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(54) **Silver halide light-sensitive photographic material.**

(57) A sliver halide light-sensitive photographic material which comprises a support and, provided on at least one side thereof, at least two photographic layers,
at least one of which photographic layers being a silver halide emulsion layer containing silver halide grains, of which silver bromide content is not less than 80 mol% and the average grain size is not less than 0.4 micro meters,
and at least one other of which photographic layers being a non-light-sensitive layer provided contiguous to said silver halide emulsion layer,
characterized in that at least one of said photographic layers contains a 1-phenyl-3-pyrazolidone compound and said non-light-sensitive layer contains a heterocyclic compound having therein a mercapto group or a derivative thereof.

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SILVER HALIDE LIGHT-SENSITIVE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide light-sensitive photographic material, and more particularly to a silver halide light-sensitive photographic material which is stable in the photographic characteristics against changes in the developing condition.

BACKGROUND OF THE INVENTION

In recent years the processing of silver halide light-sensitive photographic materials has a tendency toward rapid processing, and at the same time the control procedure for the processing has a trend toward being simplified. It is because of saving the labors and expenses required for maintaining the development processes. Such trends can be seen in the movements toward the reduction of the replenishing amounts of developing and other processing solutions; extension of the time interval between renewals of the processing solutions; processing under the same condition of

light-sensitive materials which had been conventionally processed independently under different conditions; and the like.

Such movements to speed up and simplify the development processes have prompted devising means for light-sensitive materials to reduce the dependence of the photographic characteristics upon the processing: for example, the addition of those hydroquinone compounds as desicribed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 39928/1975; the addition of those 1-phenyl-3-pyrazolidones as described in Japanese Patent O.P.I. Publication No. 19739/1982; and the like are known as such means. These techniques all are of compounds for use as developing agents in ordinary photographic developing solutions, and, by incorporating such developing agents in advance into light-sensitive materials, are aimed at making light-sensitive materials hardly subject to changes in the developing condition.

As has been mentioned, recently there is an increasing trend toward processing under the same condition light-sensitive materials which had been conventionally processed independently under different conditions: for example, there are cases where photo-typesetting films use and photo-sensitive papers for photo-typesettingr and other films or

papers for graphic arts, are processed under the same conditions, respectively.

Photographic film, since it has generally a large coating amount of silver compared to photographic paper, tends to be processed at a high temperature or for a long period of time, and therefore, photographic paper, if processed at the same time in the same solution, is supposed to be processed under a much severe condition as compared to the conventional condition under which it should be processed, thus adversely affecting the paper, increasing a fog.

On the other hand, however, where photo-typesetting paper is processed alone, more rapid processing at a lower temperature is desired. Accordingly, in the case of photo-typesetting paper, it is strongly desired to reduce the dependence of the photographic characteristics upon the processing condition.

Reducing the dependence of the photographic characteristics upon the processing condition is of course desirable for all light-sensitive materials as well as the photo-typesetting paper. Particularly in the case of a silver halide light-sensitive photographic material containing not less than 80 mole% silver bromide and silver halide grains whose average grain size is not less than 0.4μm, since the developability of the silver halide grain itself is inferior, it is very difficult to lessen the dependence thereof on the processing.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a silver halide light-sensitive photographic material whose photographic characteristics are less dependent upon the processing thereof.

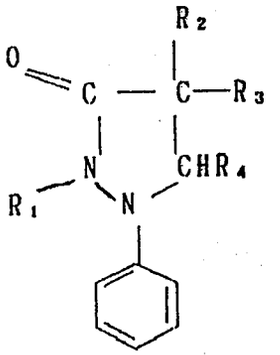
It is another object of the present invention to provide a silver halide light-sensitive photographic material which contains not less than 80 mole% silver bromide and silver halide grains whose average grain size is not less than 0.4μm and of which the photographic characteristics are less dependent upon the processing.

The above objects of the present invention are accomplished by the following: In a silver halide light-sensitive photographic material comprising a support having on at least one side thereof at least one silver halide emulsion layer containing not less than 80 mole% silver bromide and silver halide grains whose average grain size is not less than 0.4μm, the said silver halide light-sensitive photographic material wherein at least one of the photographic layers provided on the said silver halide emulsion layer-provided side comprises a 1-phenyl-3-pyrazolidone, and a nonlight-sensitive layer adjacent to the said silver halide emulsion layer comprises at least one heterocyclic compound having a mercapto group.

DETAILED DESCRIPTION OF THE INVENTION

The 1-phenyl-3-pyrazolidones usable in this invention are

those having the formula [1]:



[1]

wherein R_1 is hydrogen or an acetyl group, and R_2, R_3 and R_4 each is hydrogen or a substituted or unsubstituted alkyl group.

The term 'average grain size' used herein means an average value of the whole grain sizes.

The phrase 'having at least one silver halide photographic layer' used herein implies a layer construction comprising a support provided on at least one side thereof directly or through a nonlight-sensitive layer with a silver halide photographic emulsion layer or a layer construction wherein the said emulsion layer has thereon, if necessary, further repeated nonlight-sensitive layers, emulsion layers, and the like. And on the topmost silver halide photographic emulsion layer a protective layer may be provided.

As the support to be used in this invention those materials which will be mentioned hereinafter may be used.

The nonlight-sensitive layer adjacent to the silver

halide photographic emulsion layer in this invention includes, e.g., a subbing (undercoat) layer, antihalation layer, intermediate layer, filter layer, protective layer and the like.

The photographic layer is a general term for silver halide photographic emulsion layers and nonlight-sensitive layers mentioned above.

