

[54] **SILVER HALIDE EMULSION
SENSITIZED WITH PENTATHIEPANE**

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[58] Field of Search96/107; 260/327 R

[56]

References Cited

UNITED STATES PATENTS

3,503,758 3/1970 Wada et al.260/327 R

Primary Examiner—Norman G. Torchin

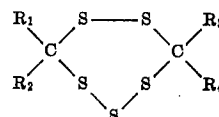
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[57]

ABSTRACT

A photosensitive silver halide photographic emulsion contain-
ing at least one compound selected from the group consisting
of compounds having the formula



wherein each of R_1 , R_2 , R_3 and R_4 is selected from the group
consisting of a hydrogen atom, an alkyl group and an aralkyl
group; and wherein R_1 and R_2 , or R_3 and R_4 can combine
to form a cycloalkyl group, is disclosed.

9 Claims, No Drawings

SILVER HALIDE EMULSION SENSITIZED WITH PENTATHIEPANE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a silver halide photographic emulsion. More particularly, the present invention relates to a silver halide photographic emulsion which is chemically sensitized with a sulfur-containing compound.

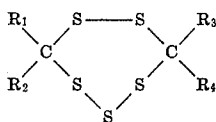
2. Description of the Prior Art

An object of the present invention is to increase the sensitivity of photosensitive silver halide photographic emulsions.

Various methods for increasing the sensitivity of photosensitive silver halide photographic emulsions during manufacture are known as a chemically sensitizing process. For example, compounds containing a labile sulfur (for example, sodium thiosulfate or thio-urea derivatives) are known as sulfur sensitizing agents. Also, a reducing agent, such as stannous chloride and hydrazine, is known as a reducing sensitizing agent. Some of these labile sulfur-containing compounds and reducing substances are considered to be contained in a natural gelatin for photography. Certain aurous or auric salts, for example aurous thiocyanate, have a chemically sensitizing action, and the method of utilizing this action is well known.

SUMMARY OF THE INVENTION

The present inventors have found that a compound represented by the general formula



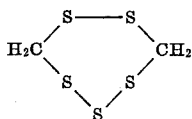
wherein each of R_1 , R_2 , R_3 and R_4 represents a hydrogen atom, an alkyl group, such as a methyl, an ethyl, a propyl, a butyl group and the like, or an aralkyl group such as benzyl, phenethyl group and the like, or wherein R_1 and R_2 , or R_3 and R_4 may together form a cycloalkyl group, such as a cyclopentyl, a cyclohexyl, a cycloheptyl, a cyclooctyl group and the like is a useful sulfur sensitizing agent for a photosensitive silver halide photographic emulsion.

DETAILED DESCRIPTION OF THE INVENTION

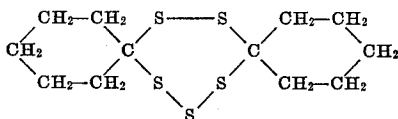
The above compound is a useful sensitizing agent regardless of whether the emulsion is a silver chloride emulsion, a silver bromide emulsion, a silver iodide emulsion, or a mixed silver halide emulsion, or, further, whether the emulsion is a water-washed or a water-unwashed emulsion.

Suitable chemical sensitizers having the above formula are as follows:

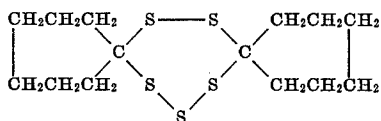
Compound 1



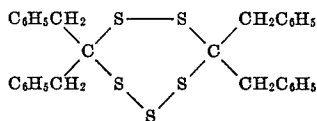
Compound 2



Compound 3



Compound 4



However, the chemical sensitizers used in the present invention are not limited to these compounds.

The optimum amount of the sulfur sensitizer having the above described formula to be used is dependent on the specific compound selected, the type of silver halide, the particle size ripening temperature, the ripening time, and the pH and the pAg of the silver halide emulsion. However, the amount generally used is in the range of from 0.01 to 100 mg per 1 mole of silver halide. However, where the sensitizer is used in combination with other sensitizers, the amount used can be smaller. Where the sensitizer is used in combination with any appropriate antifoggant, the amount can be larger.

