

[54] **PHOTOGRAPHIC EMULSIONS AND DEVELOPERS CONTAINING 2-MERCAPTO HETEROCYCLIC COMPOUNDS**

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[63] Continuation-in-part of Ser. No. 91,220, Nov. 19, 1970, abandoned.

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[58] **Field of Search**..... **96/109, 95, 66.3, 96/66.5, 107, 108**

[56] **References Cited**

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[57]

ABSTRACT

This invention relates to photographic materials designed for processing in developing agents which have a long induction period and to which fog-reducing adjuvants have been added. The induction period can be considerably shortened and the restraining action of any antifoggant overcome by the addition of certain heterocyclic nitrogen compounds which contain a mercapto substituent adjacent to the nitrogen atom and which exhibit a pKa not less than 7.7.

13 Claims, No Drawings

PHOTOGRAPHIC EMULSIONS AND DEVELOPERS CONTAINING 2-MERCAPTO HETEROCYCLIC COMPOUNDS

This application is a continuation-in-part of my co-pending application, Ser. No. 91,220, filed Nov. 19, 1970 now abandoned.

BACKGROUND OF THE INVENTION

A combination of special emulsions and developers is required to give the high contrast, sharp toe, low fog and high top density characteristic of graphic arts products such as lithographic films. Developers commonly used to obtain this curve shape are based mainly on hydroquinone as taught by Mason in "Photographic Processing Chemistry," the Focal Press (1966). This combination of emulsion-developer is mainly used for the production of halftone dot images useful in the production of letterpress, lithography and the like. It is known from Kirillov in "Problems in Photographic Research and Technology," the Focal Press (1967), pp. 100-101, and from Mess-James, "The Theory of the Photographic Process," (1966), p. 352 that these developers require an induction period prior to development whereupon so called "infectious development" occurs giving rise to the high gradient necessary for good dot quality. This phenomenon has been discussed by, for example, James in the Journal of Photographic Science, 10 (1944), p. 271 and again by James in Photographic Science and Engineering, 12 (1968), p. 67 and by Yule in the Journal of the Franklin Institute, 239 (1945), p. 221.

To hasten the induction period and, hence, increase the effective speed of developer systems, and to improve developer access time, many additives have been tried. Luppó-Cramer (Phot. Korr. 70 (1934), p. 145), for example, observed that development of exposed emulsions in mildly alkaline hydroquinone was accelerated if the emulsion was first bathed in allylthiourea. However, these researchers reported that serious fogging problems arose with the use of thiourea or its simple derivatives. The silver formed as a result of the development of non-exposed crystals of silver halide is known as "fog" and may be reduced substantially by addition of certain antifoggants to the emulsion. These anti-foggants (also known as "stabilizers" or "restrainers") retard the development of both exposed and non-exposed silver halide crystals and, hence, tend to reduce the effective speed of the resulting emulsion. These facts are well-known to the art and are discussed, for example, in the cited Mason reference. Useful organic antifoggants, e.g., benzotriazole, 6-nitrobenzimidazole, and others, are discussed in this and other references.

SUMMARY OF THE INVENTION

An object of this invention is to provide a novel photographic emulsion-developer system. A further object is to reduce the induction period of litho-type developers. Another object is to lower the induction period without alteration of the sensitometric characteristics of the emulsion. Still another object is to eliminate the need for a primary developing agent, e.g., N-methyl-p-aminophenol or a 3-pyrazolidone admixed with hydroquinone in super-additive mixtures. Yet, another object is to overcome the restraining action that occurs when antifoggants are added to the photographic sys-

tems without a subsequent deleterious increase in fogging.

