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(54) Silver halide photographic lightsensitive material.

(57) A photographic material which comprises a light-sensitive silver halide emulsion layer and a non-light-sensitive hydrophilic colloid layer provided outside of the light-sensitive silver halide emulsion layer to the supportis disclosed. Total content of gelatin of the layers at a side of the silver halide emulsion layer is 2.0 to 2.8 g/m^2 and the non-light-sensitive hydrophilic colloid layer contains a polymer latex. The material provides a high contrast image and is suitable for the use of lithography.

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SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material for graphic arts use, and more particularly to a silver halide photographic light-sensitive material for graphic arts use which is excellent in the ultra-high-speed processability as well as in the coatability.

BACKGROUND OF THE INVENTION

In the printing and graphic arts industry, there has been a growing demand for more speedup of processing and more improved image quality; for example, there has been desired a graphic arts silver halide photographic light-sensitive material which can be subjected to a ultra-high-speed processing in a dry-to-dry processing time of only 60 seconds to provide a contrasty image with a gamma value of 6.0 or more in a density of 0.3 to 3.0.

One method for achieving such a ultra-high-speed process ing as in the 60-second dry-to-dry time is to perform developing and fixing at raised temperatures, but the method is unacceptable because of affecting the preservability of processing solutions and increasing the vapor therefrom into the processing room. It is therefore desirable to manage to perform such the ultra-high-speed processing at a low temperature (not higher than 38 $^{\circ}$ C). Also, reducing the amount of silver is effective in a high-speed processing. However, there is a correction work called 'reduction' in a plate-making process, so that it is necessary to provide therefor a high silver-content silver halide photographic light-sensitive material which contains not less than 3.5g/m^2 of silver and yet adaptable to ultra-high-speed processing. A very useful means for processing at a low temperature such the high silver-content silver halide photographic light-sensitive material is to reduce the amount of the binder, particularly gelatin, contained therein. However, reducing the amount of gelatin invites deterioration of the coatability to cause an uneven and nonuniform coating or a rainbow-colored gloss on the coated surface due to changes in the thickness - so-called rainbow mottle, thus resulting in a drop of the light-sensitive material's productivity.

Another notable problem caused by reducing the amount of gelatin is the appearance of a lot of pinholes attributable to the matting agent contained usually in the outermost layer.

In a dry-to-dry ultra-high-speed processing for not longer than 60 seconds, the drying time is preferably within 15 seconds. In order to shorten the drying time, to the drying system of ordinary automatic processors (dry-to-dry 80 to 150 seconds) are taken various measures such as increasing the drying air quantity, reducing the drying air humidity, raising the drying temperature, and using a far-infrared heater, ultrasonic oscillator or microwave dryer. The difference between such drying systems largely affects the change in the dimensions of a light-sensitive material before and after the processing thereof. Therefore, it is necessary to provide a light-sensitive material capable of showing the same dimensional change even when treated in different drying conditions.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a silver halide photographic light-sensitive material which is capable of keeping its high productivity with very little coating unevenness or rainbow mottle despite its gelatin content being as small as 2.0 to 2.8g/m^2.

It is another object of the present invention to provide a silver halide photographic light-sensitive material capable of forming a contrasty image of which the gamma value in a density of 0.3 to 3.0 is not lower than 6.

It is a further object of the present invention to pro vide a silver halide light-sensitive material capable of always giving an almost constant change in its dimensions before and after processing regardless of the drying time and drying system used.

A silver halide photographic light-sensitive material of the invention comprises a support having thereon at least one light-sensitive silver halide emulsion layer and at least one non-light-sensitive hydrophilic colloid

layer provided on the outside of said silver halide emulsion layer to the support, in which the total gelatin content of said layers containing said light-sensitive silver halide emulsion layer is 2.0 to 2.8g/m^2 and at least one of said non-light-sensitive hydrophilic colloid layers contains a polymer latex.

DETAILED DESCRIPTION OF THE INVENTION

In order to make the above light-sensitive material highly contrasty, it is necessary to incorporate into at least one of the hydrophilic colloid layers thereof a tetrazolium compound or a hydrazine compound.

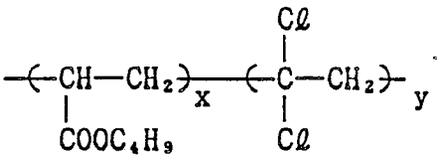
The polymer latex to be contained in the photographic light-sensitive material of the invention includes those hydrates of vinyl polymers with the acrylates, methacrylates, and styrenes described in U.S. Patent Nos. 2,772,166, 3,325,286, 3,411,911, 3,311,912 and 3,525,620; and Research Disclosure No. 19551 (195) (July, 1980).

Useful examples of the polymer latex for the invention include homopolymers of metha-alkyl acrylates such as methyl methacrylate or ethyl methacrylate; copolymers of a metha-alkyl acrylate or styrene with acrylic acid, N-methylol-acrylamide or glycidol methacrylate; homopolymers of alkyl acrylates such as methyl acrylate, ethyl acrylate or butyl acrylate, or copolymers of an alkyl acrylate with acrylic acid or N-methylol-acrylamide (acrylic acid component of the copolymer is preferably up to 30% by weight); homopolymers of butadiene or copolymers of butadiene with one or more of styrene, butoxymethylacrylamide and acrylic acid; and vinylidene chloridemethyl acrylate-acrylic acid tri-copolymers.

The following are particular examples of the polymer latex suitably usable in the invention.

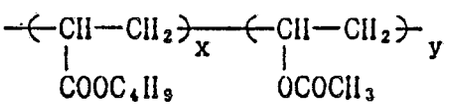
Exemplified latex compounds:

L — 1



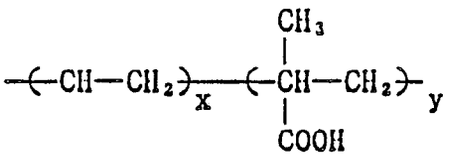
(x/y=50/50)

L — 2



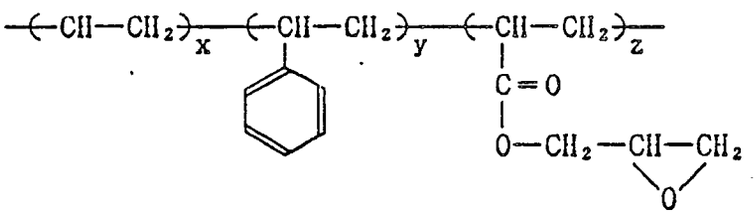
(x/y=50/50)

L — 3



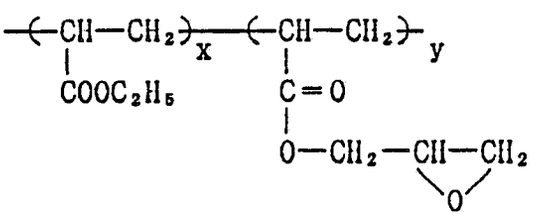
(x/y=95.6/4.4)

L — 4



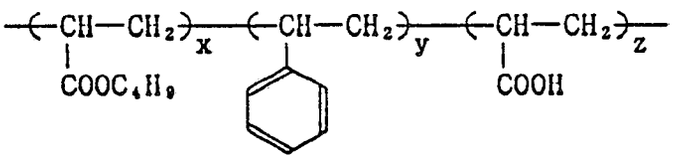
(x/y/z=40/20/40)

L — 5



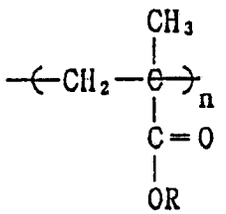
(x／y＝50／50)

L — 6



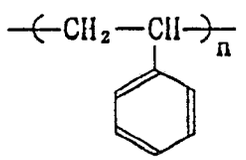
(x／y／z＝39.4／59／1.6)

L — 7

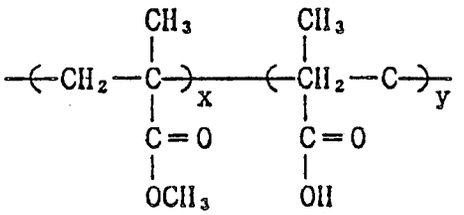


R : —CH_3, C_2H_5, C_4H_9

L — 8

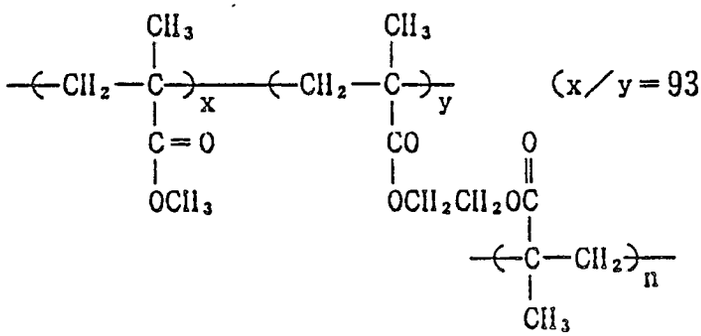


L — 9



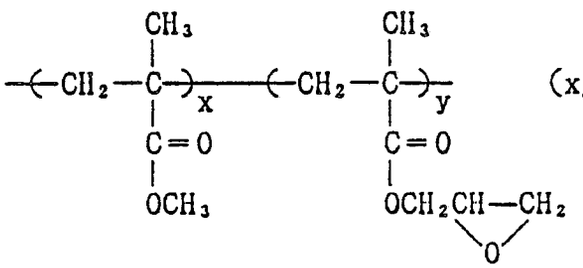
(x／y＝93／7)

L — 10



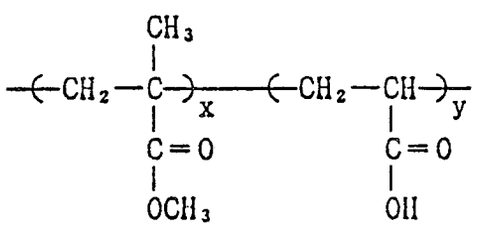
(x／y＝93／7)

L — 11



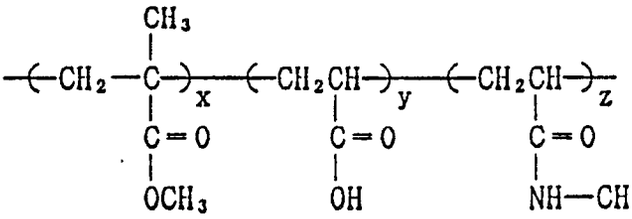
(x／y＝93／7)

L — 12



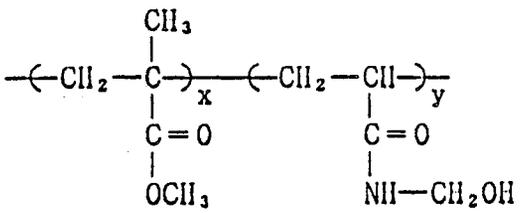
(x／y＝93／7)

