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PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIAL

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Claims priority, application Japan, Nov. 13, 1964, 39/63,973

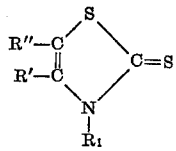
U.S. Cl. 96—107 10 Claims
Int. Cl. G03c 1/28

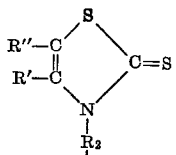
This invention relates to photographic silver halide sensitive materials and to silver halide emulsions for photographic materials.

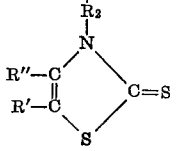
Photographic silver halide emulsions are generally produced by dispersing crystals of silver halide such as silver iodide, bromide and chloride in gelatin, polyvinyl alcohol or other high molecular electrolytes as a protective colloid and are applied as a light-sensitive material on a support of paper, glass, nitrocellulose, acetylcellulose, polyamide, polyester, polycarbonate and other synthetic high molecular materials in a thin film whereby photographic films, plates and papers are obtained.

We have found that the photographic characteristics can be remarkably improved by adding thiazoline-2-thiones to such light sensitive material during production or with the starting materials.

That is to say, the present invention is characterized by incorporating in a light sensitive material during production or with the starting materials thereof at least one of the thiazoline-2-thiones represented by the following general formula:



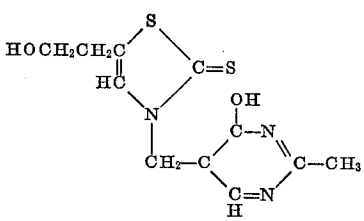




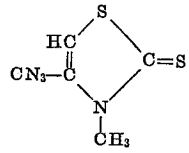
in which R_1 represents lower alkyl-, cycloalkyl-, aryl- or pyrimidyl- methyl group, R_2 represents alkylene group, R′ and R″ represent hydrogen, lower alkyl-, hydroxyalkyl- or aryl group, and R′ and R″ may be linked to each other.

Illustrative of the compounds used in this invention are:

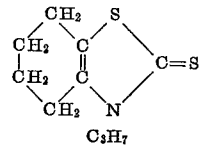
Compound 1.



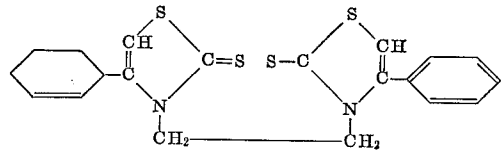
Compound 2.



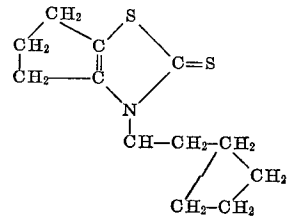
Compound 3.



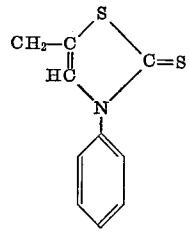
Compound 4.



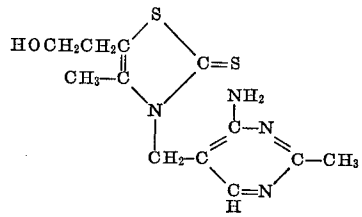
Compound 5.



Compound 6.



Compound 7.



The compound may be added in a silver halide emulsion at any step, but it is preferable to add the above compound, as the crystal or as a solution, when the crystals of silver halide are formed or ripened after washing with water, or just before the photographic silver halide emulsion is dissolved and coated on a support. The compound may be incorporated in, for example, an adjacent layer of the photographic silver halide emulsion layer (therefore, the term "silver halide emulsion layer" in the specification and claims includes the layers adjacent the emulsion layer). More particularly, if the compound contained in gelatin or other protective colloid is added during production, the dispersion thereof can be favorably effected. Moreover, a light sensitive material may be treated with a solution containing the compound.

The first object accomplished by our invention is to make a blue-black tone of developed silver image of a

light sensitive material, in particular, photographic paper or positive photographic material and the second object is to raise the sensitivity of a light sensitive material.

Example 1

20 ml. of 0.3% methanol solution of the Compound 1 was added to 1 kg. of an adherent photographic paper emulsion containing 21.5 g. of silver chloride, to which 20 ml. of 6% aqueous solution of formalin was further added, and coated on baryta paper. The thus obtained photographic paper was exposed and developed at 20° C. for 1 minute by the use of the following developer after diluting to 1:1.

