(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 097 536**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 83303599.1

(22) Date of filing: 22.06.83

(51) Int. Cl.³: G 03 C 1/06
G 03 C 1/34

(30) Priority: 23.06.82 JP 108964/82
14.03.83 JP 42778/83

(43) Date of publication of application:
04.01.84 Bulletin 84/1

(84) Designated Contracting States:
DE FR GB

(71) Applicant: KONISHIROKU PHOTO INDUSTRY CO. LTD.
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku
Tokyo 160(JP)

(72) Inventor: Machida, Katsutoshi
972-4 Yokokawa-Cho
Hachioji-Shi Tokyo 193(JP)

(72) Inventor: Sakuma, Haruhiko
No. 65-4, Takakura-Cho
Hachioji-Shi Tokyo 192(JP)

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

(54) **Silver halide photographic material.**

(57) A silver halide photographic material is disclosed. It has formed on a support at least one photographic constitution layer containing at least one compound of the formula:

$$R_1 - A - S - \underset{\displaystyle (CH_2\rightarrow)_{\overline{n}} R_3}{\overset{\displaystyle CH - R_2}{|}}$$

wherein A is a carbonyl group or a sulfonyl group; R_1 is an aliphatic group, an aromatic group or a heterocyclic group; R_2 and R_3 are each a hydrogen atom, a hydroxyl group, an alkyl group, $-SO_3M$ (wherein M is a monovalent cation), a halogen atom or $-COOR_4$ (wherein R_4 is a monovalent cation or an aliphatic or aromatic group), provided that at least one of R_2 and R_3 is $-COOR_4$; and n is an integer of 0 to 6.

EP 0 097 536 A2

SILVER HALIDE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material, and more particularly, to a silver halide photographic material having improved image quality.

BACKGROUND OF THE INVENTION

Among the many properties that are required to be met by recent versions of silver halide photographic materials, stability, high sensitivity, reduced fog and high-quality image are particularly important. For X-ray photographic materials that should provide much information with reduced personnel exposure to X-rays, the requirements are high sensitivity, high image quality and adaptability to rapid processing.

Several methods are known for increasing the sensitivity of silver halide photographic materials and they are classified into two groups. In the methods which belong to the first group, the sensitivity is increased by incorporating sensitizers in the silver halide photographic material. For example, U.S. Patents Nos. 2,521,926, 3,021,215, 3,625,697, Japanese Patent Publication No. 11116/72, and Japanese Patent Application (OPI) No. 155828/79 (the symbol OPI as used herein means an unexamined published Japanese

patent application) disclose techniques for increasing the sensitivity of the silver halide photographic material by incorporating organic thioethers in it. The essence of the methods of the second group is enhancement of the degree of development by increasing the size of silver halide grains or by incorporating sensitizers or development accelerators in developing solutions.

Methods are also known for rapidly processing silver halide photographic materials by either reducing the amount of gelatin (as binder) with respect to the silver halide or effecting development at an elevated temperature (30 - 40°C) in a developing bath of high pH value.

However, the conventional methods for increasing the sensitivity of silver halide photographic materials or achieving their rapid processing are known to provide photographic images of much inferior quality. Many reports have been made on the method for minimizing the deterioration of the quality of the photographic images formed on silver halide photographic materials. According to one method, an antifoggant or stabilizer is incorporated in a silver halide emulsion in order to inhibit the deterioration of image quality due to the coarsening of developed silver grains. Other methods are essentially the same in that they reinforce the film, on which developed

silver grains are supported, by hardening the gelatin (binder) in the photographic material. Hardeners used for this purpose include inorganic compounds such as chrome alum; aldehyde compounds such as formaldehyde and glutaraldehyde; compounds having activated halogens as described in U.S. Patent No. 3,288,755; compounds having reactive ethylenically unsaturated bonds as described in U.S. Patent No. 3,635,718; epoxy compounds as described in U.S. Patent No. 3,091,537; and organic compounds such as halogenated carboxyaldehydes (e.g. mucochloric acid). These hardeners are incorporated in silver halide emulsion layers or protective layers to harden the gelatin (binder) to such a degree that it withstands processing under severe conditions such as rapidity and elevated temperatures. However, none of these methods are capable of improving the image quality satisfactorily without impairing the other properties of the silver halide photographic materials (e.g. sensitivity, contrast and maximum density).

Therefore, it has long been desired to provide a technique for producing a high-quality image on silver halide photographic materials in spite of the use of a sensitizer in silver halide emulsions, reduction in the amount of gelatin (binder) with respect to silver halide, or rapid development under elevated temperature.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a silver halide photographic material that produces an image of good quality even if it is processed to achieve high sensitivity subjected to rapid processing using less gelatin with respect to the silver halide.

Another object of the present invention is to provide a silver halide photographic material that yields an image of good quality even if it is subjected to rapid processing under high pHs and temperatures.