The sulfur sensitizer used in the present invention can be used in combination with reducing sensitizers such as stannous chloride or thiourea dioxide, and also can be combined with auric or aurous salts, such as aurous thiocyanate, platinum salts, palladium salts, or sulfur-containing compounds such as sodium thiosulfate, thiourea derivatives, and further can be used together with polyoxyalkylene compounds having a molecular weight of above 300 or onium compounds.

The sulfur-containing compound represented by the above-described formula according to the present invention can be used not only in case of spectral sensitization but also without such sensitization. These can be usually applied to emulsions for black and white photography, for color photography, for X-ray, and for graphics.

The sulfur-containing compound represented by the above formula can be added to the photographic emulsion without any deleterious effects on stabilizers, antifoggants, hardeners, color developing agents, coating agents, and other emulsion additives.

The sulfur sensitizing agent represented by the above described formula is extremely useful for sensitizing a silver halide emulsion made of an inert gelatin and also can be used for sensitizing a silver halide emulsion in which at least one part of the protective colloid comprises other hydrophilic colloids such as a photographically labile gelatin or a polyvinylalcohol.

The sulfur sensitizing agent is particularly valuable in that the sensitizing effect is markedly increased in combination with a thiosulfate ion, i.e. a compound giving rise to a thiosulfate ion.

The synthesis of the compounds represented by the above formula is described in *Tetrahedron Letters* No. 6,576 (1966) for Compounds 1, *Acta Chemica Scandinavica* 13 1032 and 1715 (1959) for Compound 2 and 4, respectively, and *Fredge. A. Acta Chem. Scand.* 12 891 (1958) for Compound 3.

The present invention is illustrated further by reference to the following examples.

EXAMPLE 1

A highly sensitive neutral gelatino-silver bromo-iodide emulsion (5.0 percent silver iodide and 95.0 percent silver bromide) at the beginning of the chemical ripening was divided into five equal parts (Samples A to E). Samples C to E were mixed with Compound 1 in an alcohol solution and Sample B was mixed with a sensitizing natural gelatin, and were added with, as a metallic sensitizing agent, 7.5 mg of potassium chloraurate (tetrahydrate) and 150 mg of potassium thiocyanate per 1 mole of silver halide in the form of an aqueous solution, and were chemically ripened under stirring at 50° C for 60 minutes. Further to 1 kg of each emulsion were added 30 mg of 3,3'-diethyl-9-methylthiocarbocyanine bromide, 450 mg of chrome alum and 120 mg of saponine and the mixture was coated on a cellulose triacetate base film and dried to obtain a photosensitive material of 14 microns in coating thickness. Next, the material so obtained was exposed stepwise to a light source of 5,400° K for 1/50 second, developed with a developer having the following composition at 20° C for 10 minutes, fixed, washed with water, and, after drying, sen-

sitometry was carried out. The results obtained are shown in Table 1.

Developer Composition	
N-Methyl-para-aminophenol Sulfate	2.0 g
Sodium Sulfite (anhydrous)	100.0 g
Hydroquinone	5.0 g
Borax	2.0 g
Water	to 1000 ml

TABLE 1

Sample	Sulfur sensitizer	Added amount, mole/AgX	Relative sensitivity	Gamma	Fog
A	100	0.52	0.04
B	Sensitizing natural gelatin	10.0 g	1,120	1.02	0.12
C	Compound 1	55 mg	1,100	1.04	0.07
D	Compound 2	60 mg	1,240	1.07	0.09
E	Compound 3	65 mg	1,360	1.01	0.10

As can be seen from Table 1, a marked sensitizing effect was observed.