The radiation-sensitive elements of this invention have layers comprised of photographic silver halide emulsions in hardened, macromolecular, water-permeable, organic colloid binders on suitable supports. Processing of these elements in litho-type or conventional high free sulfite developers containing hydroquinone, methyl-hydroquinone, catechol, pyrogallol, and others, can be hastened by adding certain mercapto-substituted heterocyclic nitrogen compounds exhibiting a pKa not less than 7.7. These mercapto compounds, e.g., 2-mercapto pyridine and 2-mercapto quinoline, can be admixed with the emulsion in quantities of 10^{-2} millimoles to 2.5 millimoles/1.5 moles of silver halide and produce the same sensitometric curve shape at a substantial and novel increase in emulsion speed of reduction of the induction period necessary for development. Surprisingly, these useful additives do not objectionably increase the fog of the photographic film as is common with many speed increasing adjuvants. In addition, the novel compounds may be incorporated into the above-described developing solutions in the range of 0.0005 to 1.0 gram per liter of solution where they perform the same functions described above. Alternatively, when admixed in developing solutions containing substantial amounts of at least one antifoggant, such as 5-nitroindazole, 5-nitrobenzimidazole, and 1,2-naphthotriazole, they overcome the restraining action of said antifoggant and prevent speed loss without increasing the level of fog.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The water-permeable colloid silver halide emulsions which may be used to practice the invention include all of the common silver halide types used, for example, in graphic arts, medical and industrial x-ray, cine negative or positives, and color films. These aqueous silver halide emulsions, for example, silver chloride, bromide, chlorobromide, bromiodide, chloriodide, or mixtures of chloride-iodide-bromide emulsions may contain reduced amounts of gelatin and other polymer binders, such as dispersed aqueous polyethyl acrylate, and are preferably brought to their optimum sensitization by digestion with sulfur and gold in a known manner. The speed increasing additives of this invention are preferably added to the emulsion or to the developing solution. These additives are heterocyclic nitrogen compounds having attached to an intracyclic carbon atom in the alpha-position to the intracyclic nitrogen atom a mercapto group, and exhibiting a pKa not less than 7.7, and can be added to the emulsion in the range of 10^{-2} millimoles to 2.5 millimoles per 1.5 moles of silver halide and preferably at 0.1 millimoles to 1.0 millimoles per 1.5 moles of silver halide. Alternatively, they can be added to the developing solution in the range of 0.0005 gram to 1.0 gram per liter of developer and preferably at 0.01 to 0.1 gram per liter of developer. Suitable 2-mercapto compounds are selected from the group: 2-mercaptopyridine, 2-mercaptoquinoline, 2-mercaptobenzimidazole, 2-mercapto-4-phenylthiazole, 2-mercaptopyrimidine, 2-mercapto-1-methylimidazole, 2-mercaptoimidazoline, 3,4,5,6-tetrahydro-2-pyrimidinethiol, 2-mercaptoimidazole, ϵ -thiocaprolac-

tam and 2-mercaptothiazoline. While usually only one of these compounds is used in the emulsions or developer solutions, mixtures of two, three or more of the mercapto compounds can be used.

Suitable developer solutions contain the following ingredients:

Ingredients	Grams
Ammonium, sodium, or potassium sulfite	1.0 to 100.0
Sodium or potassium carbonate or borate (depending on desired degree of buffering)	3.0 to 80.0
Sodium bromide	0.0 to 30.0
Hydroquinone	1.0 to 50.0
2-mercapto compound of the invention	0.0005 to 1.0
Sodium or potassium hydroxide to adjust pH to	10.5 $\pm$ 1
Water to	1 liter