L — 13



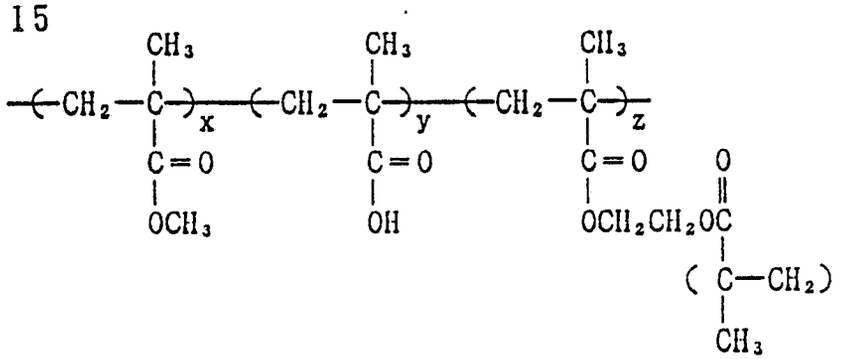
(x／y／z＝93／3／4)

L — 14



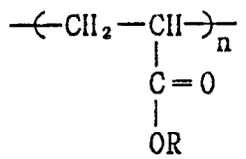
(x／y＝93／7)

L — 15



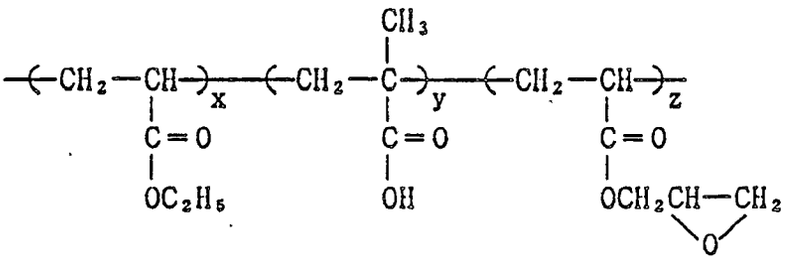
(x／y／z＝93／3／4)

L — 16



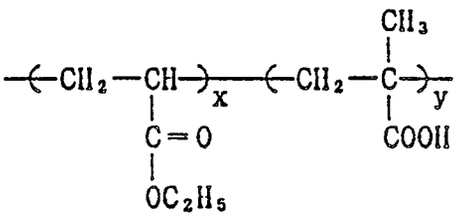
R : —CH_3, —C_2H_5, —C_4H_9

L — 17



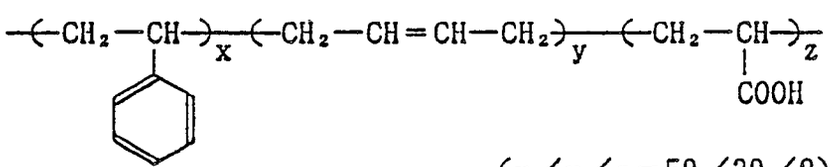
(x/y/z=93/3/4)

L — 18



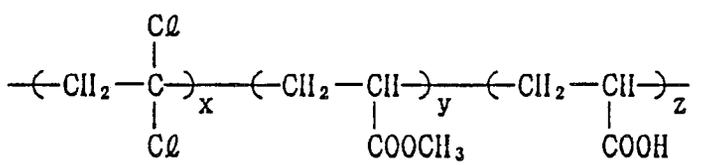
(x/y=93/7)

L — 19



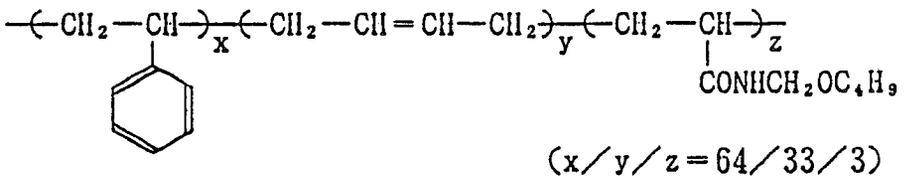
(x/y/z=59/39/2)

L — 20



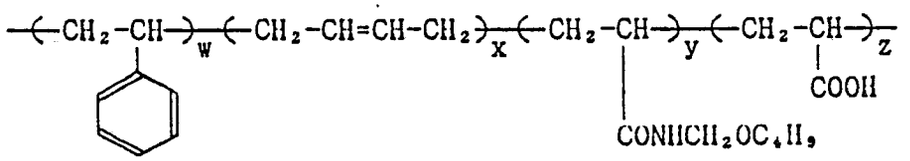
(x/y/z=85/13/2)

L — 21



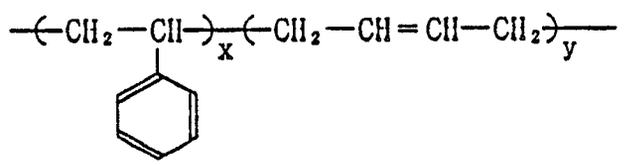
(x/y/z = 64/33/3)

L — 22



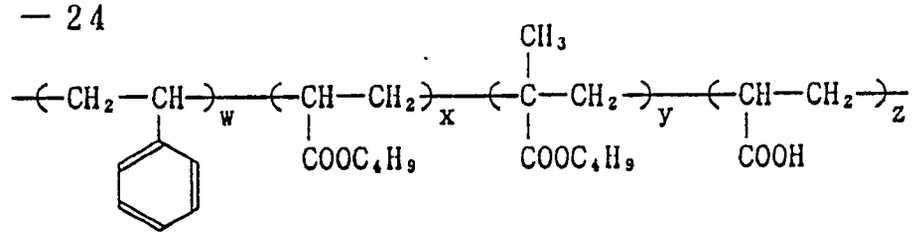
(w/x/y/z = 63/32/3/2)

L — 23



(x/y = 67/33)

L — 24



(w/x/y/z = 45/43/8/4)

The polymer latex used in the invention has an average particle size of preferably 0.005 to 1μm, more preferably 0.02 to 0.5μm, and most preferably not more than 0.1μm.

The polymer latex used in the invention may be contained on either one side or both sides of the support. When contained on both sides, the kind and/or amount of the polymer latex contained on each side may be either the same or different.

As long as the polymer latex is added to at least one of the non-light-sensitive hydrophilic colloid layers provided on the outside of the silver halide emulsion layer to the support, the polymer latex may be added also to any layers other than the non-light-sensitive hydrophilic colloid layer. Where contained on the side including the light-sensitive emulsion layer, the polymer latex may be contained in the emulsion layer and also in the topmost non-light-sensitive colloid layer as a protective layer, not to mention other layers such as a subbing layer and an intermediate layer, if any, between the silver halide emulsion layer and the

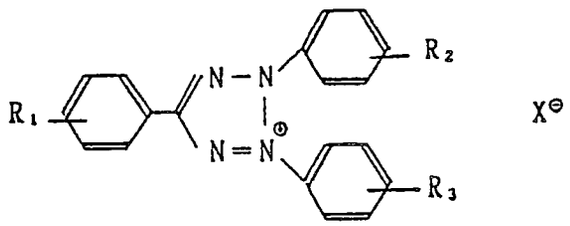
topmost layer. Further, the polymer latex, if present on the multilayer side of the support, may be contained in any single layer.

In the invention, the amount of the polymer latex with a particle size of not more than 1μm dispersedly contained in at least one of the non-light-sensitive hydrophilic colloid layers provided outside the emulsion layer on the emulsion side of the support is preferably not less than 0.18g/m^2, and the total amount of the polymer latex contained in the whole non-light-sensitive hydrophilic colloid layers outside the emulsion layer is preferably not less than 0.2g/m^2.

The polymer latex content of at least one of the non-light-sensitive hydrophilic colloid layers on the outside of the silver halide emulsion layer to the support is preferably 0.01g/m^2 to 1.0g/m^2, and more preferably 0.02g/m^2 to 0.6g/m^2. The gelatin content of the hydrophilic colloid layer to which the polymer latex is added is preferably 0.1g/m^2 to 1.5g/m^2, and more preferably 0.3g/m^2 to 1.2g/m^2. Also, in the invention, the polymer latex is contained preferably in an amount of not less than 0.05g/m^2 in at least one emulsion layer and not less than 0.1g/m^2 in the whole emulsion layers. The gelatin content of the emulsion layers is preferably 0.3 to 2.2g/m^2, and more preferably 0.5 to 2.2g/m^2.

The tetrazolium compound used in the invention is a compound represented by the following Formula I:

Formula I

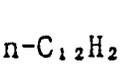


In Formula I, R_1, R_2 and R_3 each represents an alkyl group such as methyl, ethyl, cyclopropyl, propyl, isopropyl, cyclobutyl, butyl, isobutyl, pentyl or cyclohexyl; an amono group; an acylamino group such as acetylamino; a hydroxyl group; an alkoxy group such as methoxy, ethoxy, propoxy, butoxy or pentoxy; an acyloxy group such as acetyloxy; a halogen atom such as fluorine, chlorine or bromine; a carbamoyl group; an acylthio group such as acetylthio; an alkoxycarbonyl group such as ethoxycarbonyl; a carboxyl group; an acyl group such as acetyl; a cyano group, a nitro group, a mercapto group, a sulfoxy group or an aminosulfoxy group.

X^- is an anion, including halogen ions such as a chloride ion, a bromide ion and an iodide ion; acid radicals of inorganic acids such as nitric acid, sulfuric acid and perchloric acid; acid radicals of organic acids such as sulfonic acid and carboxylic acid; anionic activators including lower alkylbenzenesulfonic acid anions such as p-toluenesulfonic acid anion; higher alkylbenzenesulfonic acid anions such as p-dodecylbenzenesulfonic acid anion; higher alkyl sulfonate anions such as lauryl sulfate anion; boric acid anions such as tetraphenylboron; dialkylsulfo succinate anions such as di-2-ethylhexylsulfo succinate anion; polyether-alcohol sulfate anions such as polyethenoxy cetyl alcohol sulfate anion; higher aliphatic anions such as stearic acid anion; and those polymers provided with acid radicals such as polyacrylic acid anions.

Examples of the compound represented by Formula I usable in the invention are listed in Table 1, but the invention is not limited by the examples

Table 1

Compound No.	R_1	R_2	R_3	$X^{\ominus}$
I − 1	H	H	H	$Cl^{\ominus}$
I − 2	H	p-CH_3	p-CH_3	$Cl^{\ominus}$
I − 3	H	m-CH_3	m-CH_3	$Cl^{\ominus}$
I − 4	H	o-CH_3	o-CH_3	$Cl^{\ominus}$
I − 5	p-CH_3	p-CH_3	p-CH_3	$Cl^{\ominus}$
I − 6	H	p-OCH_3	p-OCH_3	$Cl^{\ominus}$
I − 7	H	m-OCH_3	m-OCH_3	$Cl^{\ominus}$
I − 8	H	o-OCH_3	o-OCH_3	$Cl^{\ominus}$
I − 9	p-OCH_3	p-OCH_3	p-OCH_3	$Cl^{\ominus}$
I − 10	H	p-C_2H_5	p-C_2H_5	$Cl^{\ominus}$
I − 11	H	m-C_2H_5	m-C_2H_5	$Cl^{\ominus}$
I − 12	H	p-C_3H_7	p-C_3H_7	$Cl^{\ominus}$
I − 13	H	p-OC_2H_5	p-OC_2H_5	$Cl^{\ominus}$
I − 14	H	p-OCH_3	p-OCH_3	$Cl^{\ominus}$
I − 15	H	p-OCH_3	p-OC_2H_5	$Cl^{\ominus}$
I − 16	H	p-OC_5H_{11}	p-OCH_3	$Cl^{\ominus}$
I − 17	H	p-OC_8H_{17}-n	p-OC_8H_{17}-n	$Cl^{\ominus}$
I − 18	H	p-$C_{12}H_{25}$-n	p-$C_{12}H_{25}$-n	$Cl^{\ominus}$
I − 19	H	p-$N(CH_3)_2$	p-$N(CH_3)_2$	$Cl^{\ominus}$
I − 20	H	p-NH_2	p-NH_2	$Cl^{\ominus}$
I − 21	H	p-OH	p-OH	$Cl^{\ominus}$
I − 22	H	m-OH	m-OH	$Cl^{\ominus}$
I − 23	H	p-Cl	p-Cl	$Cl^{\ominus}$
I − 24	H	m-Cl	m-Cl	$Cl^{\ominus}$
I − 25	p-CN	p-CH_3	p-CH_3	$Cl^{\ominus}$
I − 26	p-SH	p-OCH_3	p-OCH_3	$Cl^{\ominus}$
I − 27	H	p-OCH_3	p-OCH_3	n-$C_{12}H_{25}$-  -$SO_3^{\ominus}$

These tetrazolium compounds of the invention can be easily synthesized in accordance with those methods described in the Chemical Reviews, vol.55, pp.335 to 483.