Subsequently, the 1-phenyl-3-pyrazolidones to be used in this invention will be described below. Out of the compounds those having the foregoing formula [1] is preferred, of which typical examples will be given in the following (A-1) through (A-8). It goes without saying that the compounds usable in this invention are not limited to the following exemplified compounds.

(A-1) 1-phenyl-3-pyrazolidone

(A-2) 1-phenyl-4-methyl-3-pyrazolidone

(A-3) 1-phenyl-4,4-dimethyl-3-pyrazolidone

(A-4) 1-phenyl-5-methyl-3-pyrazolidone

(A-5) 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone

(A-6) 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone

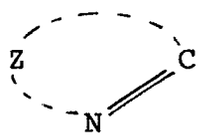
(A-7) 1-phenyl-4,4-di-n-propyl-3-pyrazolidone

(A-8) 1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone

The preferred adding amount range of any 1-phenyl-3-pyrazolidone is from 0.2g to 5 g per mole of silver halide. If the amount is less than 0.2g, the effect of the compound

can lessen, while if it exceeds 5g, the shelf stability, i.e., stability with the passage of time can be deteriorated. The 1-phenyl-3-pyrazolidone may be added to any layer of the photographic layers on the emulsion layer side, and the addition of it to the emulsion layer is particularly effective.

As the heterocyclic compound having a mercapto group to be used in this invention those having the following formula [2] may be suitably used:



[2]

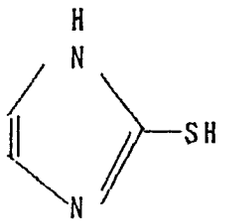
wherein Z is a group of nonmetallic atoms necessary to form a 5- to 6-member heterocyclic ring; and X is a hydrogen atom, an alkali metallic atom, ammonium or an organic amine residue.

In the above general formula, the 5- or 6-member heterocyclic ring including Z is preferably selected from the group consisting of an imidazole, a thiazole, an oxazole, a benzimidazole, a benzothiazole, a benzoxazole, an oxadiazole, a thiadiazole, a triazole, a tetrazole, a pyrimidine, a triazine, a tetrazaindene, or the like.

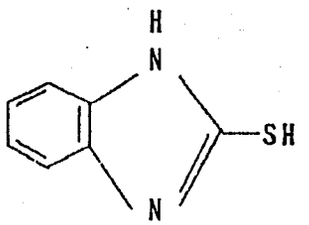
Typical compounds represented by the above general formula [2] will be given in the following [B-1] through

[B-30]. It goes without saying that the compounds usable in this invention are not limited to the following exemplified compounds.

〔B－1〕



〔B－2〕



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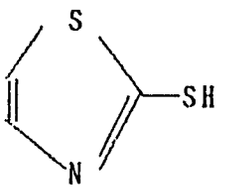

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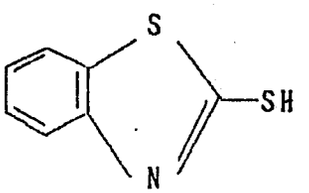

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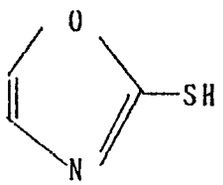

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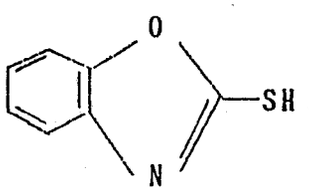

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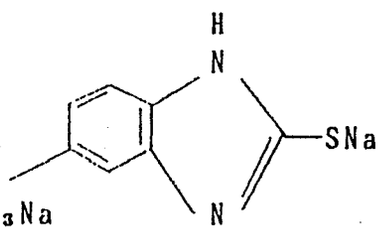

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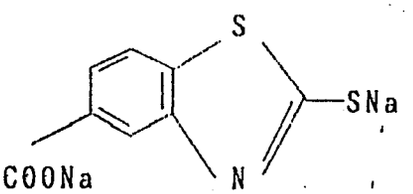

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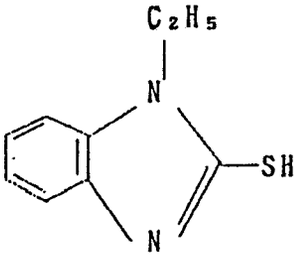

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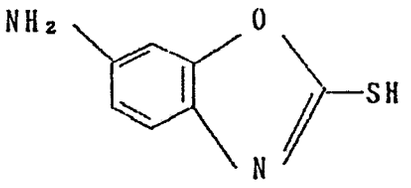

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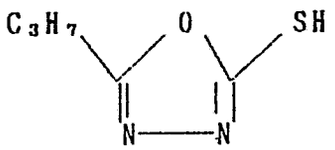

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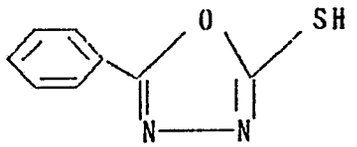

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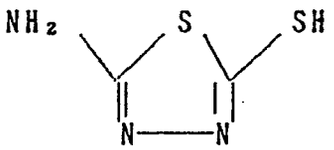

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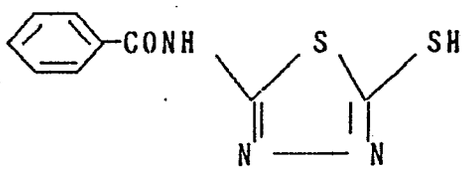

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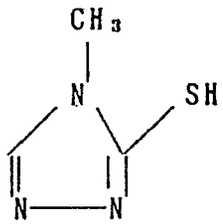