As a result of various studies to develop a product that can attain these objects, we have found that they can be achieved by a silver halide photographic material that has formed on a support at least one photographic constitution layer containing at least one compound of the following formula:

$$R_1 - A - S - \underset{\displaystyle (CH_2)_n}{\overset{\displaystyle |}{CH}} - R_2 \qquad R_3$$

wherein A is a carbonyl group or a sulfonyl group; R_1 is an aliphatic group, an aromatic group or a heterocyclic group; R_2 and R_3 are each a hydrogen atom, a hydroxyl group, an alkyl group, $-SO_3M$ (wherein M is a monovalent cation), a halogen atom or $-COOR_4$ (wherein R_4 is a monovalent cation or an aliphatic or aromatic group), provided that at least one of R_2 and

R_3 is $-COOR_4$; and n is an integer of 0 to 6.

Simply stated, we have found that the objects of the present invention can be accomplished by incorporating the thioether compound of the formula in at least one element in a silver halide photographic material.

DETAILED DESCRIPTION OF THE INVENTION

The thioether compound incorporated in a photographic element according to the present invention is represented by the formula given hereinabove. Preferred aliphatic groups for R_1 and R_4 are straight-chain, branched-chain and cyclic aliphatic groups such as alkyl groups having 1 to 18 carbon atoms (e.g. methyl, n-butyl, 1-propyl, t-butyl and n-dodecyl), alkenyl groups having 2 to 18 carbon atoms (e.g. allyl, butenyl and octenyl), and cycloalkyl groups having 3 to 8 carbon atoms (e.g. cyclopentyl and cyclohexyl). These aliphatic groups may have at least one substituent such as an alkoxy group (e.g. methoxy or ethoxy), aryl group (e.g. phenyl or tolyl), aryloxy (e.g. phenoxy), amino group, dialkylamino group (e.g. dimethylamino or diethylamino), heterocyclic group (e.g. N-morpholino or N-piperidino), halogen atom (e.g. chlorine, bromine or iodine), nitro group, hydroxyl group, carboxyl group, sulfo group, or alkoxycarbonyl group (e.g. methoxycarbonyl or ethoxycarbonyl).

Preferred aromatic groups for R_1 and R_4 include

phenyl and naphthyl groups, and they may have at least one substituent such as an alkyl group (e.g. methyl or ethyl), alkoxy group (e.g. methoxy or ethoxy), hydroxyl group, halogen atom (e.g. chlorine, bromine or iodine), acylamino group (e.g. acetylamino or benzoylamino), alkoxycarbonyl group (e.g. methoxycarbonyl or ethoxycarbonyl), succinimido group, carbamoyl group or nitro group.

Preferred heterocyclic groups for R_1 are 5- or 6-membered heterocyclic groups having at least one hetero atom selected from among nitrogen, oxygen and sulfur atoms (e.g. pyrrolyl, pyridinyl, pyridyl, thiazolyl, morpholino and furanyl). These heterocyclic groups may have at least one substituent selected from among those listed as substituents for the above defined aliphatic and aromatic groups.

Preferred monovalent cations for M in the group $-SO_3M$ for R_2 and R_3, as well as for R_4 include hydrogen ion, alkali metal ion (e.g. sodium or potassium ion) and ammonium ion.

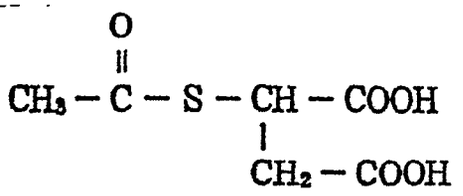
Particularly preferred compounds having the formula defined above are those wherein R_1 is an alkyl group having 1 to 8 carbon atoms, either R_2 or R_3 is a carboxyl group and the other is $-COOR_4$ (R_4 is an aliphatic or aromatic group), and A is a carbonyl group.

Typical examples of the compound having the formula noted above are listed below, but it should be

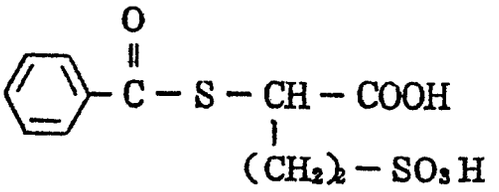
understood that they are merely illustrative and the scope of the present invention is by means limited to these examples.

(Compound)

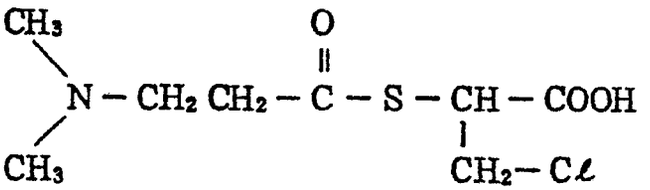
(1)



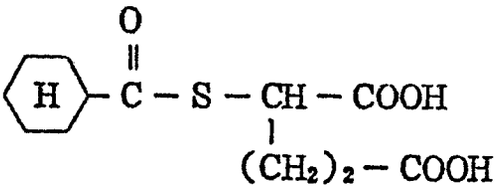
(2)



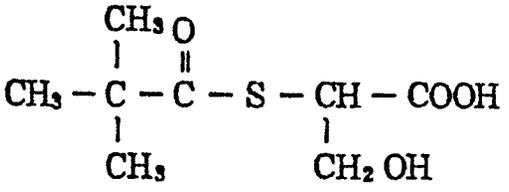
(3)