These 2-mercapto substituted heterocyclic nitrogen compounds exhibit a pKa greater than 7.7. They may be added to the emulsion at any stage of manufacture but preferably after digestion and just prior to coating. Alternatively, one may incorporate these adjuvants into the developer solution. The 2-mercapto compounds of this invention may be added alone or together with certain antifoggants which preferably include 5-nitroindazole, 5-nitrobenzimidazole, 1,2-naphthotriazole, benzotriazole, and various derivatives of these compounds. These antifoggants may be admixed with the emulsion, but are preferably added to the developing solution at 0.01 gram to 2.0 gram per liter of developer and preferably at 0.01 gram to 0.5 gram per liter of solution. When used in the emulsion, they are incorporated at a level of 0.05 millimoles to 20 millimoles per 1.5 mole of silver halide. Other antifoggants which are believed to be useful include 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzoxazole, and 5-phenyltetrazole, monoazoles, diazoles, triazoles and pyrimidines, and polyethylene oxides which are specifically useful in hydroquinone developers. The emulsions used may be silver halide emulsions of various types such as non-sensitized, x-ray, panchromatic or orthochromatic. The carrier for said emulsion may be gelatin or any other organic, macromolecular, water-permeable colloid. In place of part or all of the gelatin or other natural colloid binding agent, synthetic agents, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers and acetals containing a large number of extralinear $-\text{CH}_2-\text{CH}-\text{OH}-$ groups, hydrolyzed interpolymers of vinyl acetate, and unsaturated addition polymerizable compounds, such as maleic anhydride, acrylic and methacrylic acid, ethyl esters, and styrene may be used. Suitable colloids of the last-mentioned type are disclosed in U.S. Pat. Nos. 2,276,322; 2,276,323; and 2,347,811. Suitable mixed colloids are described in U.S. Pat. Nos. 3,142,568 and 3,203,804.

The emulsions containing the 2-mercapto compounds and/or antifoggants of this invention or to be used with the developer containing these mercapto compounds and/or anti-foggants may be coated on any conventional base or support, such as glass, metal, various waterproof papers, cellulose derivatives, super polymers, such as nylon, polyvinyl chloride, polystyrene, and polyethylene terephthalate and others. These emulsions may also contain other adjuvants, such as sensitizers, coating aids, dyes, hardeners, etc.

The invention is illustrated by, but not limited to, the examples described below. Examples I - VIII all contain the lithographic type emulsion described by Notorff in U.S. Pat. No. 3,142,568. These are aqueous gelatin/ethyl acrylate silver bromochloride emulsions which contain about 30 mole percent AgBr and about 70 mole percent AgCl, but may also contain small amounts of iodide, and have been brought to their optimum sensitivity. These emulsions contain the usual coating aids, anti-foggants, and hardeners. Just prior to coating, the 2-mercapto compounds of this invention are added in the amounts shown from solution in ethanol. In each case, an untreated control is included. The emulsions were coated on clear, 0.004-inch-thick polyethylene terephthalate film coated on both sides with a vinylidene/alkyl acrylate/itaconic acid copolymer mixed with an alkyl acrylate and/or methacrylate polymer as described by Rawlins in U.S. Pat. No. 3,443,950, on which had been coated on both sides a thin anchoring substratum of gelatin (0.5 mg/dm²). After drying, strips from the coatings were given a 20 second exposure through a $\sqrt{2}$ step wedge to a white light tungsten filament lamp followed by a 2- $\frac{1}{4}$ minute development at 68°F. in the aqueous developer solutions as shown below:

Developer Composition*

A	B
500 cc.	500 cc.
6 g.	30 g.
42.5 g.	—
—	7.5 g.
—	7.5 g.
4.5 g.	—
1.8 g.	1.6 g.
—	2.6 g.
12.5 g.	—
20 g.	22.5 g.
1.0 liter	1.0 liter
10.5	10.5

*Additional wetting agents, sequestrants and adjuvants may be incorporated as known in those skilled in the art.

Emulsion Additive (gms/1.5 mole of Silver Halide)	Additive pKa	Base + Fog	Relative Speed	Developer
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EXAMPLE I

None — Control	—	0.05	100)	A
0.1 gm. 2-mercapto-pyridine	10.5	0.03	161)	

EXAMPLE II

None — Control	—	0.05	100)	B
0.075 gm. 2-mercapto-pyridine	10.5	0.04	110)	
0.1 gm. 2-mercapto-pyridine	10.5	0.04	135)	

EXAMPLE III

None — Control	—	0.05	100)	A
0.056 gm. 2-mercapto-quinoline	10.25	0.03	114)	
0.11 gm. 2-mercapto-quinoline	10.25	0.03	123)	