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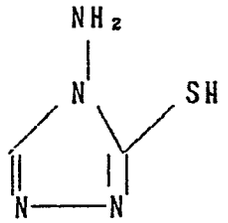
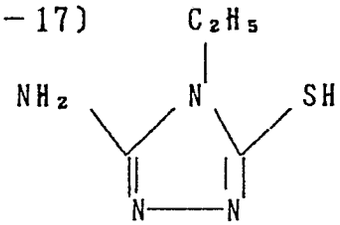


(B-17)



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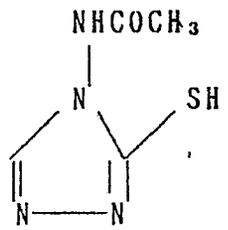

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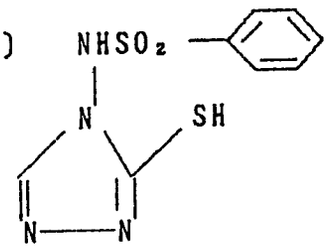

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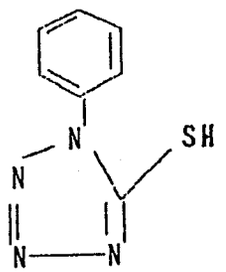

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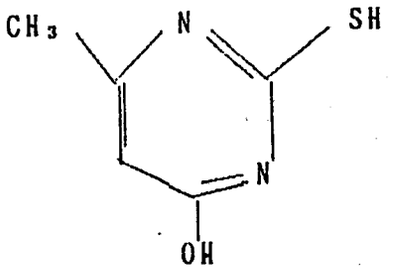

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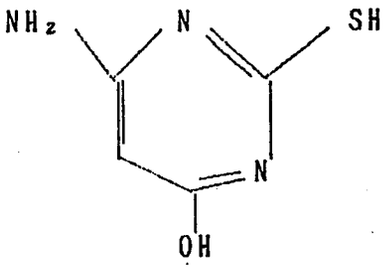

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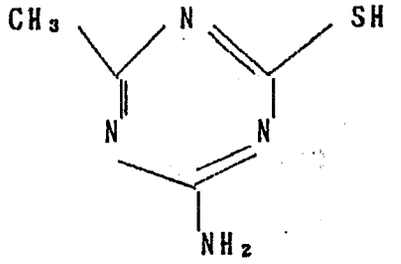

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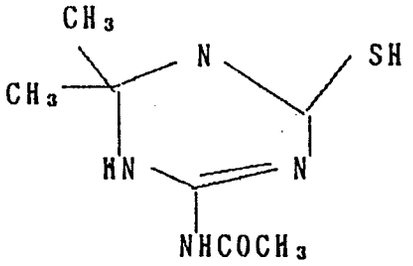

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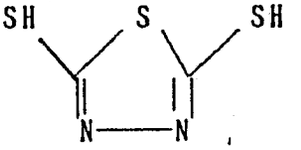

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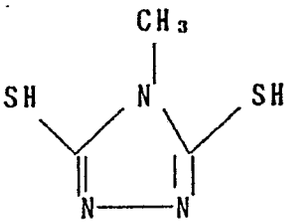

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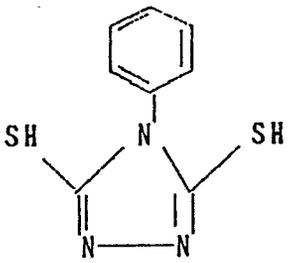

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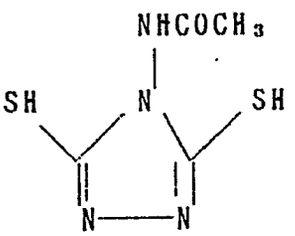

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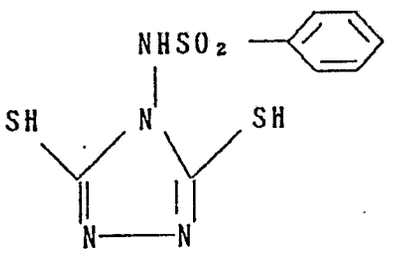

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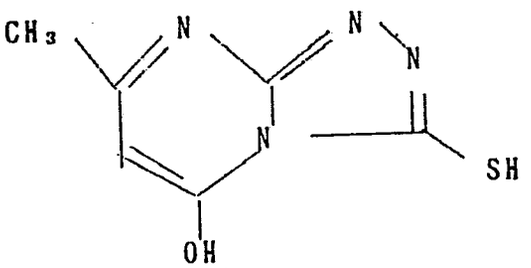


These mercapto group-having heterocyclic compounds usable in this invention may be easily synthesized in accordance with those methods as described in, e.g., U.S. Patent Nos. 3,615,501, 2,324,123, 2,384,593, 2,496,940, 3,137,578, 2,496,940, 3,082,088, 3,473,924, 3,575,699, 3,687,660, 2,271,229 and 2,496,940, and British Patent Nos. 1,141,773 and 1,376,600, or in similar manner to these methods. Also, these compounds may be easily synthesized in accordance with those methods as described in the 'Dai-Yuki-Kagaku' (Comprehensive Organic Chemistry), edited by Munio Kotake (published by Asakura Shoten, 1971) or A. Weissberger, 'The Chemistry of Heterocyclic Compounds,' (N. Y. Interscience, 1950-1964), or similar manner to these methods.

Any of these mercapto group-having heterocyclic compounds usable in this invention may be provided on the same side as the silver halide emulsion layer's and incorporated into a nonlight-sensitive layer adjacent to the emulsion layer. The nonlight-sensitive layer means, to be concrete, the subbing layer (undercoat layer), filter layer, or protective layer. The coating amount of the mercapto group-having heterocyclic compound to be used in this invention is desirable to be from 0.1 mg to 10 mg/m^2. If the amount is less than 0.1 mg/m^2, the effect of the compound can lessen, while if it exceeds 10 mg/m^2, it tends to largely deteriorate the sensitivity.