The tetrazolium compound having Formula I of the invention may be used in the amount range of about 1 mg to about 10g, and preferably about 10 mg to about 2g per mole of silver halide.

The tetrazolium compound having Formula I of the invention may be used alone or in combination of two or more kinds thereof in an arbitrary ratio. Further, the tetrazolium compound of the invention may be used in combination in an arbitrary ratio with other tetrazolium compound outside the invention.

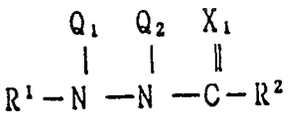
In the invention, when an anion capable of combining with the tetrazolium compound of the invention to lower the hydrophilicity thereof is used in combination therewith, particularly good results can be obtained. Examples of the anion include acid radicals of inorganic acids such as perchloric acid; acid radicals of organic acids such as sulfonic acid and carboxylic acid; anionic activators including lower alkylbenzenesulfonic acid anions such as p-toluenesulfonic acid anions, p-dodecylbenzenesulfonic acid anions, alkylnaph-

thalenesulfonic acid anions, lauryl sulfate anions, tetraphenylborons, dialkylsulfo succinate anions such as di-2-ethylhexylsulfo succinate anions, polyether-alcohol sulfate anions such as polyethenoxy cetyl alcohol sulfate anions, stearic acid anions, and polyacrylic acid anions.

Such the anion may, after being mixed with a tetrazolium compound of the invention, be added to a hydrophilic colloid layer or may be added alone to a silver halide emulsion layer containing or not containing a tetrazolium compound of the invention or to a hydrophilic colloid layer.

The hydrazine compound used in the invention is preferably a compound represented by the following Formula II:

Formula II



wherein R^1 is a monovalent organic residue; R^2 is a hydrogen atom or a monovalent organic residue; Q_1 and Q_2 each represents a hydrogen atom, an alkylsulfonyl group including one having a substituent, or an arylsulfonyl group including one having a substituent; and X_1 is an oxygen atom or a sulfur atom. Preferred among those compounds represented by Formula II is one in which X_1 is an oxygen atom and R_2 is a hydrogen atom.

The monovalent organic residue represented by the above R^1 or R^2 includes an aromatic residue, a heterocyclic residue and an aliphatic residue.

The aromatic residue includes a phenyl group, a naphthyl group and the same groups having a substituent such as an alkyl group, an alkoxy group, an acylhydrazino group, a dialkylamino group, an alkoxycarbonyl group, a cyano group, a carboxy group, nitro group, an alkylthio group, a hydroxy group, a sulfonyl group, a carbamoyl group, a halogen atom, an acylamino group, a sulfonamido group, or a thiourea group. Examples of the phenyl group having such substituents include a 4-methylphenyl group, a 4-ethylphenyl group, a 4-oxyethylphenyl group, a 4-dodecylphenyl group, a 4-carboxyphenyl group, a 4-diethylaminophenyl group, 4-octylaminophenyl group, a 4-benzylaminophenyl group, 4-acetamido-2-methylphenyl group, a 4-(3-ethylthioureido)phenyl group, a 4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl group, and a 4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl group.

The heterocyclic residue is a 5- or 6-member single ring or condensed ring which has at least one atom selected from the group consisting of oxygen, nitrogen, sulfur and selenium atoms and which may have a substituent. Examples of the residue ring include a pyrroline ring, a pyridine ring, a quinoline ring, an indole ring, an oxazole ring, a benzoxazole ring, a naphthoxazole ring, an imidazole ring, a benzimidazole ring, a thiazoline ring, a thiazole ring, a benzothiazole ring, a naphthothiazole ring, a selenazole ring, a benzoselenazole ring, and a naphthoselenazole ring.

These heterocyclic rings may be substituted by an alkyl group having 1 to 4 carbon atoms such as a methyl group or an ethyl group, an alkoxy group having 1 to 4 carbon atoms such as a methoxy group or an ethoxy group, an aryl group having 6 to 18 carbon atoms such as a phenyl group, a halogen atom such as chlorine or bromine, an alkoxycarbonyl group, a cyano group or an amino group.

The aliphatic residue includes a straight-chain or branched-chain alkyl group, a cycloalkyl group, the same groups having a substituent, an alkenyl group and an alkinyl group.

The straight-chain or branched-chain alkyl group is an alkyl group having 1 to 18 carbon atoms, preferably 1 to 8 carbon atoms, such as a methyl group, an ethyl group, an isobutyl group and a 1-octyl group.

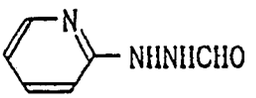
The cycloalkyl group is one having 3 to 10 carbon atoms, such as a cyclopropyl group, a cyclohexyl group and an adamantyl group.

A substituent to the above alkyl group or cycloalkyl group includes an alkoxy group such as methoxy, ethoxy, propoxy or butoxy; an alkoxycarbonyl group; a carbamoyl group; a hydroxy group; an alkylthio group; an amido group; an acyloxy group; a cyano group; a sulfonyl group; a halogen atom such as chlorine, bromine, fluorine or iodine; and an aryl group such as phenyl, halogen-substituted phenyl, alkyl-substituted phenyl. Examples of the group substituted include a 3-methoxy propyl group, an ethoxycarbonylmethyl group, a 4-chlorocyclohexyl group, a benzyl group, a p-methylbenzyl group, and a p-chlorobenzyl group. The above alkenyl group includes an allyl group, and the alkinyl group includes a propargyl group.

The following are preferred examples of the hydrazine compound of the invention.

II-1 1-formyl-2-{4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine.
II-2 1-formyl-2-(4-diethylaminophenyl)hydrazine.
II-3 1-formyl-2-(p-tolyl)hydrazine.
II-4 1-formyl-2-(4-ethylphenyl)hydrazine.
II-5 1-formyl-2-(4-acetamido-2-methylphenyl)hydrazine.
II-6 1-formyl-2-(4-oxyethylphenyl)hydrazine.
II-7 1-formyl-2-(4-N,N-dihydroxyethylaminophenyl)hydrazine.
II-8 1-formyl-2-[4-(3-ethylthioureido)phenyl]hydrazine.
II-9 1-thioformyl-2-{4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine.
II-10 1-formyl-2-(4-benzylaminophenyl)hydrazine.
II-11 1-formyl-2-(4-octylaminophenyl)hydrazine.
II-12 1-formyl-2-(4-dodecylphenyl)hydrazine.
II-13 1-acetyl-2-{4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine.
II-14 4-carboxyphenylhydrazine.
II-15 1-acetyl-1-(4-methylphenylsulfonyl)-2-phenylhydrazine.
II-16 1-ethoxycarbonyl-1-(4-methylphenylsulfonyl)-2-phenylhydrazine.
II-17 1-formyl-2-(4-hydroxyphenyl)-2-(4-methylphenylsulfonyl)hydrazine.
II-18 1-(4-acetoxyphenyl)-2-formyl-1-(4-methylphenylsulfonyl)hydrazine.
II-19 1-formyl-2-(4-hexanoxyphenyl)-2-(4-methylphenylsulfonyl)hydrazine.
II-20 1-formyl-2-[4-(tetrahydro-2H-pyran-2-yloxy)phenyl]-2-(4-methylphenylsulfonyl)hydrazine.
II-21 1-formyl-2-[4-(3-hexylureidophenyl)]-2-(4-methylphenylsulfonyl)hydrazine.
II-22 1-formyl-2-(4-methylphenylsulfonyl)-2-[4-(phenoxythiocarbonylamino)phenyl] hydrazine.
II-23 1-(4-ethoxythiocarbonylaminophenyl)-2-formyl-1-(4-methylphenylsulfonyl)hydrazine.
II-24 1-formyl-2-(4-methylphenylsulfonyl)-2-[4-(3-methyl-3-phenyl-2-thioureido)phenyl]hydrazine.
II-25 1-{{4-{3-[4-(2,4-bis-t-amylphenoxy)butyl]ureido}phenyl}}-2-formyl-1-(4-methylphenylsulfonyl)-hydrazine.

II-26



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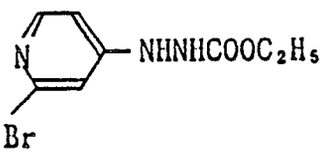

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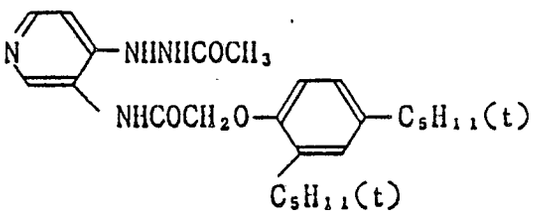

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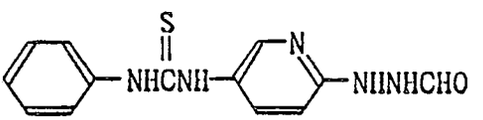

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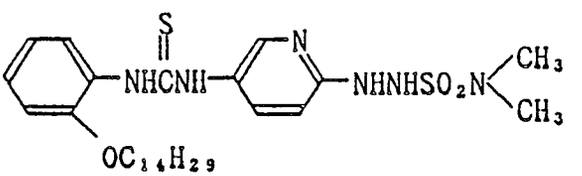

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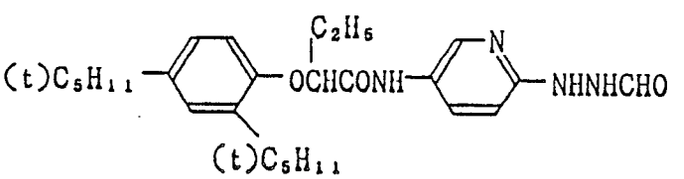

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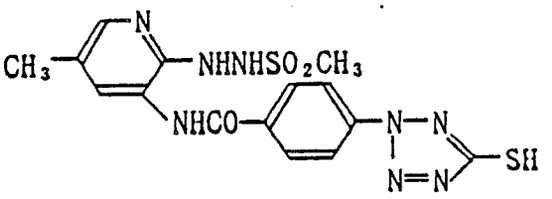

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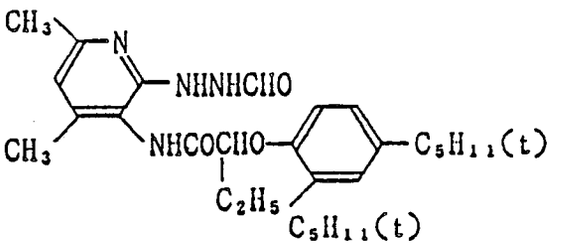