EXAMPLE IV

None — Control	—	0.05	100)	A
0.125 gm. 2-mercapto-4-phenyl thiazole	7.7	0.03	119)	

EXAMPLE V

None — Control	—	0.08	100)	
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Emulsion Additive (gms/1.5 mole of Silver Halide)	Additive pKa	Base + Fog	Relative Speed	Developer
EXAMPLE I				
0.06 gm. 2-mercapto-pyridine	10.5	0.04	130)	B
0.12 gm. 2-mercapto-pyridine	10.5	0.04	140)	
0.06 gm. 4-mercapto-pyridine	8.86	0.06	69)	
EXAMPLE VI				
None — Control	—	0.04	100)	B
0.1 gm. 2-mercapto-pyridine	10.5	0.04	117)	
0.12 gm. 2-mercapto-benzimidazole		0.06	151)	
10				
EXAMPLE VII				
None — Control	—	0.04	100)	A
0.15 gm. 2-mercapto-benzoxazole		0.04	100)	
	6.6		)	
0.15 gm. 2-mercapto-benzothiazole		0.04	100)	
	7.4		)	
0.25 gm. 8-mercapto quinoline	—	0.04	100)	

All of the above examples shown gave the same curve shape, gamma and top density when the H & D curves were plotted and compared. The examples which exhibit a pKa not less than 7.7 and have a mercapto substituent adjacent to the nitrogen, gave a considerable and surprising increase in speed.

EXAMPLE VIII

In this Example, the emulsion was like that in Examples I - VII, but no mercapto compound was added; instead, 0.1 g. of 2-mercaptopyridine was added per liter of developing Solution A of Examples I - VII with the following results:

Sample	Base + Fog	Relative Speed
Control	0.06	100
With 2-mercapto-pyridine	0.06	223

As can be seen from this example, addition of the speed increasing 2-mercapto compound adjuvant to the developer more than doubles the speed of the resulting film. Exposure and developing times were the same as reported in Examples I - VII.

EXAMPLE IX

An optically unsensitized, large grained, silver halide emulsion is produced containing about 0.35% gelatin, 5% polyvinyl alcohol and about 10% silver halide and brought to its optimum sensitivity by digestion with gold and sulfur. The silver halide consists of 98 weight percent AgBr and 2 weight percent AgI. After digestion, the usual coating aids, antifoggers, hardeners, etc. are added and the emulsion is coated on 0.007-inch thick polyethylene terephthalate base subbed and prepared as described by Alles in U.S. Pat. No. 2,779,684, Example IV. After drying, strips from this coating were given a 10^{-1} second exposure through a $\sqrt{2}$ step wedge on the Mark 6 Sensitometer produced by E.G. & G. Co. which uses the GE Type FT-118 Xenon Flash

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Tube. The sensitometer contained a 2.0 neutral density filter and a No. 207763, 10^{-2} compensating attenuator grid. These exposed strips were then developed in the developer composition listed below with or without the 2-mercapto compounds of this invention. The induction period, or time needed to show the first signs of the highest exposure region (E_{20}) of the step wedge, was noted and the results are given below:

Developer Composition

K₂SO₃ (anhydrous — 40 g./liter
K₂CO₃ (anhydrous) — 20 g./liter
KOH — 5 g./liter
KBr — 10 g./liter
Benzotriazole — 1 g./liter
Developing Agent — as shown below
pH — 10.5
H₂O to — 1.0 liter

Developing Agent	Sensitizer Used (0.1 gm./liter of developer)	pKa	Induction Time
25 Hydroquinone (25 g./l) Do. Do.	None — Control 2-mercaptopyridine 1-phenyl-5-mercapto- tetrazole *	— 10.5 4	about 10 min. 1.5 min. >12 min.
30 Chlorohydro- quinone (33 g/l) Do. Methylhydro- quinone (28 g/l) Do. Catechol (25 g/l) Do. Pyrogallol (26 g/l) Do.	None — Control 2-mercaptopyridine None — Control 2-mercaptopyridine None — Control 2-mercaptopyridine None — Control 2-mercaptopyridine	— 10.5 — 10.5 — 10.5 — 10.5	75 sec. 30 sec. 90 sec. 12 sec. 210 sec. 140 sec. 35 sec. 25 sec.
35 Hydroquinone (25 g/l) Do. Do.	None — Control 2-mercaptopyrimidine 2-mercapto-1-methyl-imidazole	— 7.8 10.6	about 10 min. 18 sec. 18 sec.