The mercapto group-having heterocyclic compound to be

used in this invention may, if necessary, be incorporated also into the emulsion layer. However, from the viewpoint of the objects of this invention to lessen the dependence of the photographic characteristics upon the development, it is advantageous to incorporate the compound into the protective layer, so that the adding amount of the compound to the emulsion layer is desirable to be kept down to the minimum of its necessary range.

The silver halide to be used in this invention is not subjected to any particular restriction; any silver halides, for example, silver bromide, silver chloride, silver iodidobromide, silver chloroiodobromide, etc., may be widely used. The crystal form or crystal habit of these silver halides is not placed under restriction either and can be freely selected, and further may be of either the surface latent image type or the internal latent image type. The pAg and pH of the silver halide emulsion may also be widely selected.

The silver halide emulsion to be used in this invention may be prepared by any of various methods; e.g., the acid method, neutral method, alkaline method, ammoniacal method, and also, orderly mixing method, inversely mixing method, simultaneously mixing method, pAg-controlled double-jet method, conversion method, and the like. Further, a core/shell-type emulsion may also be used.

The silver halide emulsion to be used in this invention, in the course of the formation of the grains thereof or of the physical ripening thereof, may be present together with a cadmium salt, zinc salt, lead salt, thalium salt, iridium salt or a complex salt thereof, rhodium salt or a complex salt thereof, iron salt or iron complex salt, or the like.

Gelatin is usually used as a binder or protective colloid for the silver halide emulsion to be used in this invention, and in addition to gelatin, other materials may also be used which include, for example, proteins such as gelatin derivatives, graft polymers of gelatin with other high-molecular materials, albumin, casein, etc.; sugar derivatives such as agar-agar, sodium alginate, starch derivatives, etc.; and various synthetic hydrophilic high-molecular materials like homo- or copolymers such as polyvinyl alcohols, poly-N-vinylpyrolidones, polyacrylic acids, polyacrylamides, polyvinyl imidazoles, polyvinyl pyrazoles, etc.; and the like.

The silver halide emulsion to be used in this invention may be chemically sensitized by using various sensitizers. The sensitization may be carried out by the single or combined use of, for example, sulfur sensitizers (e.g., hypo, thiourea, active gelatin), noble-metallic sensitizers (e.g., gold sensitizers such as gold chloride, gold thiocyanate, etc., platinum salt, palladium salt, iridium salt, rhodium salt, ruthenium salt), reduction sensitizers (e.g., stannous

chloride, thiourea dioxide, hydrazine derivatives), those selenium sensitizers as desicribed in U.S. Patent No. 3,297,446, those polyalkylene-polyamine compounds as described in U.S. Patent No. 2,518,698, and the like.

The silver halide emulsion to be used in this invention may be sensitized by using appropriate sensitizing dyes to desired spectral wavelength regions. As the sensitizing dye various-type sensitizing dyes may be used alone or in combination of two or more thereof. Examples of the sensitizing dye usable in this invention include methine dyes and styryl dyes, such as cyanines, merocyanines, hemicyanines, rhodacyanines, oxonoles, hemioxonoles, and the like.

Hardening agents usable in this invention include organic hardening agents such as vinylsulfone-type, cyanur-chloride-type, acryloyl-type and ethylene-imine-type hardening agents, and inorganic hardening agents such as chrome alum, potassium alum, etc., which may be used alone or in combination of two or more thereof.

The photographic light-sensitive material of this invention may use various-type surface active agents including nonionic surface active agents such as saponin, polyalkylene glycol ether, etc., and anionic surface active agents such as alkylbenzenesulfonates, alkyl sulfates, sulfosuccinates, etc.

The photographic light-sensitive material of this invention may, if necessary, use various other photographic

additives including, e.g., stabilizers, coating aids, layer's physical property improving agents, ultraviolet absorbing agents, brightening agents, oxidation inhibitors, antistain agents, metallic ion blocking agents, viscosity increasing agents, matting agents, antihalation agents, antiirradiation agents, and the like.

Materials usable as the support for the photographic light-sensitive material of this invention include paper, glass, cellulose acetate, cellulose nitrate, polyester, polyamide, polystyrene, polypropylene, and two or more substrates-laminated materials such as paper-polyolefin (e.g., polyethylene, polypropylene) laminates, and the like.

Developing agents for use in developing the silver halide light-sensitive photographic material of this invention include various discretional developing agents to be used according to the light-sensitive material produced. For example, they are typified by the following: The most typical one as the HO-(CH=CH)n-OH-type developing agent is hydroquinone, and other examples representative of it include catechol, pyrogallol and derivatives thereof and ascorbic acid, such as chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhydroquinone, 2,3-dibromohydroquinone, 2,5-dihydroxyacetophenone, 2,5-diethylhydroquinone, 2,5-di-p-phenethylhydroquinone, 2,5-dibenzoyl-

aminohydroquinone, catechol, 4-chlorocatechol, 3-phenylcatechol, 4-phenylcatechol, 3-methoxycatechol, 4-acetylpyrogallol, 4-(2-hydroxybenzoyl)pyrogallol, sodium ascorbate, and the like.