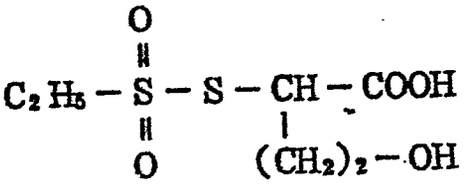
(4)



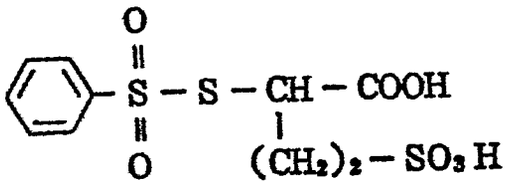
(5)



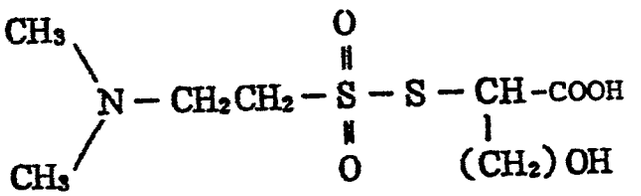
(6)



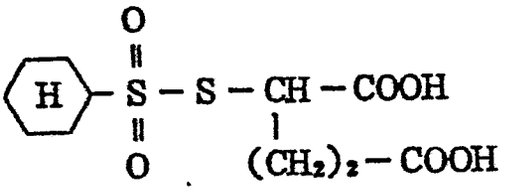
(7)



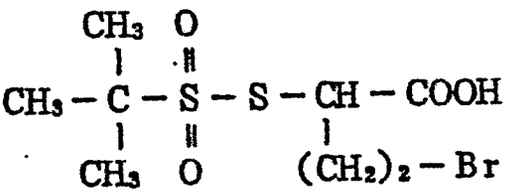
(8)



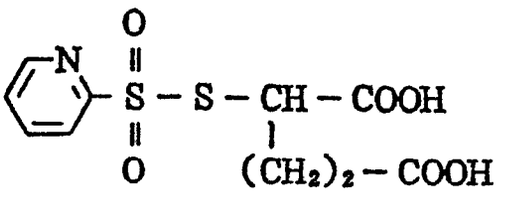
(9)



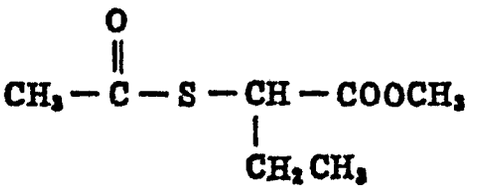
(10)



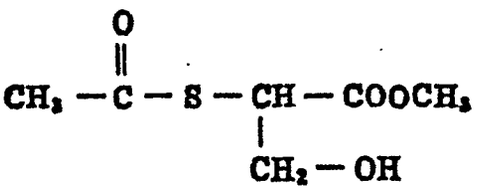
(11)



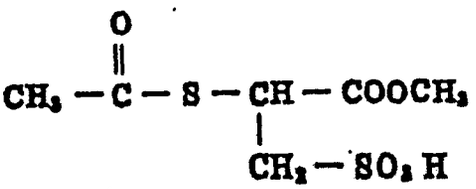
(12)



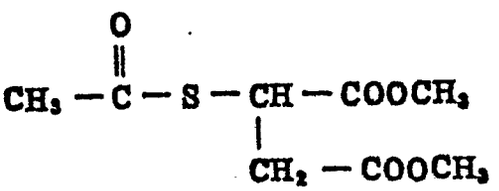
(13)



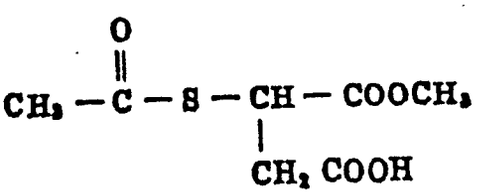
(14)



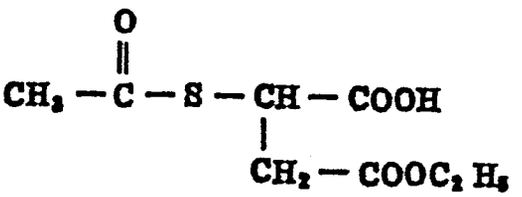
(15)



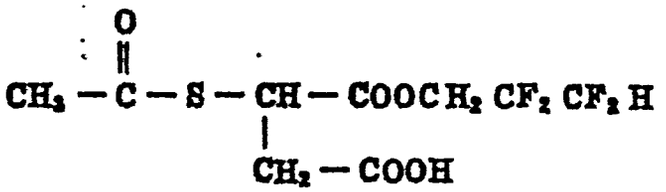
(16)



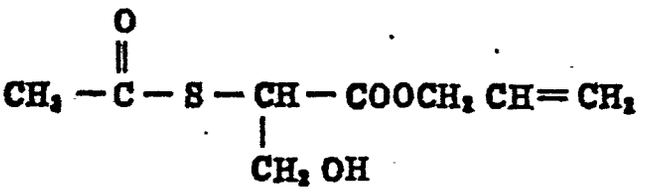
(17)



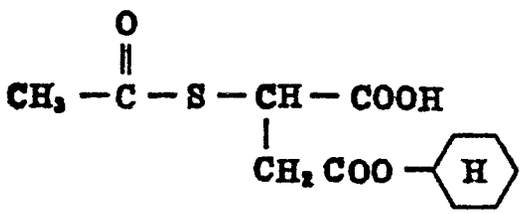
(18)