EXAMPLE 2

A neutral gelatino-silver bromochloride emulsion (58.0 mole percent silver bromide and 42.0 mole percent silver chloride) for a fine grained positive film at the beginning of chemical ripening was divided into three equal parts (Samples F to H). Compound 2 in a methyl alcohol solution was added to Sample H and a sensitive natural gelatin was added to Sample G in the amount as shown in Table 2. Next, after ripening at 52° C for 3 minutes to 1 kg of each emulsion were added 300 mg of 4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene, 450 mg of chrome alum, and 120 mg of saponine, and the mixture was coated on a cellulose triacetate film base and dried to obtain a photosensitive material of 12 microns in coating thickness. The material so obtained was exposed stepwise to a light source of 2,660° K for 1/20 second, developed with a developer having the following composition, fixed, washed with water and, after drying, sensitometry was conducted. The results obtained are shown in Table 2.

Developer Composition	
N-Methyl-para-aminophenol Sulfate	1.4 g
Isomeric Potassium Bisulfite	8.0 g
Hydroquinone	6.0 g
Sodium Carbonate (mono hydrate)	22.5 g
Citric Acid	0.7 g
Potassium Bromide	0.9 g
Water	to 1000 ml

As can be seen from the results in Table 2, a marked sensitizing effect was obtained.

TABLE 2

Sample	Sulfur sensitizer	Added amount, mole/AgX	Relative sensitivity	Gamma	Fog
F	100	1.30	0.04
G	Sensitizing natural gelatin	14 g	870	2.52	0.05
H	Compound 2	120 mg	1,050	2.71	0.05

EXAMPLE 3

A highly sensitive neutral gelatino-silver bromoiodide emulsion for an outer type reverse color film at the beginning of chemical ripening was divided into five equal parts (Samples I to M) and Compound 2 in a methyl alcohol solution was added to each of samples K to M, and a sensitizing natural gelatin was added to Sample J in the amount as shown in Table 3. Next, to each of these five types of emulsions were added 7.5 mg of potassium chloroaurate tetrahydrate and 150 mg of potassium thiocyanate per 1 mole of silver halide in the form

of an aqueous solution and was chemically ripened at 50° C under stirring for 70 minutes. Further, to 1 kg of the emulsion were added 30 g of 1,3'-diethyl-5'-methoxy-6-methyl-seleno-2-cyanineiodide, 450 mg of chrome alum and 120 mg of saponine, and the mixture was coated on a cellulose triacetate film base and dried to obtain a sensitive material of 8 micron in coating thickness. Next, the material so obtained was exposed stepwise to a light source of 5,400° K for 1/20 second, developed using a developer having the following composition at 27° C for 3½ minutes, fixed, washed with water and, after drying, sensitometry was carried out. The results obtained are shown in Table 3.

Developer Composition	
N-Methyl-para-aminophenol Sulfate	1.0 g
Sodium Sulfite (anhydrous)	60.0 g
Hydroquinone	10.0 g
Potassium Bromide	5.0 g
Potassium Thiocyanate	1.5 g
Potassium Iodide (0.1%)	5.0 ml
Sodium Hydroxide	2.0 g
Water	to 1000 ml

TABLE 3

Sample	Sulfur sensitizer	Added amount, mole/AgX	Relative sensitivity	Gamma	Fog
I	100	0.49	0.09
J	Sensitizing natural gelatin	100 g	980	0.84	0.19
K	Compound 2	45 mg	1,020	0.87	0.19
L	do	50 mg	1,150	0.97	0.13
M	do	55 mg	1,290	0.85	0.15

As can be seen from the results shown in Table 3, a marked sensitizing effect was obtained.

EXAMPLE 4

A semi-ammonium process gelatino-silver bromoiodide emulsion (1.5 mole percent silver iodide and 98.5 mole percent silver bromide) at the beginning of chemical ripening was divided into three equal parts (Samples N to P) and to Sample O to P were respectively added compounds 1 and 2 in a methylalcohol solution in the amount shown in Table 4. Next, to Sample N were added 4.7 mg of sodium thiosulfate (pentahydrate) and 1.2 mg of sodium aurous thiosulfate (dihydrate) $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ in the form of an aqueous solution per 1 mole of silver halide. In the same manner, Sample O was added with 4.7 mg and 3.2×10^{-2} mg of these salts per 1 mole of silver halide, respectively. Sample P was added with only 1.2 mg of sodium aurous thiosulfate (dihydrate) per 1 mole of silver halide.