Also, examples representative of the $HO-(CH=CH)_n-NH_2$-type developing agent include o- and p-aminophenols and aminopyrazolone, such as 4-aminophenol, 2-amino-6-phenylphenol, 2-amino-4-chloro-6-phenylphenol, 4-amino-2-phenylphenol, 3,4-diaminophenol, 3-methyl-4,6-diaminophenol, 2,4-diaminoresorcinol, 2,4,6-triaminophenol, N-methyl-p-aminophenol, N-ß-hydroxyethyl-p-aminophenol, p-hydroxyphenylaminoacetic acid, 2-aminonaphthol, and the like.

Further, examples of the $H_2N-(CH=CH)n-NH_2$-type developing agent include, e.g., 4-amino-2-methyl-N,N-diethylaniline, 2,4-diamino-N,N-diethylaniline, N-(4-amino-3-methylphenyl)-morpholine, p-phenylenediamine, 4-amino-N,N-dimethyl-3-hydroxyaniline, N,N,N,N-tetramethylparaphenylenediamine, 4-amino-N-ethyl-N-(ß-hydroxyethyl)-aniline, 4-amino-3-methyl-N-ethyl-N-(ß-hydroxyethyl)-aniline, 4-amino-N-ethyl-(ß-methoxyethyl)-3-methyl-aniline, 4-amino-3-methyl-N-ethyl-N-(ß-methylsulfonamidoethyl)-aniline, 4-amino-N-butyl-N-γ-sulfobutylaniline, 1-(4-aminophenyl)-pyrolidine, and the like.

Examples of the heterocyclic-type developing agent include 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-

hydroxymethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, etc., and 1-phenyl-4-amino-5-pyrazolone, 1-(p-aminophenyl)-3-amino-2-pyrazoline, 1-phenyl-3-methyl-4-amino-5-pyrazolone, 5-aminouracil, and the like.

In addition to these compounds, those developing agents as described in T. H. James, "The Theory of the Photographic Process," Fourth Edition, pp. 291-334 and Journal of the American Chemical Society, Vol. 73, p. 3,100 (1951) may also be effectively used in this invention. These developing agents may be used either alone or in combination of two or more thereof, and the being used in combination is preferred. The effect of this invention will not be reduced even though, e.g., sodium sulfite or potassium sulfite, etc., as a preservative is added to the developing solution to be used for the light-sensitive material of this invention; this is one of the characteristics of this invention. In addition, hydroxylamine, hydrazide compounds may also be used as the preservative. Aside from the above, providing the developer solution with pH adjustment and buffer function by use of a caustic alkali, carbonate alkali or amine which is usually used for general black-and-white developer solution, and the addition to the developer solution of an inorganic development restrainer such as potassium bromide; an organic development restrainer such as benzotriazole; a metallic ion capturing agent such as ethylenediaminetetraacetic acid; a development

accelerator such as methanol, ethanol, benzyl alcohol, polyalkylene oxides, etc.; a surface active agent such as a sodium alkylarylsulfonate, natural saponin, saccharide, or an alkyl ester of the above compound; a hardening agent such as glutaraldehyde, formalin, glyoxal, etc.; an ionic strength adjusting agent such as sodium sulfate; and the like may be carried out arbitrarily.

The developer solution to be used in this invention may contain an alkanolamine or a glycol as an organic solvent.

The pH value of the above-composition-having developer solution is preferably from 9 to 12, and more preferably from 10 to 11 from the standpoint of the preservability and photographic characteristics.

The silver halide light-sensitive photographic material of this invention may be processed under various conditions. As for the processing temperature, for example, the developing temperature is preferably not more than 50°C, and particularly preferably between 30°C and 40°C. The developing time is generally within 3 minutes, and particularly preferably within 2 minutes, which, in most cases, results in satisfactory results. Those processing steps other than the above development, such as, e.g., washing, stopping, stabilizing, fixation, and further, if necessary, prehardening, neutralizing and the like processes, may be adopted arbitrarily, and some of these processes may be omitted

according to circumstances. Further, these processes may be carried out either in manual way such as by tray development or frame development or in mechanical way such as by roller development, hanger development, or the like.

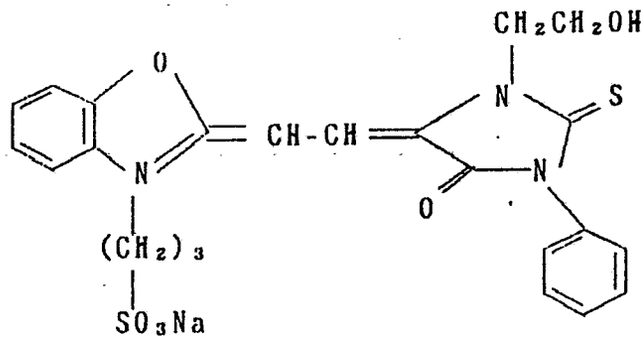
The present invention will be further illustrated in detail by the following examples. It goes without saying that the invention is not limited to and by the examples.

EXAMPLE-1

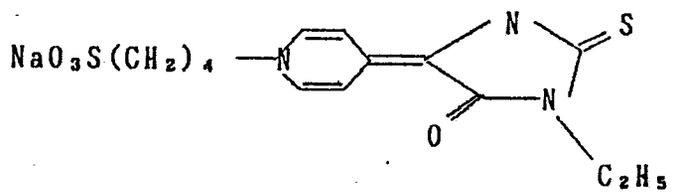
A silver halide emulsion containing tetradecahedral silver halide crystalline grains comprised in composition of 90 mole% silver bromide, 9 mole% silver chloride and 1 mole% silver iodide, whose average grain size is 0.6μm, was prepared and then subjected to gold sensitization and sulfur sensitization. To this emulsion were added 100mg each per mole of Ag of sensitizing dyes having the following Formulas (I) and (II), and further added 1 g per mole of Ag of a stabilizer 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene; a mercapto group-having heterocyclic compound as given in Table 1; 1 g per mole of Ag of a coating aid sodium tripropylnaphthalene-sulfonate; 40 g per mole of Ag of liquid paraffin in the form of an emulsifiedly dispersed product and 20 g per mole of Ag of diethylene glycol both as layer's physical property improving agents; 5 g per mole of Ag of a styrene-maleic anhydride copolymer as a viscosity increasing agent; 30 mg per gram of gelatin of the reaction product of tetrakis(vinyl-

sulfonylmethyl)methane and taurine potassium salt (1:0.25) as a hardening agent, and then the pH of the mixture was adjusted to 5.5, whereby an emulsion coating liquid was prepared.