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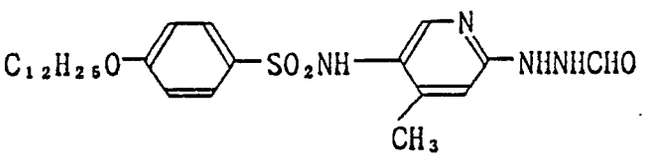

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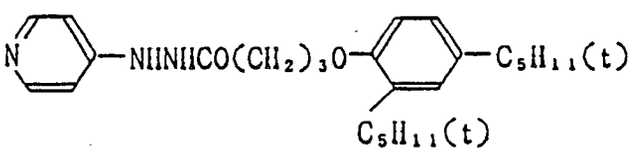

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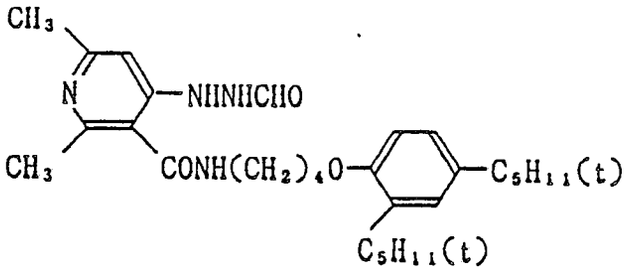

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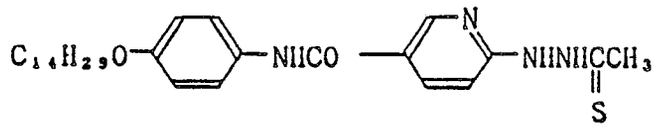

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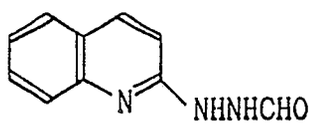

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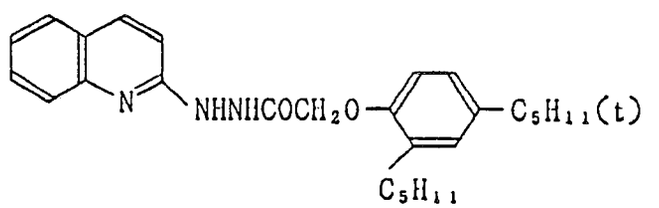

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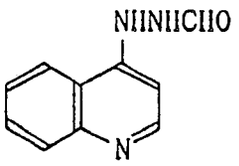

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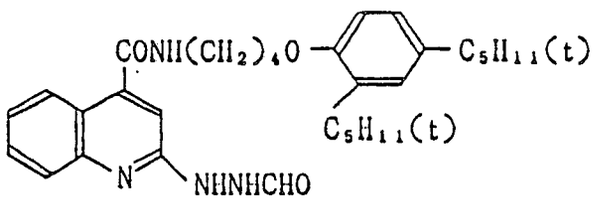

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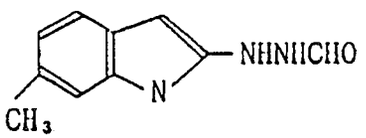

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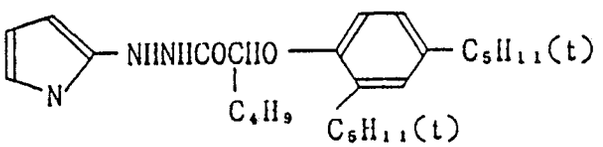

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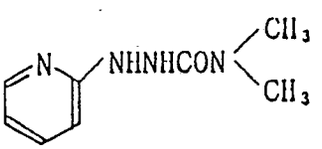

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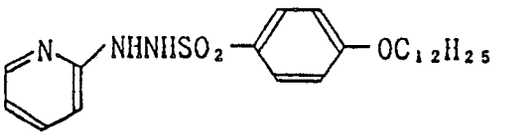

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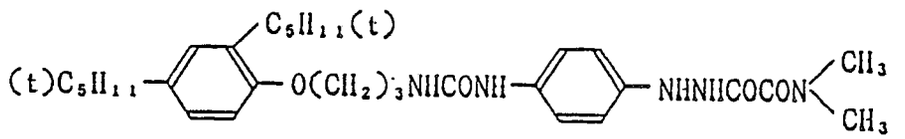

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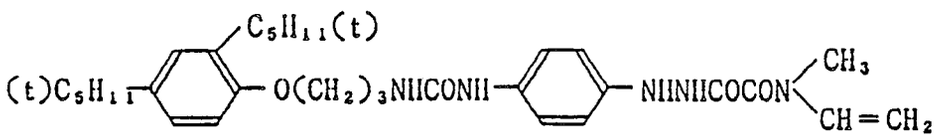

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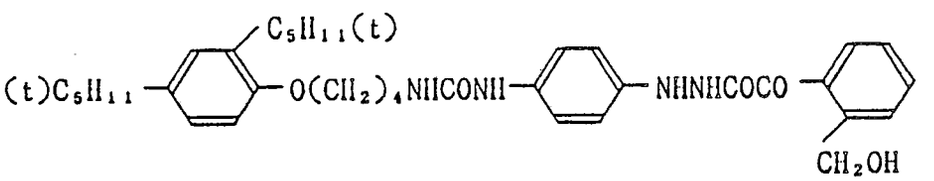

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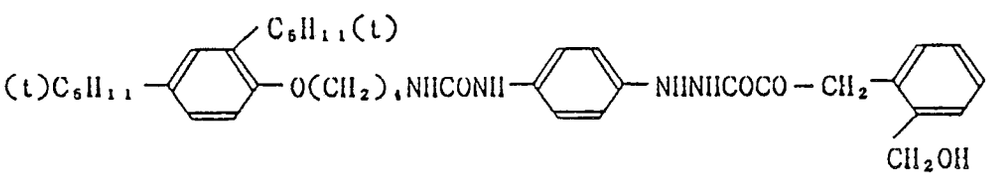

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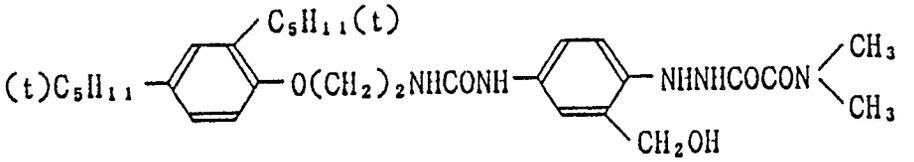

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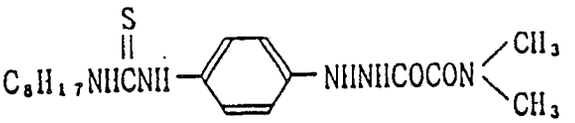

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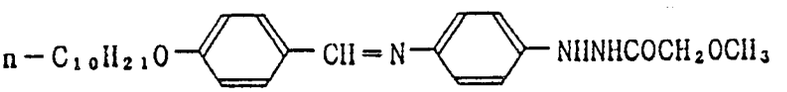

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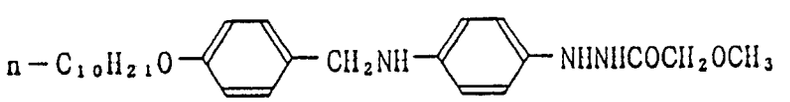

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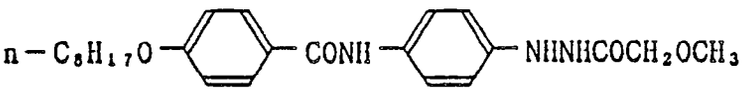

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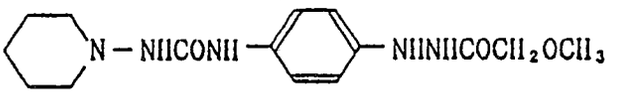

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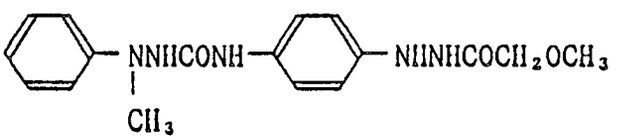

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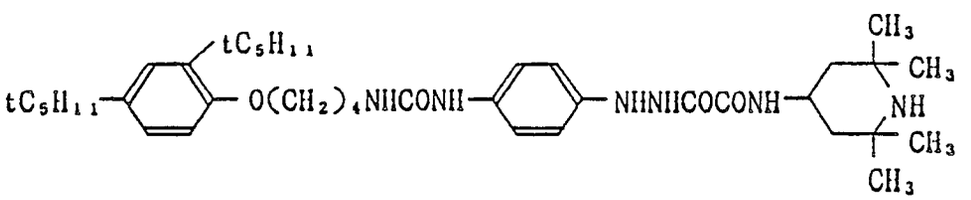


The place into which is incorporated a hydrazine compound represented by Formula II is a silver halide emulsion layer and/or a non-light-sensitive layer located on the silver halide emulsion layer side of the support, and preferably the silver halide emulsion layer and/or a layer thereunderneath. The adding amount of the hydrazine compound is preferably 10^{-5} to 10^{-1} mole, and more preferably 10^{-4} to 10^{-2} mole per mole of silver.

The silver halide of the silver halide emulsion used in the light-sensitive material of the invention may be any arbitrary one for conventional silver halide emulsions, such as silver bromide, silver iodobromide, silver chloride, silver chlorobromide or silver chloroiodobromide, and preferably a silver chlorobromide containing more than 50 mole% silver chloride for a negative-type silver halide emulsion. The silver halide grain may be one that is obtained by any of an acid method, a neutral method and an ammoniacal method. The silver halide emulsion used in the invention may be either of a single composition or of a plurality of grains different in the composition, which may be contained together in a single layer or separately in a plurality of layers.

Configuration of the silver halide grain of the invention is not restricted, but one preferred example is a cubic grain having a {100} face as a crystal surface. The grain may also be of an octahedral, tetradecahedral or dodecahedral configura tion, which may be prepared in accordance with those methods described in U.S. Patent Nos. 4,183,756 and 4,225,666; Japanese Patent O.P.I. Publication No. 26589/1980, and Japanese Patent Examined Publication No. 42737/1980; and the Journal of Photographic Science, 21.

39 (1973). Further, the grain may also be a crystal having a twin plane.

The silver halide grains of the invention may be either grains of unified form or mixed grains of varied forms.

The silver halide grains may be of any grain size distribution; the emulsion used may be an emulsion of a wide grain size distribution (referred to as a polydisperse emulsion), a single emulsion or a mixture of different emulsions having a narrow grain size distribution (referred to as monodisperse emulsions), or a mixture of a polydisperse emulsion and a monodisperse emulsion.

The silver halide emulsion may be a mixture of separately prepared two or more different emulsions.

In the invention, the monodisperse emulsion is preferred. The monodisperse silver halide grains in the monodisperse emulsion are such that the weight of the silver halide grains included within the grain size range of 20% ± average grain size $\bar{r}$ account for not less than 60%, more preferably not less than 70%, and most preferably not less than 80% of the weight of the whole silver halide grains.

The average grain size $\bar{r}$ herein is defined as the grain diameter ri obtained when the product ni x ri^3 of the frequency ni of a grain having a grain diameter ri and ri^3 becomes maximum (calculated and rounded to three places of decimals).

