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3,625,697

SENSITIZATION OF LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSIONS

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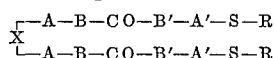
Int. Cl. G03c 1/28, 1/34

U.S. Cl. 96—107

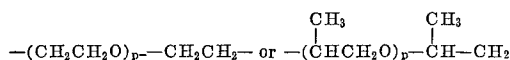
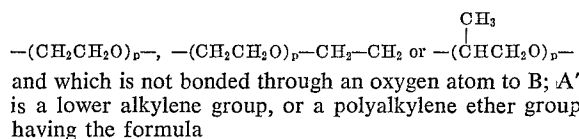
5 Claims

ABSTRACT OF THE DISCLOSURE

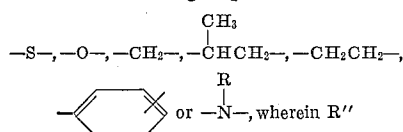
Light-sensitive silver halide emulsions are sensitized by incorporating into the emulsion, a sensitizing amount (0.1–1000 mg./kg.) of a compound of the formula:



wherein A is a lower alkylene group, or a polyalkylene ether group, having the formula:



provided that A and A' are not both polyalkylene ether groups at the same time, and p is an integer of 2 to 30; B and B' are —NH— or —O—, provided that both are not —O— at the same time; R is a lower alkyl group, a phenyl group, an aralkyl group or —(CH₂)_q—COOR', wherein q is an integer of 1 to 3, and R' is a lower alkyl group; and X is a divalent group of the formula:



This invention relates to a light-sensitive silver halide photographic emulsion sensitized by incorporating therein a sulfur-containing compound which will be described below.

Numerous methods are known for the sensitization of light-sensitive silver halide photographic emulsions. Typical of these is chemical sensitization using either a sulfur compound capable of yielding a silver sulfide or a suitable reducing compound; or a noble metal salt. Further, it is well known that the joint use of said compounds can further increase the sensitivity of the emulsion (refer, for example, to The Theory of the Photographic Process, third edition (1967), pages 113–117).

However, the known chemical sensitization process of this kind is severely restricted as far as the amount of the compound to be added, and has such disadvantages that if the amount exceeds a definite limit, the emulsion is greatly increased in fog and becomes low in stability during storage of the resulting film at an elevated temperature. Further, if a photographic emulsion is subjected to high temperature ripening in the presence of such a sensitizer as mentioned above, usually, only fogging of the emulsion is increased while the desired increase in sensitivity can not be attained after a definite sensitivity has been reached.

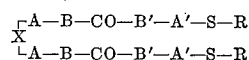
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The object of the present invention is to provide silver halide photographic emulsions improved in photographic properties, which are less in fog formation and which are increased in sensitivity.

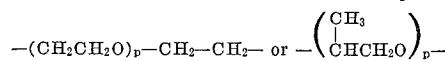
As the result of various studies, we have found that the above object can be effectively achieved by applying the novel sensitizing compounds mentioned below to silver halide photographic emulsions.

The compounds employed in the present invention have many characteristics different from those of the conventional chemical sensitizers. For example, they are usable as additives prior to coating and, when used in combination with chemical sensitizers, they can further increase the sensitivity of silver halide photographic emulsions without any accompanying fog formation.

The sensitizing compounds useful in the present invention are represented by the formula

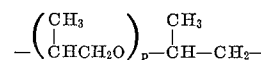


wherein A is a lower alkylene group, or a polyalkylene ether group of the formula —(CH₂CH₂O)_p—,



and which is not bonded through an oxygen atom to B;

A' is a lower alkylene group, or a polyalkylene ether group of the formula —(CH₂CH₂O)_p—CH₂—CH₂— or

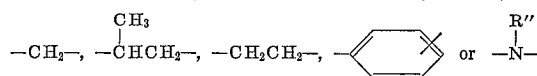


provided that A and A' are not both polyalkylene ether groups at the same time, and p is an integer of 2 to 30;

B and B' are —NH— or —O—, provided that both are not —O— at the same time;

