydrogène ; M_1 est un atome d'hydrogène, un atome de métal alcalin ou un groupe ammonium ; m est égal à un nombre entier qui vaut 0, 1 ou 2 ; M_2 est un atome d'hydrogène, un groupe alkyle ayant 1 à 4 atomes de carbone, un atome de métal alcalin, un groupe aryle ou un groupe aralkyle n'ayant pas plus de 15 atomes de carbone.

2. Agent de développement selon la revendication 1, qui contient ledit composé représenté par la formule 1 ou 2 dans une proportion de 1×10^{-5} à 3×10^{-2} mole par litre.

3. Agent de développement selon la revendication 2, qui contient ledit composé représenté par la formule 1 ou 2 dans une proportion de 1×10^{-4} à 3×10^{-2} mole par litre.

4. Agent de développement selon l'une quelconque des revendications précédentes, qui contient un composé 1,4-dihydroxybenzène.

5. Agent de développement selon la revendication 4, qui contient ledit composé 1,4-dihydroxybenzène dans une proportion de 0,01 mole à 0,5 mole par litre.

6. Agent de développement selon la revendication 5, qui contient ledit composé 1,4-dihydroxybenzène dans une proportion de 0,1 mole à 0,5 mole par litre.

7. Agent de développement selon l'une quelconque des revendications précédentes, qui contient un composé p-aminophénol ou un composé pyrazolidone.

8. Agent de développement selon la revendication 7, qui contient ledit composé p-aminophénol ou ledit composé pyrazolidone dans une proportion de 0,0005 mole à 0,2 mole par litre.

9. Agent de développement selon la revendication 8, qui contient ledit composé p-aminophénol ou ledit composé pyrazolidone dans une proportion de 0,001 mole à 0,1 mole par litre.

10. Agent de développement selon la revendication 1, comprenant un composé représenté par la formule 1 ou la formule 2 dans une proportion de 1×10^{-4} à 3×10^{-2} mole par litre, un composé 1,4-dihydroxybenzène dans une proportion de 0,1 mole à 0,5 mole par litre et un composé p-aminophénol ou un composé pyrazolidone dans une proportion de 0,001 mole à 0,1 mole par litre.