	G.
N-methyl-p-aminophenol sulphate	2
Anhydrous sodium sulfite	30
Hydroquinone	7
Sodium carbonate (monohydrate)	53
Potassium bromide	1.5
Water to 1000 ml.	

After the developing treatment, it was dipped in a stop bath of 1.5% acetic acid solution for 15–20 seconds, fixed for 10 minutes in an acidic hardening fixing solution and washed with water for 60 minutes in water flow. Thereafter, the developed material was then subjected to the hot-glaze or natural drying.

In carrying out this invention, images having a satisfactory blue-black tone could be obtained, while images having a brownish-black tone were obtained in the case of no addition of the compound (development, stopping fixing, water washing and drying were similar to in the former).

Example 2

30 ml. of 0.3% methanol solution of the Compound 2 was added to 1 kg. of an enlargement photographic paper emulsion containing 25 g. of silver chlorobromide (silver bromide 30 mol percent), coated on a support similarly to Example 1 and dried. The resulting photographic paper, being exposed similarly to Example 1, was developed for 2 minutes at 20° C., fixed and washed with water. In this photographic paper to which the Compound 2 had been added, the initial developing velocity was rapid, the sensitivity was increased by 10% and images having a blue-black tone were obtained, as compared with images having a brownish-black tone in another photographic paper to which it had not been added.

Example 3

30 ml. of 0.3% methanol solution of the Compound 2 and 15 ml. of 0.1% aqueous solution of 1-phenyl-5- mercaptotetrazole as a fog inhibitor were added to 1 kg. of an adherent photographic paper emulsion containing 23 g. of silver chlorobromide (silver bromide 7 mol percent), coated on a support similarly to Example 1 and dried. The resulting photographic paper, being exposed as in Example 1, was developed at 20° C. for 1 minute 30 seconds, fixed, washed with water and dried. In this photographic paper, no fog increase was observed and an image having a blue-black tone was obtained without delaying the initial development, as compared with an image having a neutral black tone in the case of no addition of the compound.

Example 4

When the procedure as in Example 1 was repeated using 60 ml. of a 0.3% methanol solution of Compound 4 instead of Compound 1, almost same brown-black images as in Example 1 were obtained.

Example 5

40 ml. of 0.2% methanol solution of the Compound 6 was added to 1 kg. of a micro-positive emulsion containing 35 g. of silver chlorobromide (silver bromide 45 mol percent), coated on a triacetylcellulose film support to which a subbing layer had been previously applied, and

dried. The film thus resulting, being exposed similarly to Example 1, was developed at 20° C. for 2 minutes, fixed, washed with water and dried. This film gave a good image of neutral black tone, as compared with an image of brownish-black tone obtained in the case of no addition of the compound.

Example 6

To 1 kg. of a fine grain positive emulsion containing 50 g. of silver iodobromide (silver iodide 1.5 mol percent) was added the compound of our invention as shown in Table I. The composition was coated on a triacetylcellulose film support having a subbing layer, followed by drying. The thus obtained film, after exposure, was developed at 20° C. for 5 minutes by the use of the following developer and then was fixed, washed with water and dried.

	G.
N-methyl-p-aminophenol sulphate	0.3
Anhydrous sodium sulfite	38.0
Hydroquinone	6.0
Sodium carbonate (monohydrate)	22.5
Citric acid	0.7
Potassium bromide	0.9
Potassium metabisulfite	1.4
Water to 1000 ml.	

TABLE I

Compound	Amount added	Specific sensitivity	Gamma	Fog
	0	100	3.1	0.05
2	6×10^{-3}	107	3.1	0.05
	2×10^{-2}	129	3.3	0.05
	6×10^{-2}	162	3.5	0.05
	2×10^{-1}	200	3.5	0.06
3	6×10^{-3}	110	3.1	0.05
	2×10^{-2}	135	3.3	0.05
	6×10^{-2}	170	3.3	0.06
	2×10^{-1}	230	3.5	0.07
5	6×10^{-3}	105	3.1	0.05
	2×10^{-2}	125	3.1	0.05
	6×10^{-2}	150	3.1	0.05
	2×10^{-1}	180	3.3	0.05

In the case of thus carrying out our invention, the sensitivity alone could be raised, by increasing the amount of the compound, without substantially affecting the gamma and fog.

Example 7

To 100 g. of a photographic emulsion containing 2.8 g. of silver chloride was added a M/100 methanol-acetone (4:1) solution of the Compound 1, 2 or 7 in an amount as shown in Table II, coated on a glass plate to be 6 ml. emulsion/200 cm.^{2} and dried.