The grain diameter, in the case of a spherical silver halide grain, is its diameter and, in the case of a non-spherical grain, is the diameter of a circular image equivalent in the area to its projection image.

The grain diameter can be obtained by measuring the diameter of a grain image on a photographed print or the area of a projected image obtained by magnifying the grain 10,000 to 50,000 times by an electron microscope, provided that the number of grains to be measured is 1000 or more selected at random.

The particularly preferred high monodisperse emulsion of the invention is one in which the grain size distribution width defined by

$$\frac{\text{Grain sizes standard deviation}}{\text{Average grain size}} \times 100 = \text{distribution width (\%)}$$

is 20% or less, and more preferably 15% or less.

Herein, the average grain size and the grain size standard deviation are to be found from the previously defined ri.

The monodisperse emulsion can be prepared by making reference to Japanese Patent O.P.I. Publication Nos. 48521/1979, 49938/1983 and 122935/1985.

The light-sensitive silver halide emulsion, although allowed to be used remaining unchemically-sensitized, i.e., in a primitive emulsion, is usually subjected to chemical sensitization. The chemical sensitization may be carried out in accordance with appropriate ones of those methods described in the publications by Glafkides and Zelikman, and the 'Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden', Akademische Verlagsgesellschaft, 1968, compiled by H. Frieser.

Namely, a sulfur sensitization method which uses an active gelatin or a compound containing sulfur capable of reacting with silver ions; a reduction sensitization method which uses a reducing substance; and a noble-metal sensitization method which uses a gold compound or other noble metal compounds may be used alone or in combination. As the sulfur sensitizer, a thiosulfate, a thiourea, a thiazole, a rhodanine and other compound may be used, examples of which are described in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668 and 3,656,955. As the reduction sensitizer, a stannous salt, an amine, a hydrazine derivative, formamizinesulfinic acid, and a silane compound may be used, examples of which are described in U.S. Patent Nos. 2,478,850, 2,419,974, 2,518,698, 2,983,609, 2,983,610 and 2,694,637. For the noble metal sensitization, a complex salt of a metal such as platinum, iridium or palladium, belonging to Group VII of the periodic table, can be used, examples of which are described in U.S. Patent Nos. 2,399,083 and 2,448,060, and British Patent No. 618,061.

The conditions of pH, pAg and temperature for the chemical sensitization are not particularly restricted; pH is preferably 4 to 9, particularly 5 to 8; pAg is preferably 5 to 11, particularly 8 to 10; and temperature is preferably 40 to 90 ° C, particularly 45 to 75 ° C.

The photographic emulsion used in the invention may be chemically sensitized by combined use of the above-mentioned sulfur sensitization, gold-sulfur sensitization, reduction sensitization and noble-metal sensitization.

As for the light-sensitive emulsion, the foregoing emulsion may be used alone or in a mixture of two or more kinds thereof.

In practicing the invention, for the emulsion, after completion of the above chemical sensitization, may

be used 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 5-mercapto-1-phenyltetrazole, 2-mercaptobenzothiazole, and various other stabilizers. Further, if necessary, a silver halide solvent such as thioether, a mercapto group-containing compound, and a crystal habit control agent such as a sensitizing dye may be used.

The silver halide grain for the emulsion of the invention may contain in the inside thereof and/or on the surface thereof metallic ions by adding thereto in the grain forming and/or growing process a cadmium salt, a zinc salt, a lead salt, a thalium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, or an iron salt or a complex salt thereof.

The emulsion of the invention may have its useless soluble salt either removed therefrom after completion of the growth of the silver halide grain or remain contained therein. The removal of the salt can be carried out in accordance with the method described in Research Disclosure 17643.

In the silver halide photographic light-sensitive material of the invention, the emulsion may be spectrally sensitized to relatively longer wavelength-having blue, green and red lights or infrared light by using sensitizing dyes. The dyes to be used include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. The particularly useful ones are cyanine dyes, merocyanine dyes and complex merocyanine dyes. The basic heterocyclic nucleus of these dyes may be any one of those nuclei usually applied to cyanine dyes, which includes a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, a pyridine nucleus; a nucleus formed by the fusion of an alicyclic hydrocarbon ring with one of these nuclei; and a nucleus formed by the fusion of an aromatic hydrocarbon ring with one of these nuclei, such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. Any of these nuclei may have a substituent on a carbon atom thereof.

The ketomethylene structure-having nucleus of the merocyanine dye or complex merocyanine dye may be a 5- or 6-member heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazlidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, rhodanine nucleus, a thiobarbituric acid nucleus.

The sensitizing dye for use in the invention is used in the same concentration as used in conventional negative-type silver halide emulsions. Particularly, it is advantageous to use the sensitizing dye in a concentration range substantially not to deteriorate the inherent sensitivity of the silver halide emulsion; preferably about 1.0×10^{-5} to 5×10^{-4} mole of the sensitizing dye per mole of silver halide, and particularly preferably about 4×10^{-5} to 2×10^{-4} mole per mole of silver halide.

The sensitizing dye of the invention may be used alone or in combination of two or more kinds thereof. Useful examples of the sensitizing dye of the invention are as follows:

The sensitizing dyes for the blue-sensitive silver halide emulsion include those described in West German Patent No. 929,080; U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,956, 3,672,897, 3,694,217, 4,025,349 and 4,046,572; British Patent No. 1,242,588; Japanese Patent Examined Publication Nos. 14030/1969 and 24844/1977; and Japanese Patent O.P.I. Publication Nos. 73137/1973 and 172140/1986. The sensitizing dyes for the green-sensitive silver halide emulsion include those cyanine dyes, merocyanine dyes, and complex cyanine dyes described in U.S. Patent Nos. 1,939,201, 2,072,908, 2,739,149 and 2,945,763; British Patent No. 505,979; and Japanese Patent Examined Publication No. 42172/1973. And, the sensitizing dyes for the red-sensitive emulsion and infrared-sensitive emulsion include those cyanine dyes, merocyanine dyes and complex cyanine dyes described in U.S. Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629 and 2,776,280; Japanese Patent Examined Publication No. 17725/1974; and Japanese Patent O.P.I. Publication Nos. 62425/1975, 29836/1986 and 80841/1985.

These sensitizing dyes may be used alone or in combination. Combination of such sensitizing dyes is often used for the purpose of supersensitization. Typical examples of the combination are described in U.S. Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707; British Patent Nos. 1,344,281 and 1,507,803; Japanese Patent Examined Publica tion Nos. 4936/1968 and 12375/1978; and Japanese Patent O.P.I. Publication Nos. 110618/1977 and 109925/1977.

The silver halide photographic light-sensitive material of the invention may contain in the hydrophilic colloid layers thereof a water-soluble dye as a filter dye or for the antiirradiation, antihalation and some other purposes. Examples of such the dye include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Of these dyes, the oxonole dyes, hemioxonol dyes and merocyanine dyes are particularly useful.

In the silver halide photographic light-sensitive material of the invention, where the hydrophilic colloid layers thereof contain a dye or a ultraviolet absorbing agent, the dye or the agent may be mordanted by a

cationic polymer.

To the emulsion of the light-sensitive material, in order to prevent its sensitivity deterioration or fogging during the course of the manufacture, storage or processing thereof, may be added various compounds; e.g., those compounds known as stabilizers, which include azoles such as a benzothiazolium salt, a nitroindazole, a triazole, a benzotriazole, a benzimidazole (particularly nitro- or halogen-substituted one), a heterocyclic mercapto compound such as a mercaptothiazole, a mercaptorbenzothiazole, a mercaptobenzimidazole, a mercaptothiadiazole, a mercaptotetrazole (particularly 1-phenyl-5-mercaptotetrazole): mercaptopyridines; heterocyclic mercapto com pounds, similar to the above, having a water-soluble group such as a carboxyl group or sulfone group; thioketo compounds such as oxazolinethione; azaindenes such as a tetrazaindene (particularly a 4-hydroxy-substituted (1,3,3a,7)-tetrazaindene); benzenethiosulfonic acids and benzenesulfinic acids.

Some examples of the compound usable in the invention are detailed in K. Mees, The Theory of the Photographic Process, 3rd ed., 1966.

More detailed examples and the use of such compounds can be found in U.S. Patent Nos. 3,954,474, 3,982,947 and 4,021,248; and Japanese Patent Examined Publication No. 28660/1977.

The silver halide photographic light-sensitive material of the invention may contain the following various additives: Those materials as viscosity increasing agents or plasticizers such as a styrene-sodium maleate copolymer and dextran sulfate as described in U.S. Patent Nos. 2,960,404 and 3,767,410; Japanese Patent Examined Publication Nos. 4939/1968 and 15462/1970; West German DAS Patent No. 1,904,604; Japanese Patent O.P.I. Publication No. 63715/1973; and Belgian Patent Nos. 762,833 and 558,143; hardeners such as aldehyde-type, epoxy-type, ethyleneimine-type, active halogen-type, vinylsulfone-type, isocyanate-type, sulfonate-type, carbodiimide-type, mucochloric acid-type and acyloyl-type compounds; ultraviolet absorbing agents including those compounds as described in U.S. Patent No. 3,253,921 and British Patent No. 1,309,349, such as 2-(2′-hydroxy-5-tert-butylphenyl)benzotriazole, 2-(2′-hydroxy-3′,5′-di-tert-butylphenyl)-benzotriazole. 2-(2-hydroxy-3′-tert-butyl-5′-butylphenyl)-5-chlorobenzotriazole, and 2-(2′-hydroxy-3′,5′-di-tert-butylphenyl)-5-chlorobenzotriazole; and surfactants useful as coating aids, emulsification agents, agents for improving the permeability into processing solutions, deforming agents or for controlling various physical properties of the light-sensitive material, which include those anionic, cationic, nonionic and amphoteric compounds as described in British Patent Nos. 548,532 and 1,216,389; U.S. Patent Nos. 2,026,202 and 3,514,293; Japanese Patent Examined Publication Nos. 26580/1969, 17922/1968, 17926/1968, 13166/1968 and 20785/1973; French Patent No. 202,588; Belgian Patent No. 773,459; and Japanese Patent O.P.I. Publication No. 101118/1973. Preferred among these surfactants are sulfone group-having anionic surfactants such as sulfonated succinates, sulfonated alkylnaphthalenes, and sulfonated alkylbenzenes.

In the manufacturing process of the invention, the pH range of the coating liquid is preferably 5.3 to 7.5. In the case of multilayer coating, a mixture of the respective layers' coating liquids mixed in proportion of their coating amounts is preferred to have a pH of 5.3 to 7.5. If the pH is 5.3 or lower, the hardening makes slow progress, while if the pH exceeds 7.5, it badly affects the photographic characteristics.

The component layers of the light-sensitive material of the invention may also contain a lubricant, examples of which include those higher alcohol esters of higher fatty acids described in U.S. Patent Nos. 2,588,756 and 3,121,060; the casein described in U.S. Patent No. 3,295,979; those higher fatty acid's calcium salts described in British Patent No. 1,263,722; and those silicon compounds described in British Patent No. 1,313,384, U.S. Patent Nos. 3,042,522 and 3,489,567. Liquid paraffin-dispersed products may also be used for this purpose.

The light-sensitive material may also contain a brightening agent, examples of which include stilbene-type, triazine-type, pyrazoline-type, cumarine-type and acetylene-type compounds.