The 1-phenyl-5-mercaptotetrazole is included to demonstrate that a compound with a pKa less than 7.7 will not function according to this invention, and gives a wholly different result.

The above example serves to demonstrate further the novelty of the compounds and also their effectiveness when used with other developing agents exhibiting long induction periods and to demonstrate the use of other emulsions and binder systems. Complete development can be accomplished in almost as short a period of time as when developer solutions containing a mixture of hydroquinone and N-methyl-p-aminophenol hydrochloride or hydrosulfate (Metol) or of hydroquinone and a 3-pyrazolidone, as disclosed in Kendall U.S. Pat. No. 2,289,367, July 14, 1942, e.g., 1-phenyl-3-pyrazolidone, are used.

EXAMPLE X

Another emulsion was prepared, coated, and exposed, as described in Examples I - VII, except that no mercapto compound was added. Strips of this coating were developed $2\frac{1}{4}$ min. at 68°F. in Developer B of Examples I - VII, in which the pH of the developing solution had been adjusted to 9.5. To one-half of this developer was added 0.1 g. of 2-mercaptopyridine/liter

of developer. The other half was kept untreated for control. Results were as follows:

Developer B (pH 9.5)	D _{min}	D _{max}	First Exp. Step observable
Control — No Addition	0.05	0.10	E ₁₅
With 2-mercaptopyridine	0.05	1.95	E ₄

At a lower pH, the shelf-life of hydroquinone developers is known to be much longer. One can see the enormous advantage when the compounds of this invention are used.

Examples I — X demonstrate the usefulness of the addition of the 2-mercapto compounds of this invention alone. The following Examples show how these compounds may also be used to overcome the restraining action of specific antifoggants without a deleterious increase in fog.

EXAMPLE XI

A large grained silver halide emulsion free from optical sensitizing dyes and consisting of about 98 weight per cent Ag Br and about 2 weight per cent AgI and said emulsion containing about 5% gelatin and about 0.5% dextran and about 10% silver halide, was brought to its optimum sensitivity and coated as described in Example VIII. Various strips from the coated film were given the same exposure in the equipment described in Example VIII, followed by development at 78°F. in the following developer:

K₂SO₄ (anhydrous) — 40 g./liter
 K₂CO₃ (anhydrous) — 20 g./liter
 KOH — 5 g./liter
 Hydroquinone — 25 g./liter
 Antifoggant — As indicated
 2-mercapto compound — As indicated
 pH — Adjusted to 10.2
 H₂O — to 1.0 liter

In this Example, the antifoggant, 5-nitroindazole, was added to the developer solution at 0.1 g./liter and strips of the exposed film developed in various portions of this solution to which had been added the 2-mercapto compounds shown below with the following results:

2-Mercapto Compound	Amount (g./l.)	pKa	Induction Time (Sec.)	Relative Speed	Fog
None — Control	—	—	100	100	0.01
2-Mercapto-benzimidazole	0.04	10.0	30	1100	0.01
Do.	0.08	do.	20	800	0.01
2-Mercapto-quinoline	0.08	10.25	45	1100	0.04
Do.	0.12	do.	50	800	0.01
2-Mercapto-pyridine	0.08	10.5	28	1600	0.06
Do.	0.12	do.	20	1600	0.02
Do.	0.16	do.	15	2200	0.02
2-Mercapto-imidazole	0.01	11.1	6	2200	0.02
Do.	0.02	do.	4	4400	0.08
Do.	0.04	do.	4	6400	0.16
2-Mercapto-1-methylimidazole	0.04	10.6	15	3200	0.06
Do.	0.08	do.	7	1600	0.04