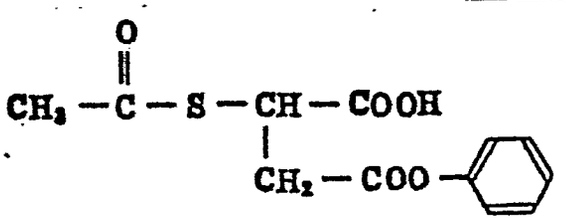
(19)



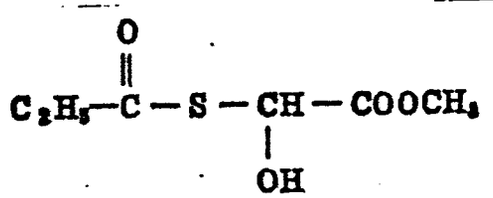
(20)



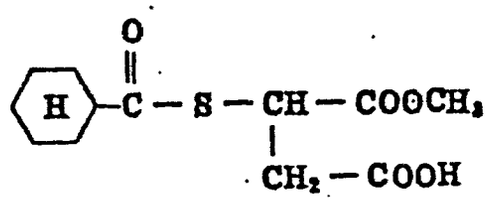
(21)



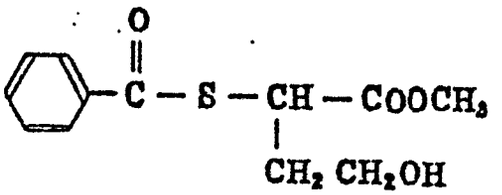
(22)



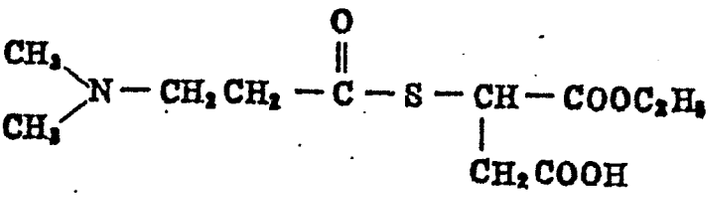
(23)



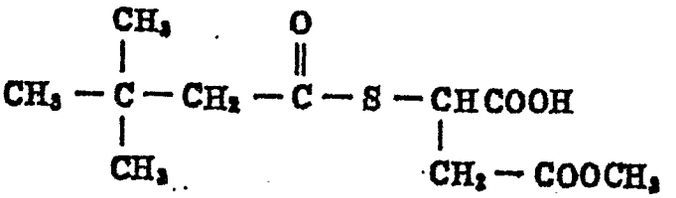
(24)



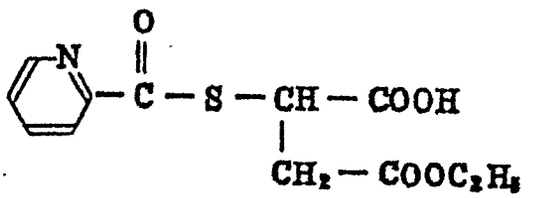
(25)



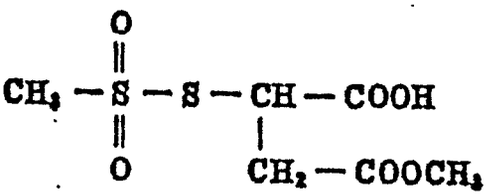
(26)



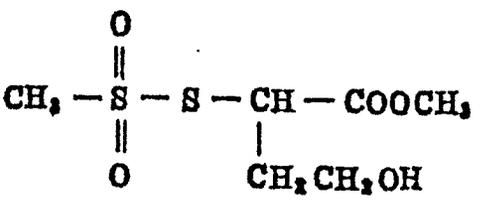
(27)



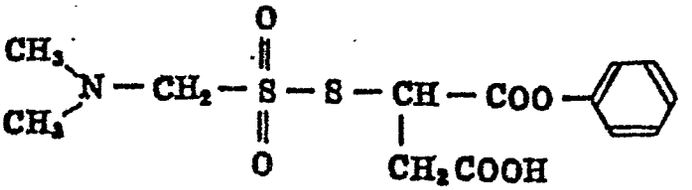
(28)



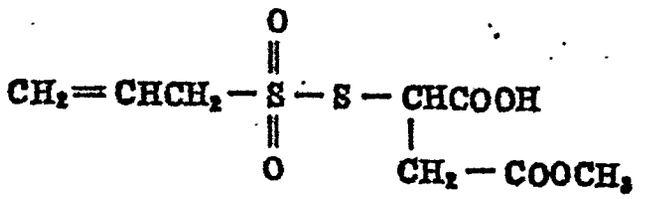
(29)



(30)



(31)



These compounds may be synthesized by the methods described in Chemical Abstracts, vol. 35, pp. 2114, 1941 and Journal of the Chemical Society, pp. 2123-2125, 1951.

The compounds according to the present invention are effective not only in increasing the sensitivity but also in inhibiting fog and minimizing the deterioration of image quality, and in this respect, the compounds are advantageous over conventional organic thioether compounds that can increase the photographic sensitivity only at the expense of other photographic characteristics.