(Sensitizing Dye I)



(Sensitizing Dye II)



Subsequently, to a gelatin binder were added 30 mg/m of silica particles as a matting agent whose average particle size is 4 μm; 30 mg/m^2 of 2-sulfonate succinic acid bis(2-ethylhexyl) ester sodium salt as a coating aid; 20 mg/m^2 of the following compound [A] as a fluorine-containing surface active agent; 100 mg/m^2 of a styrene-maleic anhydride copolymer as a viscosity increasing agent; and 30 mg per gram of gelatin of the reaction product of tetrakis(vinylsulfonyl-methyl)methane with taurine potassium salt (1:0.25) as a

hardening agent, and further were added a mercapto group-having heterocyclic compound in a quantity as given in Table 1, and then the pH of the mixture was adjusted to 5.5, whereby a protective layer coating liquid was prepared.

Both the thus prepared emulsion coating liquid and protective layer coating liquid were coated superposedly on the nonbacking-layer-side surface of a 110 μm-thick polyethylene-coated paper having a hydrophilic colloid backing layer (provided on the reverse to the at least one silver halide emulsion layer-having side of the support) and an undercoat layer, provided that a mixture solution of a 1-phenyl-3-pyrazolidone in a quantity as given in Table 1 and 4 g per mole of Ag of the following Compound [B] was added to the emulsion coating liquid immediately (within 10 seconds) before the coating.

The coating amount of silver was 1.4 g/m^2, and the coating amount of gelatin was 2.5 g/m^2 for the emulsion layer and 1.2 g/m^2 for the protective layer.

[A] $$\begin{array}{l} CH_2\text{-}COOCH_2\text{-}(CF_2)_6\text{-}H \\ | \\ NaO_3S\text{-}CH\text{-}COOCH_2\text{-}(CF_2)_6\text{-}H \end{array}$$

[B] $HO\text{-}CH_2\text{-}SO_3Na$

The thus obtained sample was subjected to 10^{-6} second flash exposure by use of a xenon speed light unit through an optical wedge, and then developed under two different conditions: 15 seconds at 32°C and 30 seconds at 38 C in a

developer solution having the following composition [I]. The developing process was then followed by fixation, washing and drying in usual manner.

Developer Solution [I]:

Pure water (ion-exchanged water)	approx.3,200 ml
Potassium sulfite	60 g
Disodium ethylenediaminetetraacetate	2 g
Potassium hydride	10.5g
5-methylbenzotriazole	300 mg
Diethylene glycol	25 g
1-phenyl-4,4-dimethyl-3-pyrazolidinone	300 mg
1-phenyl-5-mercaptotetrazole	60 mg
Potassium bromide	3.5g
Hydroquinone	20 g
Potassium carbonate	15 g
Add pure warter (ion-exchanged water) to make	4,000 ml

The obtained resultes are shown in Table 1, wherein the sensitivity is of a value expressed in -log E when an exposure necessary to obtain a density of 1.0 is regarded as E.

As is apparent from Table 1, Samples 1-3, 1-6 and 1-9 which satisfy the present invention are stable in the three photographic characteristics, the sensitivity, Dmax, and Dmin, against the change in the developing condition.