EXAMPLE XII

Strips from the coating prepared in Example XI were developed in a developer solution of that Example, containing the same antifoggant, except that the developing temperature was lowered to 72°F. Still other 2-mercapto compounds were added with the results shown below:

2-Mercapto Compound	Amount (g./l.)	pKa	Induction Time (sec.)	First Exposure Step Visible	Fog
None — Control	—	—	>120	None	0.02
3,4,5,6-Tetra-hydro-2-pyrimidineethiol	0.01	11.00	11	E-8	0.09
Do.	0.02	do.	5	E-7	0.14
Do.	0.04	do.	4	E-8	0.34
2-Mercapto-imidazole	0.01	10.2	20	E-9	0.03
Do.	0.02	do.	15	E-8	0.03
Do.	0.04	do.	10	E-8	0.03
ε-Thiocaprolactam	0.01	11.0	45	E-9	0.03
Do.	0.02	do.	40	E-9	0.03
Do.	0.04	do.	40	E-9	0.03

EXAMPLE XIII

Strips from the coated film of Example XI were developed in the same developer, except 0.1 g./liter of 5-nitro-benzimidazole were added as the antifoggant and various 2-mercapto compounds with results shown below:

2-Mercapto Compound	Amount (g./l.)	Induction Time (sec.)	Relative Speed	Fog
None — Control	—	28	100	0.02
2-Mercapto-benzimidazole	0.02	20	140	0.02
Do.	0.04	15	100	0.02
2-Mercapto-quinoline	0.032	20	140	0.01
Do.	0.064	15	100	0.04
2-Mercapto-pyridine	0.08	12	200	0.02
Do.	0.16	8	140	0.04
2-Mercapto-1-methyl-imidazole	0.02	12	280	0.06
Do.	0.04	10	200	0.01
Do.	0.06	6	140	0.01

EXAMPLE XIV

Strips from the coated film of Example XI were developed in the same developer, except 0.125 g./liter of 1,2-naphthotriazole were added as the antifoggant and the various 2-mercapto compounds with results shown below:

2-Mercapto compound	Amount (g./l.)	Induction Time (sec.)	Relative Speed	Fog
None — Control	—	22	100	0.04
2-Mercapto-benzimidazole	0.024	22	100	0.04
2-Mercapto-quinoline	0.032	22	140	0.04
Do.	0.064	20	140	0.04
Do.	0.096	15	140	0.04
2-Mercapto-pyridine	0.08	15	200	0.08
Do.	0.144	10	200	0.04
2-Mercapto-1-methylimidazole	0.02	13	175	0.10
Do.	0.04	11	175	0.12
Do.	0.06	6	140	0.06

EXAMPLE XV

Strips from the coated film of Example XI were developed in the same developer, except 0.5 g./liter of benzotriazole were added as the antifoggant and the various 2-mercapto compounds with results shown below:

2-Mercapto Compound	Amount(g./l)	Induction Time (Sec.)	Relative Speed	Fog
None — Control	—	70	100	0.02
2-Mercapto-benzimidazole	0.016	40	280	0.02
Do.	0.032	30	200	0.02
2-Mercapto-quinoline	0.024	60	100	0.01
Do.	0.048	65	280	0.01
Do.	0.072	40	100	0.01
2-Mercapto-pyridine	0.048	20	800	0.01
Do.	0.096	15	800	0.02
Do.	0.144	12	400	0.04
2-Mercapto-1-methylimidazole	0.016	18	1600	0.05
Do.	0.032	15	2200	0.04
Do.	0.048	13	1100	0.03

The emulsions of this invention may be modified and sensitized by the addition of such general emulsion sensitizers as phenyl isothiocyanate, sodium thiosulfate and alkylthiocyanate; metal compounds as for example, gold, platinum, palladium, iridium, rhodium, lead, etc.; additional anti-foggants or stabilizers such as the triazindenes and the tetrazindenes; the polyoxyethylene compounds described in U.S. Patents of Stanton 2,531,832, Blake et al. 2,400,532, and Balke 2,533,99-0; hardeners such as glutaraldehyde, formaldehyde and other aliphatic aldehydes, dimethylol urea, trime-thylol melamine; chrome alum and other chromium compounds, and other emulsion adjuvants.