These compounds may be either water-soluble ones or insoluble ones to be used in the form of dispersion.

The foregoing anionic surfactant is preferably one containing an acid group such as a carboxy group, a sulfo group, a phospho group, a sulfate group or a phosphate group, examples of which surfactant include alkylcarboxylic acid salts, alkylsulfonic acid salts, alkylbenzenesulfonic acid salts, alkylnaphthalenesulfonic acid salts, alkylsulfuric acid esters, alkylphosphoric acid esters, N-acyl-alkyltaurines, sul fosuccinic acid esters, sulfoalkylpolyoxyethylenealkylphenyl ethers, and polyoxyethylenealkylphosphoric acid esters.

Preferred compounds as the amphoteric surfactant include amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric or phosphoric esters, alkylbetaines, and amine oxides.

Preferred compounds as the cationic surfactant include alkylamines aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts such as pyridium and imidazolium, and aliphatic or heterocyclic ring-containing phosphonium or sulfonium salts.

Useful examples of the nonionic surfactant include saponin (steroid type); alkylene oxide derivatives

such as polyethylene glycol, polyethylene glycol/polypropylene glycol condensate, polyethylene glycol-alkyl ethers or polyethylene glycol-alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or -amides and silicone-polyethylene oxide adducts; glycidol derivatives such as alkenylsuccinic acid polyglycerides, alkylphenol polyglycerides; polyhydric alcohol's fatty acid esters; and sugar's alkylesters.

As the matting agent, there may be suitably used any of those organic matting agents described in British Patent No. 1,055,713; U.S. Patent Nos. 1,939,213, 2,221,873, 2,268,662, 2,332,037, 2,376,005, 2,391,181, 2,701,245, 2,992,101, 3,079,257, 3,262,782, 3,516,832, 3,539,344, 3,591,379, 3,754,924 and 3,767,448, and those inorganic matting agents described in West German Patent No. 2,592,321; British Patent Nos. 760,775 and 1,260,772; and U.S. Patent Nos. 1,201,905, 2,192,241, 3,053,662, 3,062,649, 3,257,206, 3,322,555, 3,353,958, 3,370,951, 3,411,907, 3,437,484, 3,523,022, 3,615,554, 3,635,714, 3,769,020, 4,021,245 and 4,029,504.

Suitably usable as the antistatic agent are those compounds described in British Patent No. 1,466,600:Research Disclosure 15840, 16258 and 16630; U.S. Patent Nos. 2,327,828, 2,861,056, 3,206,312, 3,245,833, 3,428,451, 3,775,126, 3,963,498, 4,025,342, 4,025,463, 4,025,691 and 4,025,704.

The particularly preferred embodiment of the invention is to use a tetrazolium compound, a polyethylene oxide derivative, a quaternary phosphate compound or a hydrazine compound as a tone control agent for increasing contrast as described in Japanese Patent O.P.I. Publication Nos. 210458/1987 and 139546/1987.

Also, there may be used a technique for improving dimensional stability by incorporating a polymer latex into the silver halide emulsion layer or backing layer. Examples of such the technique are disclosed in Japanese Patent Examined Publication Nos. 4272/1964, 17702/1964 and 13482/1968; U.S. Patent Nos. 2,376,005, 2,763,625, 2,772,166, 2,852,386, 2,853,457 and 3,397,988.

As a binder for the light-sensitive material of the inven tion, gelatin is normally used. The binder may be composed of gelatin in combination with other hydrophilic colloid materials including gelatin derivatives.

The gelatin usable includes lime-treated gelatin, acid-treated gelatin, the oxygen-treated gelatin described in Bull. Soc. Sci. Phot. Japan No.16, p.30 (1966), hydrolyzed gelatin and enzyme-decomposed gelatin.

The gelatin derivative includes those obtained by the reaction of gelatin with various compounds such as an acid halide, an acid anhydride, an isocyanate, bromoacetic acid, an alkanesultone, a vinylsulfonamide, a maleic imide compound, a polyalkylene oxide, and epoxy compound. Examples of the gelatin derivative are described in U.S. Patent Nos. 2,614,928, 3,132,945, 3,186,846 and 3,312,553; British Patent Nos. 861,414, 1,033,189 and 1,005,784; and Japanese Patent Examined Publication No. 26845/1967.

The light-sensitive material of the invention may further contain various additives according to purposes. These additives are detailed in Research Disclosure vol.176, Item 17643 (Dec. 1978) and vol.187, Item 18716 (Nov. 1979). The relevant pages and columns in the publications are listed in the following table.

Additives	RD 17643	RD 18716
1. Chemical sensitizers	p.23	p.648, right col.
2. Sensitivity increasing agents		p.648, right col.
3. Spectral sensitizers, supersensitizers	p.23 to 24	p.648, right col. to p.649, right col.
4. Brightening agents	p.24	
5. Antifoggants and stabilizers	p.24 to 25	p.649. right col.
6. Light-absorbing agents, filter dyes, UV absorbing agents	p.25 to 26	p.649, right col. to p.650, left col.
7. Antistain agents	p.25, right col.	p.650, left col. to right col.
8. Dye image stabilizer	p.25	
9. Hardeners	p.26	p.651, left col.
10. Binders	p.26	p.651, left col.
11. Plasticizers, lubricants	p.27	p.650, right col.
12,. Coating aids, surfactants	p.26 to 27	p.650, right col.
13. Antistatic agents	p.27	p.650, right col.

The support used for the light-sensitive material of the invention includes an elastic reflection support such as a paper laminated with an α-olefin polymer such as polyethylene, polypropylene, ethylene/butene copolymer, or a synthetic paper; a film support composed of a semisynthetic or synthetic high molecular material such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate or polyamide; an elastic support obtained by providing a reflection layer on the above film; and a metallic support. The most preferred among these supports is a polyethylene terephthalate support.

A subbing layer usable in the invention includes those of the organic solvent type including polyhydroxybenzenes described in Japanese Patent O.P.I. Publication No. 3972/1974, and those aqueous latex subbing layers described in Japanese Patent O.P.I. Publication Nos. 11118/1974, 104913/1977, 19941/1984, 19940/1984, 18945/1984, 112326/1976, 117617/1976, 58469/1976, 114120/1976, 121323/1976, 123139/1976, 114121/1976, 13920/1977, 65422/1977, 109923/1977, 119919/1977, 65949/1980, 128332/1982 and 19941/1984.

The subbing layer may have its surface usually subjected to chemical or physical treatment for surface activation, such as treatment with chemicals, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet ray treatment, high-frequency treatment, glow discharge treatment, active plasma treatment, laser treatment, mixed acid treatment and ozone-oxidation treatment.

The subbing layer is distinguished from the provided layers for the invention in that no restrictions be put on its coating point of time and conditions.

In the invention, dyes may be used as filter dyes and for antihalation and various other purposes. The dyes for such purposes include triallyl dyes, oxanol dyes, hemioxanol dyes, merocyanine dyes, cyanine dyes, styryl dyes and azo dyes. Especially, the oxanol dyes, hemioxanol dyes and merocyanine dyes are useful. Usable examples of such dyes include those described in West German Patent No. 616,007; British Patent Nos. 584,609 and 1,177,429; Japanese Patent Examined Publication Nos. 7777/1951, 22069/1964 and 38129/1979; Japanese Patent O.P.I. Publication Nos. 85130/1973, 99620/1974, 114420/1974, 129537/1974, 28827/1975, 108115/1977, 185038/1982 and 24845/1984; U.S. Patent Nos. 1,878,961, 1,884,035, 1,912,797, 2,098,891, 2,150,695, 2,274,782, 2,298,731, 2,409,612, 2,461,484, 2,527,583, 2,533,472, 2,865,752, 2,956,879, 3,094,418, 3,125,448, 3,148,187, 3,177,078, 3,247,127, 3,260,601, 3,282,699, 3,409,433, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 3,865,817, 4,070,352 and 4,071,312; PB Report 74175; and Photo. Abstr. 1 28 (21).

Particularly, these dyes may be suitably used for roomlight reversing light-sensitive materials; it is particularly preferable to use such dyes so as to make the sensitivity to 400nm light more than 30 times as high as that to 360nm light.

Further, in practicing the invention, there may also be used an organic desensitizer as described in

Japanese Patent O.P.I. Publication No. 26041/1986, whose sum of the anode potential and the cathode potential in a polarographic analysis is positive.

The light-sensitive material of the invention can be exposed to an electromagnetic wave light in the spectral region to which the component emulsion layer thereof is sensitive. Exposure of the light-sensitive material can be carried out by using any one of known light sources including natural light (sunlight), tungsten lamp light, fluorescent lamp light, iodine quartz light, mercury vapor lamp light, microwave-emitting UV light, xenon arc light, carbon arc light, xenon flash light, cathod ray tube flying spot, various laser lights, light-emitting diode light, and those lights released from a phosphor excited by electron beam, X-rays, γ-rays and α-rays. Good results can be obtained also when exposing the light-sensitive material to light from the UV light sourse disclosed in Japanese Patent O.P.I. Publication No. 210458/1987 to which is attached a filter absorbing the 370nm and shorter wavelength regions or from a UV light source in the wavelength regions of from 370 to 420nm.

The exposure time may be not only a shorter time than 1 millisecond to 1 second which are used in usual camera exposure but also a much shorter time than 1 microsecond such as from 100 nanosecond to 1 microsecond by a cathode ray tube or xenon flash tube. And it is also possible to use a longer exposure time than 1 second. The exposure may be made either continuously or intermittently.

The invention can be applied to various light-sensitive materials such as graphic-arts, X-ray, general negative-type, general reversal-type, general positive-type and direct positive-type light-sensitive materials, but can exhibit remarkable effects particularly when applied to a graphic-arts light-sensitive material which requires a very high dimensional stability.

The light-sensitive material of the invention may be subjected to known black-and-white, color or reversal processing, but is particularly effective when subjected to a high-contrast processing for graphic arts light-sensitive materials.

A fixer solution for use in the processing of the light-sensitive material of the invention may contain a thiosulfate, a sulfite, various acids, salts, a fixing accelerator, a wetting agent, a surfactant, a chelating agent and a hardener; for example, the thiosulfate and sulfite include potassium, sodium and ammonium sulfates and sulfites; the acids include sulfuric acid, hydrochloric acid, nitric acid, boric acid, formic acid, acetic acid, propionic acid, oxalic acid, tartaric acid, citric acid, malic acid and phthalic acid; and the salts include potassium salts, sodium salts and ammonium salts of these acids. The fixing accelerator includes those thiourea derivatives and intramolecular triple bond-having alcohols as described in Japanese Patent Examined Publication No. 35754/1970, Japanese Patent O.P.I. Publication Nos. 122535/ 1983 and 122536/1983; those thioethers described in U.S. Patent No. 4,126,459, anion-liberating cyclodextran ethers, crown ethers, diazabicycloundecene and di-(hydroxyethyl)butamine. The wetting agent includes alkanolamines and alkylene glycols. The chelating agent includes nitrilotriacetic acid and amino acids such as EDTA. The hardener includes chrome alum potassium alum and other aluminum compounds.

The fixer solution in the invention, in order to increase the hardening of the light-sensitive material, contains preferably an aluminum compound. The aluminum compound content of the fixer solution is preferably 0.1 to 3g/liter in aluminum equivalent.