The silver halide photographic material comprising a support having formed thereon a photographic element that contains the compound of the formula is

hereunder described in detail. The term "photographic element" as used in this specification includes silver halide emulsion layers formed on the support, as well as auxiliary layers formed on the same side of the support (e.g. a protective layer, an intermediate layer, a subbing layer and an anti-halation layer). According to the present invention, at least one of these layers contains the compound of the formula.

The compound of the formula is preferably contained in the photographic element in an amount of from 0.1 to 1,000 mg per mol of silver halide. The range of from 1 to 100 mg is particularly preferred. The compound is usually employed in the form of a 0.1 to 1% solution of methanol or fluorine-containing alcohol. The compound may be added at any stage before the coating and drying of the photographic material. A particularly preferred photographic element for incorporation of this compound is a silver halide emulsion layer, but it may be incorporated in other elements such as the intermediate layer, the protective layer or the subbing layer.

Silver halides that can be incorporated in the silver halide photographic emulsion according to the present invention are silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chloroiodobromide, and mixtures thereof. Silver iodobromide is the most preferred.

Gelatin is the most preferred for use as a binder or hydrophilic colloid in the present invention. If necessary, gelatin may be used in combination with other polymers such as gelatin derivatives, colloidal albumin, agar, gum arabic, alginic acid, cellulose derivatives, acrylamide, imidated polyacrylamide, casein, vinyl alcohol polymers, polyvinyl alcohol, polyvinyl pyrrolidone and hydrolyzed polyvinyl acetate.

The silver halide photographic emulsion that is used in the present invention may contain various known photographic additives such as chemical sensitizers, spectral sensitizers, antifoggants, hard toning agents, gelatin hardeners, surfactants, agents to modify the film properties, thickeners and dot improving agents. Suitable chemical sensitizers include active gelatin; noble metal sensitizers such as water-soluble gold salts, water-soluble platinum salts, water-soluble palladium salts, water-soluble rhodium salts, and water soluble-iridium salts; sulfur sensitizers; selenium sensitizers; and reduction sensitizers such as polyamines and stannous chloride. These chemical sensitizers may be used either alone or in combination. There is no particular limitation on the spectral sensitizers that can be used in the present invention. For example, cyanine or merocyanine dyes such as zeromethine, monomethine, dimethine and trimethine dyes may be used either alone

or in combination. For more details of the sensitizing techniques, see U.S. Patents Nos. 2,688,545, 2,912,329, 3,397,060, 3,615,635, 3,628,964, U.K. Patents Nos. 1,195,302, 1,242,588, 1,293,862, German Patent Applications (OLS) Nos. 2,030,326, 2,121,780, and Japanese Patent Publications Nos. 4936/68 and 14030/69. Suitable sensitizers should be selected depending upon the sensitization spectra, the sensitivity desired, and the object or use of the photographic material.

The silver halide photographic emulsion according to the present invention may contain other additives such as stabilizers or antifoggants (e.g. azaindenes, triazoles, tetrazoles, imidazolium salts, tetrazolium salts and polyhydroxy compounds); hardeners (e.g. aldehyde, aziridine, isoxazole, vinylsulfone, acryloyl, carbodiimide, maleimide, methansulfonate ester and triazine compounds); development accelerators (e.g. benzyl alcohol and polyoxyethylene compounds); image stabilizers (e.g. chroman, chraman, bisphenol and phosphite ester compounds); and lubricants (e.g. wax, glycerides of higher aliphatic acids, and higher aliphatic acid esters of higher alcohols). Surfactants may be used as coating aids, agents to improve the penetrability of processing solutions, deforming agents or materials for controlling the physical properties of the photosensitive material. Anionic, cationic, nonionic or amphoteric surfactants

may be used for these purposes. Effective antistats are diacetyl cellulose, styrene-per-fluoroalkyllidium maleate copolymer or alkali salt of the reaction product of styrene-maleic anhydride copolymer and p-aminobenzenesulfonic acid. Latices may be added to improve the film properties, and suitable latices are copolymers of acryl acid esters or vinyl esters and other monomers having ethylene groups. Suitable gelatin plasticizers are glycerin and glycolic compounds. Suitable thickeners include styrene -sodium maleate copolymer and alkylvinyl ether-maleic acid copolymer.

The silver halide photographic material of the present invention has the silver halide emulsion applied to a support by a known coating method, optionally through a subbing layer or an intermediate layer. Suitable supports are baryta paper, polyethylene coated paper, synthetic polypropylene paper, glass paper, cellulose acetate, cellulose nitrate, polyvinyl acetal, polypropylene, polyester (e.g. polyethylene terephthalate) and polystyrene.

As in ordinary color photographic materials, the silver halide photographic material of the present invention may have a laminated structure of silver halide emulsion layers sensitive to different colors. In this case, each emulsion layer may contain a suitable photographic coupler. That is, a blue-sensitive

emulsion layer may contain a yellow coupler, a green-sensitive emulsion layer may contain a magenta coupler, and a red-sensitive emulsion layer may contain a cyan coupler. If necessary, various combinations of emulsion layers and couplers may be used.