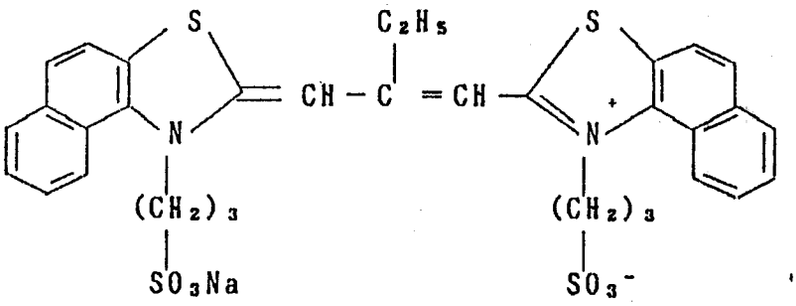
Table 1

Sample No.	1-Phenyl-3-pyrazolidone		Mercapto cpd. (EM layer)		Mercapto cpd. (Pro. layer)		Sensitivity (in log E)			Dmax			Dmin			Remarks
	Cpd.	Adding amount	Cpd.	Coating amount	Cpd.	Coating amount	15sec 32°C	30sec 38°C	Change	15sec 32°C	30sec 38°C	Change	15sec 32°C	30sec 38°C	Change	
1-1	-	-	B-20	0.8mg/m²	-	-	1.00	1.60	0.60	1.25	1.78	0.53	0.05	0.05	0	Comparative
1-2	A-1	1g/molAg	B-20	0.8mg/m²	-	-	1.42	1.72	0.30	1.66	1.80	0.14	0.05	0.08	0.03	Comparative
1-3	A-1	1g/molAg	B-20	0.8mg/m²	B-20	0.8mg/m²	1.38	1.68	0.30	1.65	1.80	0.15	0.05	0.06	0.01	Invention
1-4	A-1	1g/molAg	B-20	1.6mg/m²	-	-	1.28	1.66	0.38	1.48	1.76	0.28	0.05	0.06	0.01	Comparative
1-5	A-5	2g/molAg	B-20	0.8mg/m²	-	-	1.40	1.72	0.32	1.65	1.80	0.15	0.05	0.07	0.02	Comparative
1-6	A-5	2g/molAg	B-20	0.8mg/m²	B-20	0.8mg/m²	1.35	1.68	0.33	1.65	1.80	0.15	0.05	0.05	0	Invention
1-7	A-5	2g/molAg	B-20	1.6mg/m²	-	-	1.28	1.67	0.39	1.45	1.76	0.31	0.05	0.05	0	Comparative
1-8	A-5	2g/molAg	B-18	1.0mg/m²	-	-	1.42	1.74	0.32	1.66	1.80	0.14	0.05	0.08	0.03	Comparative
1-9	A-5	2g/molAg	B-18	1.0mg/m²	B-18	1.0mg/m²	1.40	1.72	0.32	1.64	1.80	0.16	0.05	0.06	0.01	Invention
1-10	A-5	2g/molAg	B-18	2.0mg/m²	-	-	1.32	1.70	0.38	1.45	1.78	0.33	0.05	0.06	0.01	Comparative

EXAMPLE-2

A silver halide emulsion having cubic silver halide crystalline grains comprised in composition of 98 mole% silver bromide and 2 mole% silver iodide, whose average grain size is 0.5 μm, was prepared, and then subjected to gold sensitization and sulfur sensitization treatments. To this emulsion were added 2 g per mole of Ag of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer; 150 mg per mole of Ag of a compound having the following Formula [III] as a sensitizing dye; a compound as given in Table 2 as a mercapto group-having heterocyclic compound; 10 g per mole of Ag of saponin as a coating aid; 80 g per mole of Ag of polyethylene acrylate latex as a layer's physical property improving agent; 5 g per mole of Ag of a styrene-maleic anhydride copolymer as a viscosity increasing agent; and 10 mg per gram of gelatin of formalin as a hardening agent, and the pH of this mixture was adjusted to 5.5, whereby an emulsion coating liquid was prepared.

(Sensitizing Dye III)

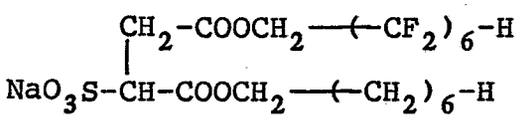


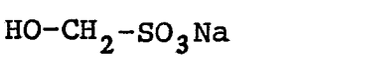
Subsequently, to a gelatin binder were added 0.1 g/m² of methyl methacrylate with an average particle size of 3.5 μm as a matting agent; 30 mg/m² of 2-sulfonate succinic acid bis(2-ethylhexyl)ester sodium salt as a coating aid; 20 mg/m² of a compound having the following Formula [A] as a fluorine-containing surface active agent; 100 mg/m² of a styrene-maleic anhydride copolymer as a viscosity increasing agent; 10 mg per gram of gelatin of formalin as a hardening agent; and further a mercapto group-having heterocyclic compound in an amount as given in Table 2, and then the pH of this mixture was adjusted to 5.5, whereby a protective layer coating liquid was prepared.

Both the thus prepared emulsion coating liquid and protective layer coating liquid were coated superposedly on the nonbacking layer-side surface of a 100 μm-thick polyethylene terephthalate film support having a hydrophilic colloid backing layer, provided that a mixture solution of 15

g per mole of Ag of hydroquinon, a 1-phenyl-3-pyrazolidone in an amount as given in Table 2 and 8 g per mole of Ag of a compound having the following Formula [B] was added to the emulsion coating liquid immediately (within 10 seconds) before the coating thereof.

The coating amount of silver was 3.8 g/m², and the coating amount of gelatin was 2.0 g/m² for the emulsion layer and 1.2 g/m² for the protective layer.

[A] 

[B] 

The thus obtained sample was subjected to 10^{-6} second flash exposure by using a xenon speed light unit through an optical wedge, and then developed under two different conditions: 20 seconds at 35°C and 40 seconds at 38°C in the same developer solution [I] as in Example-1. The developing process was then followed by fixation, washing and drying in usual manner.

The obtained results are shown in Table 2, wherein the sensitivity is expressed in -log E when an exposure necessary to obtain a density of 3.0 is regarded as E.

As is apparent from the results shown in Table 2, Samples 2-3, 2-6 and 2-9 which satisfy the present invention are stable in the three photographic characteristics, the sensitivity, Dmax, and Dmin, against the change in the

developing condition.