The sulfite content of the fixer solution is preferably 0.03 to 0.4 mole/liter, and more preferably 0.04 to 0.3 mole/liter.

The fixer solution has a pH of preferably 3.9 to 6.5. The pH range of the fixer solution not only provides satisfactory photographic characteristics but has remarkable effects upon packaging materials of the invention. The most preferred pH of the solution is 4.2 to 5.3.

The light-sensitive material of the invention is developed at a temperature of preferably not higher than 50 °C, and more preferably 25 °C to 40 °C, for a period of normally within two minutes; particularly 5 to 25 seconds high spped processing also gives a good photographic image. Those processes other than the developing and fixing process, such as washing, stopping, stabilizing and prehardening or neutralizing processes may be excluded.

The present invention exhibits its merits largely even when the light-sensitive material of the invention is subjected to a ultra-high-speed processing, whose processing time is as short as 20 to 60 seconds.

The 'ultra-high-speed processing' herein means a processing by an antomatic processor in which the quotient obtained when the overall period of time from the insertion of the leading end of a light-sensitive material traveling through the developer bath, crossover section, fixer bath, crossover section, washing bath and drying section until the ejection of the leading end therefrom, i.e., the overall length of the processing line, is divided by the line transport speed is 20 seconds to 60 seconds. The reason why the crossover sections are included, although well-known to those skilled in the art, is that even in the crossover sections, the solution in the preceding process remains in a transported light-sensitive material to have its processing effect substantially make progress.

EXAMPLES

The present invention is illustrated in detail by the following examples.

EXAMPLE 1

Negative-type silver halide light-sensitive material samples as roomlight reversing light-sensitive materials were prepared in the following manner:

Preparation of emulsions

Silver chlorobromide emulsions, containing 2 mole% silver bromide and 50 mole% silver chloride, were prepared in the following manner:

A silver nitrate aqueous solution and an aqueous solution containing potassium pentabromorhodium in an amount of 23.9mg per 60g of silver nitrate, sodium chloride and potassium bromide were simultaneously mixed into a gelatin aqueous solution with stirring in 25 minutes at 40 °C, whereby silver chlorobromide emulsions each having an average grain size of 0.20μm were prepared.

These emulsions, after adding 200mg of a stabilizer 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene thereto, were washed and desalted.

The emulsions, after adding thereto further 20mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene, were subjected to sulfur sensitization. After the sulfur sensitization, respectively necessary amounts of gelatin and a stabilizer 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene were added, and then water was added to each of the emulsions to make its quantity 260ml.

Preparation of latex (L) to be added to the emulsions

A mixture liquid of 4.51kg of n-butyl acrylate, 5.49kg of styrene and 0.1kg of acrylic acid was added spending an hour to, with stirring at 81 °C under a nitrogen atmosphere, a solution of 0.25kg of KMDS (dextran sodium sulfate) produced by Meito Industry Co. and 0.05kg of ammonium persulfate dissolved into 40 liters of water, and then 0.005kg of ammonium persulfate was added. After that, the liquid was stirred for 1.5 hours, cooled and then adjusted to pH 6 with ammonia water.

The obtained latex liquid was filtered through a GF/D filter manufactured by Whotman Co., and the quantity of the filtrate was made 50.5kg by adding water thereto, whereby a monodisperse latex L-6 having an average particle size of 0.25μ was prepared.

To the foregoing emulsions were added the following additives, and silver halide emulsion coating liquids were prepared in the following manner.

Preparation of emulsion coating liquids

Each of the emulsions, after adding thereto 9mg of phenol as a fungicide, was adjusted to pH 6.5 with a 0.5N sodium hydroxide solution, to which were then added in sequence 360mg of the following compound T, 5ml of a 20% saponin solution per mole of silver halide, 180mg of sodium dodecylbenzenesulfonate, 80mg of 5-methylbenzenetriazole 43ml of the above latex liquid L-6, 60mg of the following compound M and 280mg of an aqueous styrene-maleic acid copolymer, and added water to make the whole quantity 475ml, whereby emulsion coating liquids were prepared.

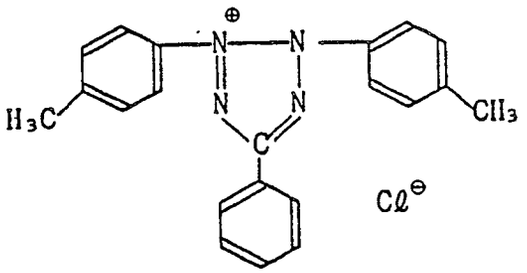
Next, a protective layer coating liquid was prepared in the following manner.

Preparation of a protective layer coating liquid

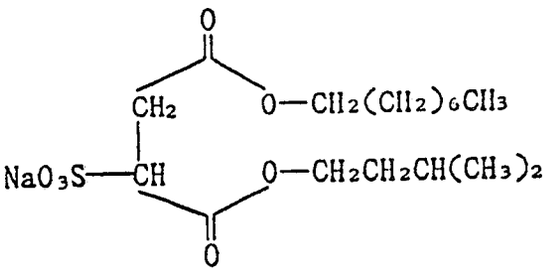
Pure water was added to gelatin in various amounts. The gelatin, after swelling, was dissolved at 40 °C, and then to this were added in sequence a 1% solution of the following compound Z as a coating aid, the

following compound N as a filter dye, an amorphous silica as a matting agent, the following compound B, and pH of the mixture was adjusted to 6.0 with citric acid, and then further added the latex L-6 in the amounts shown in Table 1, and added water to make the whole a given quantity, whereby a protective layer coating liquid was prepared.

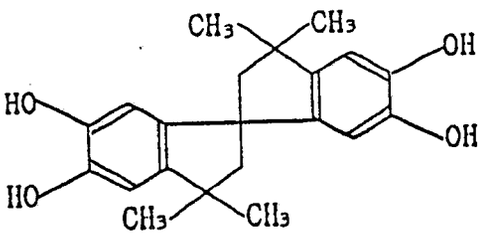
Compound T



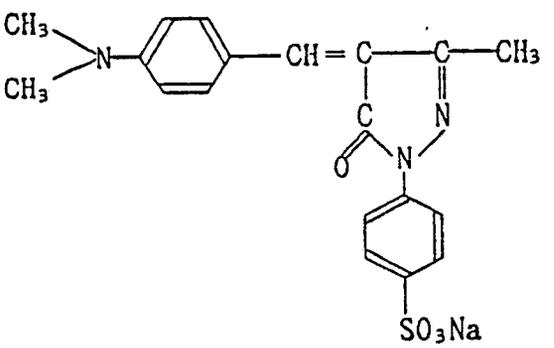
Compound Z



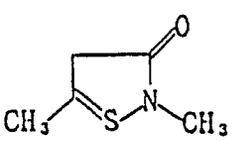
Compound M



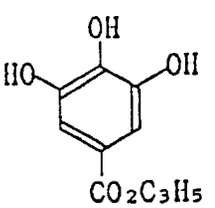
Compound N



Compound A



Compound B

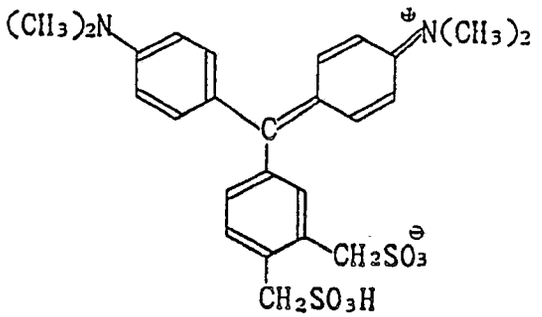


Subsequently, a backing layer coating liquid was prepared in the following manner.

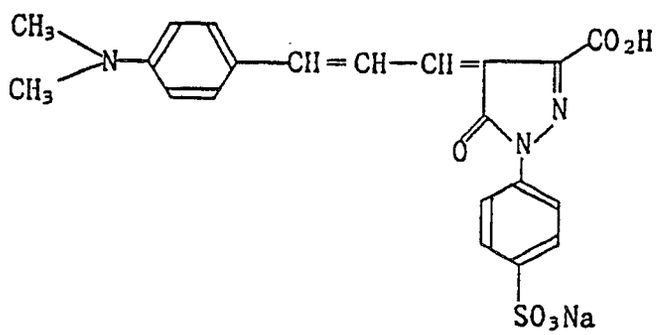
Preparation of backing layer coating liquid B-1

Thirty-six grams of gelatin were swelled with water and dissolved by heating, and to this were added 1.6g of the following compound C-1, 310mg of compound C-2 and 1.9g of compound C-3 as dyes, 2.9g of the above compound N in the form of an aqueous solution, 11ml of a 20% saponin aqueous solution, 5g of the following compound C-4 as a physical property adjusting agent, and 63mg of the following compound C-5 in the form of a methanol solution. This liquid, after adding thereto 800g of an aqueous styrene-maleic acid copolymer for viscosity adjustment, was adjusted to pH 5.4 with citric acid. Finally, 144mg of glyoxal were added, and then water added to make the whole quantity 960ml, whereby a BC coating liquid B-1 was prepared.

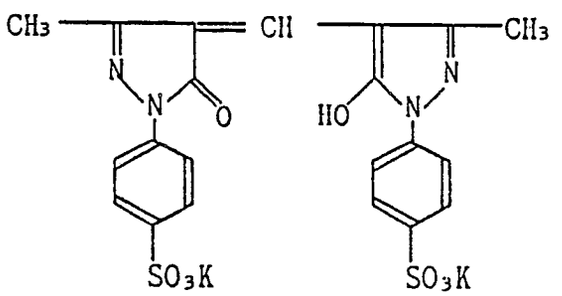
Compound C-1



Compound C-2

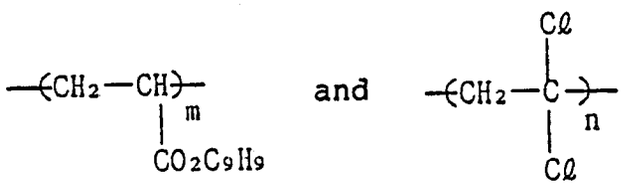


Compound C-3



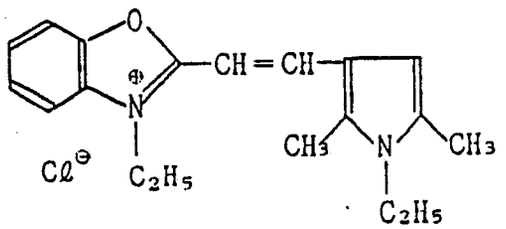
Compound C-4

Copolymer latex of



wherein m:n = 1:1

Compound C-5



A protective layer coating liquid B-2 for protection of the backing layer was prepared in the following manner.

Preparation of protective layer coating liquid B-2

Fifty grams of gelatin were swelled with water and dissolved by heating, and to this were added 340mg of sodium 2-sulfonate-succinic acid-bis (2-ethylhexyl)ester, 1.7g of polymethyl methacrylate having an average particle size of 0.4μ as a matting agent, 3.4g of sodium chloride, 1.1g of glyoxal and 540mg of mucochloric acid, and then added water to make the whole quantity 1000ml, whereby a protective layer coating liquid B-2 was prepared.