An advantage of using the novel adjuvants of this invention lies in the rapidity with which the film reduces the induction period of developers such as hydroqui-none. Yet, another advantage lies in the use of a lower pH and/or anti-foggants, the reduction in speed loss, and the longer developer shelf life of the developers.

These advantages are achieved without sacrifice of the sensitometric or physical characteristics of the film. Still other advantages will be apparent to those skilled in the art.

The embodiments of the invention in which an ex-clusive property or privilege is claimed are defined as follows:

1. In a photographic gelatino silver halide emulsion which has been brought to its optimum sensitization by digestion with an emulsion sensitizer, the improvement wherein said emulsion contains at least one 2-mercapto substituted heterocyclic compound having: intracyclic nitrogen and carbon atoms, a mercapto group attached

to an intracyclic carbon atom in the alpha position to the intracyclic nitrogen atom, and a pKa not less than 7.7.

2. An emulsion according to claim 1 wherein said compound is present in an amount of 10⁻² to 2.5 milli-moles per 1.5 moles of silver halide.

3. An emulsion according to claim 2 which is a gelatino-silver chlorobromide emulsion.

4. An emulsion according to claim 3 wherein said ni-trogen compound is 2-mercaptopyridine.

5. An emulsion according to claim 3 wherein said ni-trogen compound is 2-mercaptoquinoline.

6. An emulsion according to claim 3 wherein said ni-trogen compound is 2-mercaptobenzimidazole.

7. An emulsion according to claim 2 wherein said compound is selected from the group consisting of 2-mercaptopyridine, 2-mercaptoquinoline, 2-mercaptobenzimidazole, 2-mercapto-4-phenylthiazole, 2-mercaptopyrimidine, 2-mercapto-1-methylimida-zole, 2-mercaptoimidazoline, 3,4,5,6-tetrahydro-2-pyrimidinethiol, 2-mercaptoimidazole, ε-thiocapro-lactam, and 2-mercaptothiazoline.

8. An emulsion according to claim 2 wherein at least one antifoggant selected from the group consist-ing of 5-nitroindazole, 5-nitrobenzimidazole, 1,2-naphthotriazole and benzotriazole is present in an amount of 0.05 - 20 millimoles per 1.5 moles of silver halide.

9. In a photographic developer solution comprising an aqueous alkaline solution containing: a silver halide developing agent with a long induction period consist-ing essentially of hydroquinone or a hydroquinone de-rivative, and an alkali metal sulphite in a concentration of about 1.0 to about 100 grams per liter of solution; the improvement wherein said solution further com-prises 0.0005 to 1.0 gram per liter of at least one 2-mercapto substituted heterocyclic compound having: intracyclic nitrogen and carbon atoms, a mercapto group attached to the intracyclic carbon atom in the alpha-position to the intracyclic nitrogen atom, and a pKa not less than 7.7.

10. A developer solution according to claim 9 wherein the nitrogen compound is 2-mercaptopyridine.

11. A developer solution according to claim 9 wherein the nitrogen compound is 2-mercaptoquinoline.

12. A developer solution according to claim 9 wherein the nitrogen compound is 2-mercaptobenzimidazole.

13. A developer solution according to claim 9 wherein the developing agent is a hydroquinone, and an anti-foggant selected from the group consisting of 5-nitroindazole, 5-nitrobenzimidazole, 1,2-naphthotriazole, and a benzotriazole is present in an amount of 0.01 gram to 2.0 grams per liter of solution.

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