The silver halide photographic material of the present invention may contain a known 2- or 4-equivalent coupler. Suitable yellow couplers are extended-chain ketomethylene couplers among which benzoyl acetanilde and pivaloyl acetanilide type yellow couplers are used to advantage. Illustrative yellow couplers are described in U.S. Patents Nos. 2,875,057, 3,265,506, 3,277,155, 3,408,194, 3,415,652, 3,447,928, 3,664,841, Japanese Patent Publication No. 13576/74, Japanese Patent Applications (OPI) Nos. 29432/73, 66834/73, 10736/74, 122335/74, 28834/75, 132926/75, and Japanese Patent Application No. 145024/78. Suitable magenta couplers include pyrazolone, pyrazolotriazole, pyrazolinobenzimidazole, indazolone and cyanoacetyl compounds. Illustrative magenta couplers are described in U.S. Patents Nos. 2,600,788, 3,061,432, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,684,514, 3,888,680, British Patents Nos. 1,247,493, 1,534,349, German Patent Application (OLS) No. 2,156,111, Belgian Patents Nos. 769,116, 792,525, Japanese Patent Publication No. 60479/71, Japanese Patent Applications (OPI)

Nos. 29639/74, 111631/74, 129538/74, 13041/75, 122935/75, 20826/76, 58533/77, 80027/77, Japanese Patent Applications Nos. 98876/77, 101247/77, and 104437/77. Other couplers such as colored couplers and competing couplers may also be used.

The silver halide photographic material of the present invention may be used for processing by black-and-white or color photography. It may be used for general purposes, as well as for special purposes such as printing, X-ray photography and radiography. Especially good results are achieved if it is used as a high-sensitivity, silver iodobromide photographic material.

The silver halide photographic material of the present invention may be subjected to ordinary exposure or it may be exposed for a shorter period or only for a flash of time. The material may be processed photographically by a conventional method. The two basic processing steps are development and fixing, which may be effected consecutively or simultaneously.

The present invention is hereunder described in greater detail by reference to examples which are given here for illustrative purposes only and are by no means intended to limit its scope.

Example 1

One kilogram of a silver halide photographic emulsion containing 100 g of silver iodobromide

(containing 3.0 mol% silver iodide) and 40 g of gelatin was subjected to sulfur sensitization and gold sensitization to prepare a high-sensitivity negative emulsion. Saponin was added to this emulsion as a coating aid. The resulting emulsion was divided into 15 portions. The compounds indicated in Table 1 were added to 14 portions in the amounts also indicated in Table 1. The resulting coating solutions were applied to polyethylene terephthalate film bases. To each of the resulting silver halide emulsion layers, a gelatin solution containing a coating aid and a hardener was applied to form a protective layer in a thickness of 1.5 g/m^2. After drying, each sample was exposed to white light with a sensitometer, Model KS-1 of Konishiroku Photo Industry Co., Ltd., according to the method specified in JIS, and subsequently processed with a processor of continuous transport type which could accomplish development, fixing, washing and drying automatically. The developing solution used had the following composition.

Developing solution (development period: 30 seconds at 35°C)

Anhydrous sodium sulfite	70 g
Hydroquinone	10 g
Boric anhydride	1 g
Sodium carbonate (monohydrate)	20 g
1-Phenyl-1,3-pyrazolidone	0.35 g

Sodium hydroxide	5 g
5-Methylbenzotriazole	0.05 g
Potassium bromide	5 g
Glutaraldehyde bisulfite	15 g
Glacial acetic acid	8 g
Water to make	1,000 ml

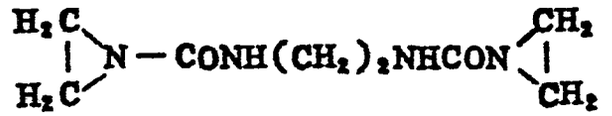
The so processed samples were subjected to sensitometry to check for their photographic characteristics, which are summarized in Table 1, wherein the figures in the column of "sensitivity" are relative values, with the sensitivity of the control (sample No. 1) taken as 100. The quality of the image formed on each sample was evaluated by visually checking the deterioration of developed silver grains at a density of 0.8, and the indices of rating were ○ (good), △ (moderate), and X (unacceptable). The combination of two indices means that the degree of deterioration was of a value between the two indices.

Table 1 demonstrates the ability of the compounds of the formula to provide an image of improved quality without sacrificing other photographic characteristics.