The resulting photographic plate, after exposure to light, was developed at 20° C. for 3 minutes by the developer having the following composition and was then fixed, washed with water and dried.

	G.
N-methyl-p-aminophenol sulphate	3
Anhydrous sodium sulfite	45
Hydroquinone	12
Sodium carbonate (monohydrate)	80
Potassium bromide	2
Water to 1000 ml.	

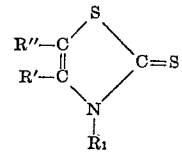
TABLE II

Compound	Amount added (ml.)	Specific Sensitivity	Tone of Image
	0	100	Brownish black.
1	2	162	Weak blue black.
	4	182	Strong blue.
	8	245	Do.
2	2	151	Weak blue black.
	4	170	Strong blue black.
	8	229	Do.
7	2	162	Do.
	4	257	Do.
	8	269	Do.

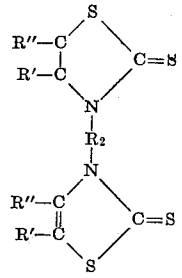
What is claimed is:

1. A photographic silver halide sensitive material comprising a support and a silver halide emulsion layer, said layer containing at least one compound selected from

the group consisting of compounds represented by the general formula:

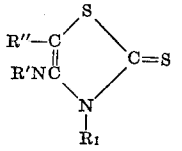


and, a compound represented by the general formula:



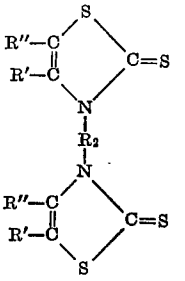
wherein R_1 represents a member selected from the class consisting of an alkyl group, a cycloalkyl group, an aryl group, and a pyrimidylmethyl group; R_2 represents an alkylene group, and R′ and R″ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, a hydroxylalkyl group, and an aryl group; and said R′ and R″ may be linked to each other.

2. A light-sensitive silver halide emulsion containing a compound selected from the group consisting of compounds represented by the general formula:



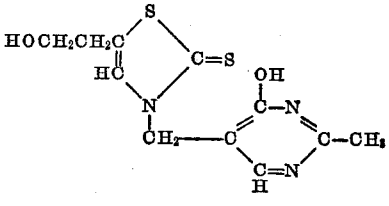
wherein R_1 represents a member selected from the class consisting of an alkyl group, a cyclo-alkyl group, an aryl group, a pyrimidylmethyl group; and R′ and R″ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, a hydroxyalkyl group, and an aryl group; said R′ and R″ being linked to each other as the case may be.

3. A light-sensitive silver halide emulsion containing a compound selected from the group consisting of compounds represented by the general formula:

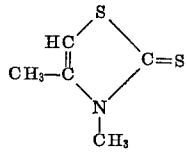


wherein R_2 represents an alkylene group and R′ and R″ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, a hydroxyalkyl group and an aryl group, said R′ and R″ being linked to each other as the case may be.

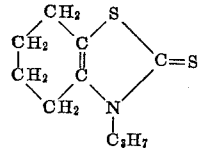
4. A material as defined in claim **1** wherein said compound is



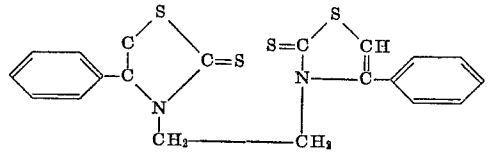
5. A material as defined in claim **1** wherein said compound is



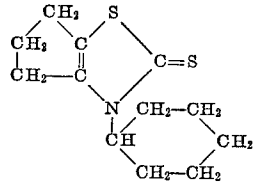
6. A material as defined in claim **1** wherein said compound is



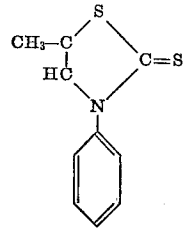
7. A material as defined in claim **1** wherein said compound is



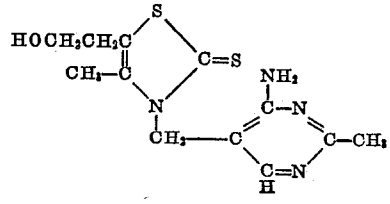
8. A material as defined in claim **1** wherein said compound is



9. A material as defined in claim **1** wherein said compound is



10. A material as defined in claim **1** wherein said compound is



References Cited

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J. TRAVIS BROWN, *Primary Examiner.*

J. R. EVERETT, *Assistant Examiner.*

U.S. Cl. X.R.

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