Preparation of samples for evaluation

The above coating liquids were coated on the both-side subbed surfaces of a 100μm-thick polyethylene terephthalate film described in Japanese Patent O.P.I. Publication No. 09941/1984, whereby the samples for evaluation listed in Table 1 were prepared.

In this instance, on one side of the subbed support was coated the backing layer coating liquid B-1 so as to make the dry gelatin weight 2g/m^2, and at the same time on the backing layer was coated the protective layer coating liquid B-2 so as to make the dry gelatin weight 1g/m^2. Subsequently, on the other side of the subbed support was coated an emulsion layer so as to make the dry gelatin weight as given in Table 1 and the weight of silver 4.3g/m^2, and at the same time on the emulsion layer was coated the protective layer coating liquid for protection of the emulsion layer, with addition thereto of formalin as a hardening agent, so as to make the gelatin dry weight and latex weight as given in Table 1, whereby evaluation samples A-1 to A-10 were prepared.

Each of the above coating liquids was coated so as to have a wet layer thickness adjusted to 64μm by a slide hopper method at a line speed of 70m/min. Exposure of each of these samples was made with its emulsion side contacted with an original placed in a roomlight printer P-627FM, manufactured by Dai-Nippon Screen Co., provided with an anelectric dis charge tube light source, manufactured by FUSION Inc. of U.S.

Each sample was processed in the following processing solutions under the following conditions. The amount of silver was analyzed by an X-ray fluorescence analyzer. The amount of silver after the processing was expressed in terms of the amount of silver in an area that gives the maximum density. As for the coating unevenness, evaluation was made by examining each sample's whole area overall exposed and processed so as to give a density of 1.3 by using the above-mentioned printer. And for the rainbow mottle, evaluation was made by examining how rainbow mottles appear on the coated side of each sample exposed and processed so as to give a density of 4.0 or more.

Developer	
Composition A:	
Pure water (ion-exchanged water)	150 ml
Disodium ethylenediaminetetraacetate	2 g
Diethylene glycol	50 g
Potassium sulfite (55% W/V aqueous solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
5-Methylbenzotriazole	200 mg
1-Phenyl-5-mercaptotetrazole	30 mg
Potassium hydroxide,	an amount necessary to adjust pH to 10.9
Potassium bromide	4.5 g
Composition B:	
Pure water (ion-exchanged water)	3 ml
Diethylene glycol	50 g
Disodium ethylenediaminetetraacetate	25 mg
Acetic acid (90% aqueous solution)	0.3 ml
5-Nitroindazole	110 mg
1-Phenyl-3-pyrazolidone	500 mg

Before use, the above compositions were dissolved in the order of A and B into 500ml of water, and water was added to make the whole quantity 1 liter.

Fixer bath	
Composition A:	
Ammonium thiosulfate (72.5% W/V aqueous solution)	230 ml
Sodium sulfite	9.5 g
Sodium acetate, trihydrated	15.9 g
Boric acid	6.7 g
Sodium citrate, dihydrated	2 g
Acetic acid (90% W/W aqueous solution)	8.1 ml
Composition B:	
Pure water (ion-exchanged water)	17 ml
Sulfuric acid (50% W/W aqueous solution)	5.8 g
Aluminum sulfate (aqueous solution, Al_2O_3 equivalent content 8.1% W/W)	26.5 g

Before use, the above compositions were dissolved in the order of A and B into 500 ml of water, and water was added to make the whole quantity 1 liter. pH of the fixer was about 4.3.

Rapid processing conditions			
Steps	Temperature	Time	Tank capacity
Developing	35 °C	15 seconds	20 liters
Fixing	35 °C	15 seconds	20 liters
Washing	18 °C	10 seconds	15 liters
Drying	40 °C	10 seconds	

The time of each step includes the transport time in the crossover section prior to the following step. Dry-to-dry time is 50 seconds.

The results are shown in Table 1.

Table 1

Sample No.	Amounts of gelatin Em/Pro	Amt of latex in protective layer	γ	Coating unevenness ranked	Effective amt of dev'd Ag	Rainbow mottle level	Pin hole level	Dimensional changes	
								Drying temp.	
								40°C	55°C
A-1 (Comp.)	2.0/1.8g/m^2	0 g/m^2	8.0	4	4.0g/m^2	2	2	23μm	45μm
A-2 (Comp.)	2.0/0.5	0	9.0	3	4.2	2	2	20	40
A-3 (Inv.)	2.0/0.8	0.2	10.1	5	4.1	5	5	18	27
A-4 (Inv.)	2.0/0.5	0.2	9.5	5	4.2	4	4	19	26
A-5 (Comp.)	1.8/1.0	0	10.2	3	4.2	2	2	21	39
A-6 (Comp.)	1.8/0.5	0	10.5	2	4.2	1	2	22	43
A-7 (Inv.)	1.8/1.0	0.2	9.8	4	4.2	5	5	20	30
A-8 (Inv.)	1.8/0.5	0.2	9.5	5	4.2	4	4	18	29
A-9 (Comp.)	1.0/1.0	0	9.9	2	4.2	3	4	21	43
A-10 (Inv.)	1.0/1.0	0.2	10.5	4	4.2	4	4	20	28
A-11 (Comp.)	2.0/1.1	0	6.3	5	3.6	5	5	23	45
A-12 (Comp.)	2.0/1.1	0.2	6.7	5	3.5	5	5	22	36

Note: Level 3 and above are ones fit for practical use.

Level 2 and below are ones unaccetable for practical use.

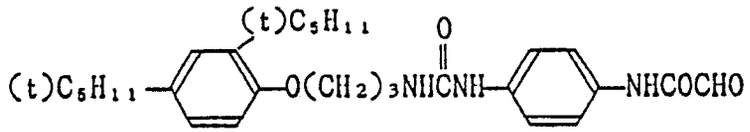
Em/Pro represents the coated weights of gelatin of the emulsion and protective layers.

EXAMPLE 2

The following hydrazine compound HD was used as a contrast increasing agent in place of the tetrazolium compound T in Example 1.

Consequently, the same results as in Example 1 were obtained.

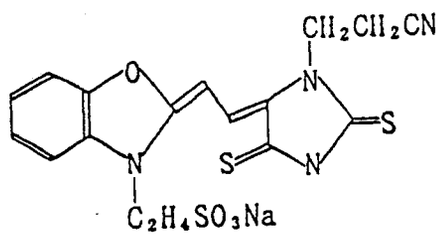
Compound HD



EXAMPLE 3

Experiments were made in the same manner as in Example 1 except that the following sensitizing dye C was added at the time of chemical sensitization for preparation of samples in Example 1, and exposure was made through the same glass wedge to a tungsten lamp, and consequently, quite the same results as in Example 1 were obtained.

Sensitizing dye C



EXAMPLE 4

Experiments were made in the same manner as in Example 1 except that the polymer latex L-6 added after the emulsion coating in Example 1 was replaced by polymer latex L-3 and the polymer latex L-6 added to the protective layer coating liquid was replaced by polymer latex L-7 (provided R: $-CH_3$). In this instance, 2.5g/m^2 of polymer latex L-3 was added as a latex component to the emulsion layer, which was coated so as to have a wet thickness of 80μm, and to the protective layer was added latex L-7 as specified in Table 2, whereby samples B-1 to B-12 were prepared. The results are shown in Table 2.

Table 2

Sample No.	Amounts of gelatin Em/Pro	Amt of latex in protective layer	γ	Coating unevenness ranked	Effective amt of dev'd Ag	Rainbow mottle level	Pin hole level	Dimensional changes	
								Drying temp.	
								40°C	55°C
B-1 (Comp.)	2.0/1.1g/m^2	0 g/m^2	6.4	5	3.2g/m^2	5	5	+18μm	+40μm
B-2 (Comp.)	2.0/0.8	0	7.8	4	4.0	2	2	+22	+37
B-3 (Comp.)	2.0/0.5	0	8.8	3	4.2	2	2	+21	+38
B-4 (Comp.)	1.8/1.0	0	10.0	3	4.2	2	2	+19	+37
B-5 (Comp.)	1.8/0.5	0	10.3	2	4.2	1	2	+19	+40
B-6 (Comp.)	1.0/1.0	0	9.7	4	4.2	3	2	+20	+39
B-7 (Comp.)	2.0/1.1	1.0	6.2	5	3.3	5	5	+18	+36
B-8 (Inv.)	2.0/0.8	1.0	9.9	5	4.1	5	5	+22	+27
B-9 (Inv.)	2.0/0.5	1.0	9.3	5	4.2	5	5	+20	+24
B-10 (Inv.)	1.8/1.0	1.0	9.6	4	4.2	5	5	+21	+24
B-11 (Inv.)	1.8/0.5	1.0	9.3	5	4.2	5	4	+22	+25
B-12 (Inv.)	1.0/1.0	1.0	10.3	4	4.2	5	5	+17	+20

Note: Level 3 and above are ones fit for practical use.

Level 2 and below are ones unaccetable for practical use.

Em/Pro represents the coated weights of gelatin of the emulsion and protective layers.

Table 2 shows that the invention can provide a light-sensitive material which is capable of forming a high-γ and high-density image excellent in the dimensional stability even in either a super-high-speed processing or a conventional processing, and which is free of pinholes and coating defects.

Claims

1. A photographic material comprising a support having thereon a light-sensitive silver halide emulsion layer and a non-light-sensitive hydrophilic colloid layer provided outside of the light-sensitive silver halide emulsion layer to the support, in which total content of gelatin of layers at a side of the silver halide emulsion layer is 2.0 to 2.8 g/m^2 and the non-light-sensitive hydrophilic colloid layer contains a polymer latex having an average particle size of 0.005 to 1 μm.

2. A photographic material as claimed in claim 1, wherein a tetrazolium compound is contained in one of the layers.

3. A photographic material as claimed in claim 1, wherein a hydrazine compound is contained in one of the layers.

4. A photographic material as claimed in claim 3 or claims 1 or 2, wherein an average particle size of the polymer latex is 0.02 to 0.5 μm.

5. A photographic material as claimed in claim 4, wherein an average particle size of the polymer latex is 0.02 to 0.1 μm.

6. A photographic material as claimed in claim 1 or claims 2 to 5, wherein the polymer latex is contained in the hydropylic colloid layer outside of the emulsion layer to the support.

7. A photographic material as claimed in claim 6, wherein the content of the polymer latex in the hydrophlic colloid layer is 0.01 to 1.0 g/m^2.

8. A photographic material as claimed in claim 7, wherein the content of the polymer latex in the hydrophlic colloid layer is 0.02 to 0.6 g/m^2.

9. A photographic material as claimed in claim 6, 7 or 8, wherein content of gelatin in the hydropylic colloid layer is 0.1 to 1.5 g/m^2.

10. A photographic material as claimed in claim 9, wherein content of gelatin in the hydropylic colloid layer is 0.3 to 1.2 g/m^2.

11. A photographic material as claimed in claim 2, wherein content of the tetrazolium compound is 1 mg to 10 g per mole of silver halide in the photographic material.

12. A photographic material as claimed in claim 11, wherein content of the tetrazolium compound is 10 mg to 2 g per mole of silver halide in the photographic material.

13. A photographic material as claimed in claim 3, wherein content of the hydrazine compound is 10^{-5} to 10^{-1} mole per mole of silver halide in the photographic material.

14. A photographic material as claimed in claim 12, wherein content of the hydrazine compound is 10^{-4} to 10^{-2} mole per mole of silver halide in the photographic material.