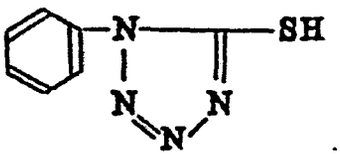
Table 1

sample No.	test compound	amount (mg/AgX1 mol)	photographic characteristics exposed to 23°C, 65% r.h. for 10 days			image quality
			fog	sensitivity	max-density	
1	——	—	0.05	100	3.50	△
2	compound (1)	10	0.04	110	3.50	○ △
3	do.	50	0.03	110	3.50	○
4	(4)	10	0.04	105	3.55	○ △
5	do.	50	0.03	110	3.55	○
6	(6)	10	0.03	105	3.50	○
7	do.	50	0.02	110	3.50	○
8	(10)	10	0.03	110	3.50	○
9	do.	50	0.02	110	3.55	○
10	(12)	10	0.04	100	3.50	○ △
11	do.	50	0.04	100	3.50	○ △
12	(16)	10	0.04	110	3.50	○
13	do.	50	0.03	105	3.50	○
14	(23)	10	0.04	105	3.55	○ △
15	do.	50	0.04	100	3.50	○
16	(26)	10	0.04	110	3.50	○
17	do.	50	0.03	105	3.50	○
18	(29)	10	0.04	100	3.55	○ △
19	do.	50	0.05	105	3.55	○ △
20	comparative compound (A)	50	0.05	95	3.40	△
21	do.	200	0.06	70	3.00	○ △
22	(B)	10	0.05	90	3.50	△
23	do.	50	0.02	55	3.45	△
24	(C)	10	0.07	105	3.50	△ X
25	do.	50	0.09	110	3.55	X

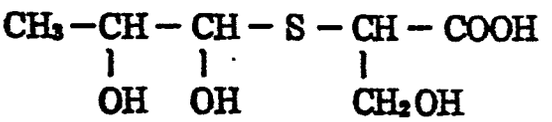
Comparative compound (A): hardener having the following structure:



Comparative compound (B): development restrainer having the following structure: and



Comparative compound (C): organic thioether compound having the following structure:



As Table 1 shows, samples 2 to 19 according to the present invention were able to retain a good image quality during the 10-day storage at 23°C and 65% r.h. without causing adverse effects on other photographic characteristics, such as reduced sensitivity and maximum density, and increased fog.

Example 2

A cellulose triacetate film base having an anti-halation layer was coated with a high-sensitivity color photographic silver iodobromide emulsion layer (first layer in a dry thickness of 5 μ) that contained 10 g of 4-chloro-1-hydroxy-2-n-octyl naphthamide

(coupler) per kilogram of a negative silver halide emulsion and which was rendered sensitive to red light. On the first layer was formed a second layer in a dry thickness of 1μ that was prepared from a 3% aqueous solution of gelatin. The second layer was overlaid with a high-sensitivity color photographic silver iodobromide emulsion layer (third layer in a dry thickness of 4 μ) that contained 10 g of 1-(3-carboxyphenyl)-3-(4-stearoylaminophenyl)-5-pyrazolone (coupler) per kilogram of a negative silver emulsion and which was rendered sensitive to green light. On the third layer was formed a yellow colloidal silver layer as a fourth layer having a dry thickness of 2 μ. The fourth layer was overlaid with a high-sensitivity color photographic silver iodobromide emulsion layer (fifth layer in a dry thickness of 7 μ) that contained 13 g of 2-dodecyloxybenzoyl acetanilide per kilogram of a negative silver halide emulsion and which was rendered sensitive to blue light. On the fifth layer was formed a sixth layer in a dry thickness of 1 μ that was prepared from a 4% aqueous solution of gelatin. Fifteen samples of this multilayer coupler-in-emulsion type negative film for color photography were prepared.

In the 2nd, 4th and 6th layers of each sample, 3 mg of formalin was incorporated as a hardener per gram of gelatin. In the 1st, 3rd and 5th layers which were silver halide emulsion layers, 4-hydroxy-6-methyl-

1,3,3a,7-tetrazaindene was incorporated as a stabilizer and saponin was added as a coating aid upon completion of the second ripening. Thereafter, the compounds listed in Table 2 were added to 14 samples in the amounts indicated in the same Table. The so prepared samples were stored at 25°C and 60% r.h. for 30 days.

These samples consisting of one control, 4 samples according to the present invention and 10 comparative samples were processed with a color developer having the formulation indicated below, and their color densities were measured with a color densitometer. The photographic characteristics determined from these measurements are listed in Table 2. The values indicated in the respective columns R, G and B as in Table 2 are those determined respectively from the values obtained through red, green and blue filters in the densitometer for color photography. The figures in the column of "sensitivity" are relative values, with the red sensitivity of the control (sample No. 26) taken as 100.

Color developer (development period: 5 minutes at 24°C)

Benzyl alcohol	3.8 ml
Anhydrous sodium sulfite	2.0 g
N-Ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5.0 g
Sodium carbonate	5. 0 g

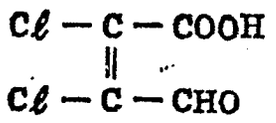
Sodium bromide	1.0 g
Water to make	1,000 ml

As Table 2 shows, samples 27 to 30 according to the present invention retained a good image quality wihtout increased fog or decreased sensitivity.