Thereafter, these emulsions were chemically ripened at 50° C for 70 minutes.

These three types of emulsions were coated on a polyethylene terephthalate film base and dried to obtain a photosensitive material of 8 microns in coating thickness. Next, the materials so obtained were exposed through a continuous wedge to a light source of 5,400° K, and developed using a developer having the following composition at 20° C for 4 minutes.

Developer Composition	
N-Methyl-para-aminophenol Sulfate	4.0 g
Sodium Sulfite (anhydrous)	60.0 g
Hydroquinone	10.0 g
Sodium carbonate (monohydrate)	53.0 g
Sodium Bromide	3.0 g
Water	to 1000 ml

After the samples were fixed, washed with water and dried, sensitometry was conducted to obtain the results shown in Table 4.

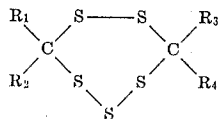
TABLE 4

Sample	Sulfur sensitizing agent	Added amount, mole/AgX (mg.)	Relative sensitivity	Gamma	Fog
N	$\{ \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \}$	4.7	100	1.75	0.15
	$\{ \text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O} \}$	1.2			
O	$\{ \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \}$	4.7	118	1.85	0.14
	$\{ \text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \}$	3.2×10^{-2}			
P	$\{ \text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O} \}$	1.2	110	1.85	0.15
	$\{ \text{Compound 2} \}$	0.13			

In case of using the sulfur sensitizing agent of the present invention in combination with sodium thiosulfate and/or sodium aurous thiosulfate $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$, Samples O and P were markedly effective in comparison with Sample N, Compounds 3 and 4 were recognized to be markedly effective in sensitization as in the above Examples 1 to 4.

What is claimed is:

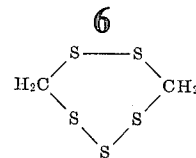
1. A photosensitive silver halide photographic emulsion containing at least one compound selected from the group consisting of compounds having the formula



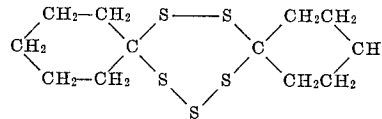
wherein each of R_1 , R_2 , R_3 and R_4 is selected from the group consisting of a hydrogen atom, an alkyl group and an aralkyl group; and wherein R_1 and R_2 , or R_3 and R_4 can combine to form a cycloalkyl group.

2. The photographic emulsion as claimed in claim 1, wherein each of R_1 , R_2 , R_3 and R_4 is selected from the group consisting of a hydrogen atom, a methyl group, an ethyl group, a propyl group, a butyl group, a benzyl group and a phenethyl group; and wherein R_1 and R_2 or R_3 and R_4 can combine to form a member selected from the group consisting of a cyclopentyl group, a cyclohexyl group, a cycloheptyl group and a cyclooctyl group.

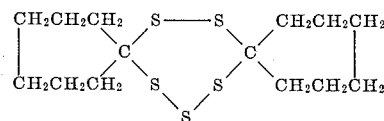
3. The photographic emulsion as claimed in claim 1, wherein said compound is



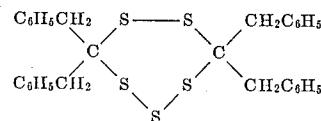
4. The photographic emulsion as claimed in claim 1, wherein said compound is



5. The photographic emulsion as claimed in claim 1, wherein said compound is



6. The photographic emulsion as claimed in claim 1, wherein said compound is



7. The photographic emulsion as claimed in claim 1, wherein said emulsion contains additionally at least one compound having a thiosulfate ion.

8. The photographic emulsion as claimed in claim 7, wherein the thiosulfate compound is selected from the group consisting of sodium thiosulfate, sodium aurous thiosulfate and mixtures thereof.

9. A photosensitive element comprising a support having thereon at least a layer of the silver halide photographic emulsion as claimed in claim 1.

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