Table 2

Sample No.	1-Phenyl-3-pyrazolidone		Mercapto cpd. (EM layer)		Mercapto cpd. (Pro. layer)		Sensitivity (in log E)			Dmax			Dmin			Remarks
	Cpd.	Adding amount	Cpd.	Coating amount	Cpd.	Coating amount	15sec 32°C	30sec 38°C	Change	15sec 32°C	30sec 38°C	Change	15sec 32°C	30sec 38°C	Change	
2-1	-	-	B-20	2.0mg/m²	-	-	1.00	1.50	0.50	4.10	5.20	1.10	0.04	0.05	0.01	Comparative
2-2	A-2	1g/molAg	B-20	2.0mg/m²	-	-	1.32	1.55	0.23	4.90	5.30	0.40	0.04	0.07	0.03	Comparative
2-3	A-2	1g/molAg	B-20	2.0mg/m²	B-20	2.0mg/m²	1.26	1.51	0.25	4.90	5.30	0.40	0.04	0.05	0.01	Invention
2-4	A-2	1g/molAg	B-20	4.0mg/m²	-	-	1.14	1.48	0.34	4.70	5.20	0.50	0.04	0.05	0.01	Comparative
2-5	A-3	2g/molAg	B-20	2.0mg/m²	-	-	1.34	1.53	0.19	4.90	5.25	0.35	0.04	0.07	0.03	Comparative
2-6	A-3	2g/molAg	B-20	2.0mg/m²	B-20	2.0mg/m²	1.30	1.50	0.20	4.90	5.25	0.35	0.04	0.05	0.01	Invention
2-7	A-3	2g/molAg	B-20	4.0mg/m²	-	-	1.21	1.48	0.27	4.65	5.10	0.45	0.04	0.05	0.01	Comparative
2-8	A-3	2g/molAg	B-4	1.0mg/m²	-	-	1.37	1.55	0.18	4.90	5.30	0.40	0.04	0.07	0.03	Comparative
2-9	A-3	2g/molAg	B-4	1.0mg/m²	B-4	1.0mg/m²	1.32	1.54	0.22	4.90	5.30	0.40	0.04	0.05	0.01	Invention
2-10	A-3	2g/molAg	B-4	2.0mg/m²	-	-	1.20	1.52	0.32	4.65	5.20	0.55	0.04	0.05	0.01	Comparative

WHAT IS CLAIMED IS:

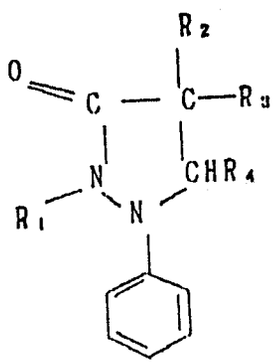
1. A silver halide light-sensitive photographic material which comprises a support and, provided on at least one side thereof, at least two photographic layers,

at least one of which photographic layers being a silver halide emulsion layer containing silver halide grains, of which silver bromide content is not less than 80 mol % and the average grain size is not less than 0.4 micro meters,

and at least one other of which photographic layers being a non-light-sensitive layer provided contiguous to said silver halide emulsion layer,

characterized in that at least one of said photographic layers contains a 1-phenyl-3-pyrazolidone compound and said non-light-sensitive layer contains a heterocyclic compound having therein a mercapto group or a derivative thereof.

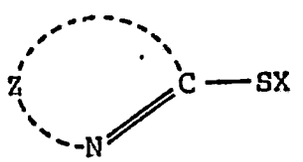
2. The silver halide light-sensitive photographic material of claim 1, wherein said 1-phenyl-3-pyrazolidone compound is represented by the general formula;



wherein, R_1 is hydrogen or an acetyl group, and R_2, R_3 and R_4 are independently selected from the group consisting of hydrogen and a substituted or unsubstituted alkyl group.

3. The silver halide light-sensitive photographic material of claim 2, wherein said 1-phenyl-3-pyrazolidone compound is one selected from the group consisting of
1-phenyl-3-pyrazolidone,
1-phenyl-4-methyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1-phenyl-5-methyl-3-pyrazolidone,
1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone,
1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone,
1-phenyl-4,4-di-n-propyl-3-pyrazolidone and
1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone.

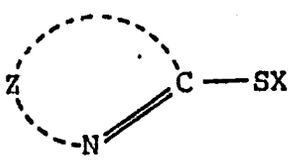
4. The silver halide light-sensitive photographic material of claim 1, wherein said heterocyclic compound is represented by general formula [2];



..... [2]

wherein, Z is a group of non-metallic atoms necessary to form a 5- or 6-membered heterocyclic ring xnd X is selected from the group consisting of hydrogen atom, an alkali metal atom, an ammonium and an organic amine residue.

5. The silver halide light-sensitive photographic material of claim 2, wherein said heterocyclic compound is represented by general formula [2];



..... [2]

wherein, Z is a group of non-metallic atoms necessary to form a 5- or 6-membered heterocyclic ring xnd X is selected from the group consisting of hydrogen atom, an alkali metal atom, an ammonium and an organic amine residue.

6. The silver halide light-sensitive photographic material of claim 4, wherein said heterocyclic ring is one selected from the group consisting of an imidazole, a thiazole, an oxazole, a benzimidazole, a benzothiazole, a benzoxazole, an oxadiazole, a thiadiazole, a triazole, a tetrazole, a pyrimidine, a triazine, and a tetrazaindene.

7. The silver halide light-sensitive photographic material of claim 5, wherein said 1-phenyl-3-pyrazolidone compound is one selected from the group consisting of
1-phenyl-3-pyrazolidone,
1-phenyl-4-methyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1-phenyl-5-methyl-3-pyrazolidone,
1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone,
1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone,
1-phenyl-4,4-di-n-propyl-3-pyrazolidone and
1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone.

8. The silver halide light-sensitive photographic material of claim 2, wherein said 1-phenyl-3-pyrazolidone compound is contained in said photographic layer in a quantity of 0.2g to 5g per mole of silver halide.

9. The silver halide light-sensitive photographic material of claim 2, wherein said heterocyclic compound is contained in a quantity of 0.1mg/m^2 to 10mg/m^2.

10. The silver halide light-sensitive photographic material of claim 1, wherein said non-light-sensitive layer is a protective layer, a subbing layer, an anti-halation layer, an intermediate layer or a filter layer.

11. The silver halide light-sensitive photographic material of claim 10, wherein said non-light-sensitive layer is a protective layer.

12. The silver halide light-sensitive photographic material of claim 10, wherein said 1-phenyl-3-pyrazolidone compound is present in a silver halide emulsion layer.