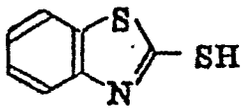
Table 2

sample No.	test compound	amount (mg/AgX 1 mol)	photographic characteristics						image quality
			fog			sensitivity			
			R	G	B	R	G	B	
26			0.07	0.07	0.07	100	110	90	△
27	compound (1)	10	0.06	0.06	0.06	105	115	95	○
28	do.	50	0.05	0.06	0.05	105	115	95	○
29	(16)	10	0.06	0.06	0.05	105	120	100	○
30	do.	50	0.05	0.06	0.05	105	115	95	○
31	comparative compound (D)	50	0.07	0.07	0.08	100	105	90	⌓
32	do.	200	0.08	0.08	0.09	95	95	80	○
33	(E)	10	0.06	0.07	0.07	95	110	90	△
34	do.	50	0.05	0.06	0.05	70	80	55	△
35	(F)	10	0.08	0.08	0.10	105	115	95	×
36	do.	50	0.10	0.10	0.12	120	120	100	×
37	(G)	10	0.09	0.08	0.10	110	115	95	×
38	(H)	10	0.08	0.09	0.08	105	115	95	△
39	do.	50	0.10	0.10	0.12	100	110	90	△
40	(I)	10	0.08	0.08	0.10	105	115	95	△

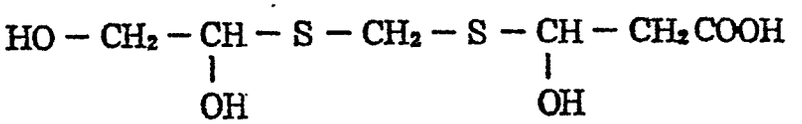
Comparative compound (D): hardener having the formula:



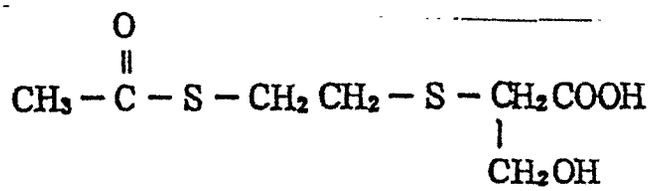
Comparative compound (E): development restrainer having the formula:



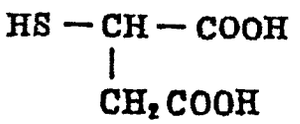
Compatative compound (F): thioether compound having the fomula:



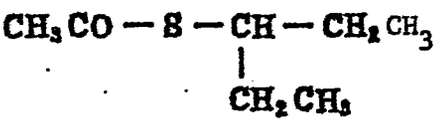
Comparative compound (G): thioether compound of the formula:



Comparative compound (H): having the formula: and



Comparative compound (I): having the formula:

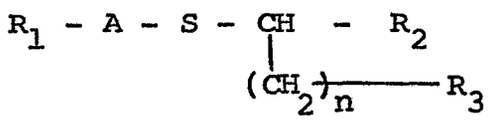


The data in Table 2 shows that samples 27 to 30 according to the present invention which contained compounds of the formula in a multilayer color photographic material provided a better image quality without sacrificing other photographic characteristics.

It is therefore concluded that the silver halide photographic material having the thioether compound of the formula in a photographic element according to the present invention can provide an improved image quality without having adverse effects on other photographic characteristics.

CLAIMS

1. A silver halide photographic material which comprises, on a support, at least one layer containing at least one compound of the formula:



wherein A is a carbonyl group or a sulfonyl group; R_1 is an aliphatic group, an aromatic group or a heterocyclic group; R_2 and R_3 are each independently a hydrogen atom, a hydroxyl group, an alkyl group, $-SO_3M$ (wherein M is a monovalent cation), a halogen atom or $-COOR_4$ (wherein R_4 is a monovalent cation or an aliphatic or aromatic group), provided that at least one of R_2 and R_3 is $-COOR_4$; and n is 0 or an integer from 1 to 6.

2. A silver halide photographic material according to claim 1, wherein said A is a carbonyl group and both of R_2 and R_3 are $-COOR_4$.

3. A silver halide photographic material according to claim 1 or 2, wherein said aliphatic group represented by R_1 and/or R_4 is an alkyl group having 1 to 18 carbon atoms, an alkenyl group having 2 to 18 carbon atoms, or a cycloalkyl group having 3 to 8 carbon atoms.

4. A silver halide photographic material according to claim 1 or 2, wherein said aromatic group represented by R_1 and/or R_4 is a phenyl group or a naphthyl group.

5. A silver halide photographic material according to claim 1 or 2, wherein said heterocyclic group represented by R_1 is a 2- or 6-membered heterocyclic group having at least one nitrogen, oxygen or

sulfur atom.

6. A silver halide photographic material according to claim 5, wherein said heterocyclic group is a pyrrolyl, pyridinyl, pyridyl, thiazolyl, morpholino or furanyl group.

7. A silver halide photographic material according to any one of claims 1 and 3 to 6, wherein said M in the group $-SO_3M$ represented by R_2 and R_3 and/or said monovalent cation represented by R_4 is a hydrogen ion, an alkali metal ion or an ammonium ion.

8. A silver halide photographic material according to any one of claims 1, 3 and 7 wherein said A is a carbonyl group, R_1 is an alkyl group having 1 to 8 carbon atoms, and one of R_2 and R_3 is a carboxyl group, and the other of R_2 and R_3 is $-COOR_4$.

9. A silver halide photographic material according to any one of claims 1 to 8, wherein said n is an integer of 1 to 3.

10. A silver halide photographic material according to any one of claims 1 to 9, wherein said compound is present in said layer in an amount of from 0.1 to 1,000 mg per mol of silver halide.

11. A silver halide photographic material according to claim 1, wherein said compound is present in an amount of from 1 to 100 mg per mol of silver halide.

12. A silver halide photographic material according to any one of claims 1 to 11, which comprises silver iodobromide.