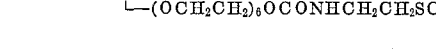
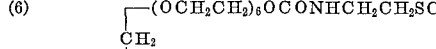
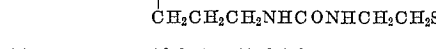
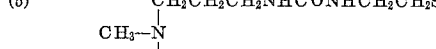
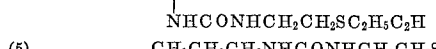
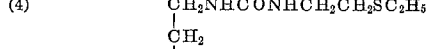
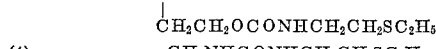
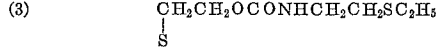
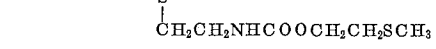
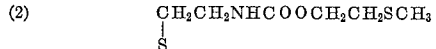
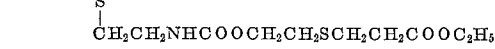
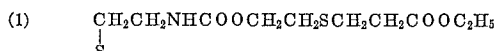
R is a lower alkyl group, a phenyl group, an aralkyl group or —(CH₂)_q—COOR', wherein q is an integer of 1 to 3 and R' is a lower alkyl group; and

X is a divalent group of the formula —S—, —O—,



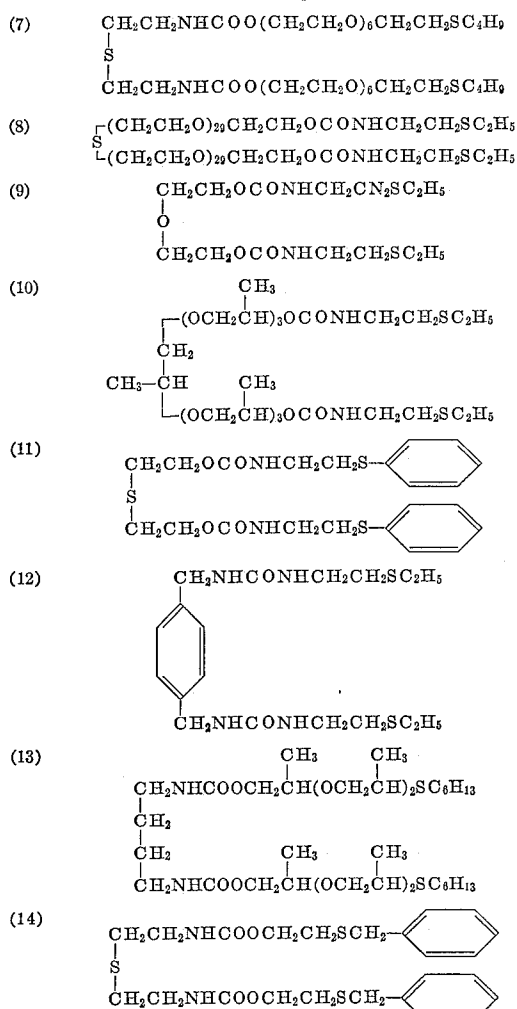
wherein R'' is a lower alkyl group.

Typical examples of the above-mentioned compounds are as follows:



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Synthesis examples of several compounds among three mentioned above are set forth immediately below.

SYNTHESIS EXAMPLE 1

Synthesis of the compound (1):

A solution of 17.8 g. of $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$ in 100 cc. of dry benzene was added with 8.6 g. of $\text{S}(\text{CH}_2\text{CH}_2\text{NCO})_2$. The mixture was refluxed for 2 hours and was then freed from the solvent by distillation under reduced pressure. The residue was dissolved in 200 cc. of ether, and was cooled and recrystallized to obtain the compound (1), M.P. 45°–46° C.

SYNTHESIS EXAMPLE 2

Synthesis of the compound (5):

A solution of 7.3 g. of $\text{CH}_3\text{---N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$ in dry benzene was added with 13.1 g. of

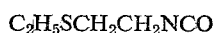


The mixture was refluxed for 2 hours in a water bath and was then cooled to deposit a crystalline mass. This mass was recrystallized from benzene to obtain the compound (5), M.P. 82°–83° C.

SYNTHESIS EXAMPLE 3

Synthesis of the compound (6):

A solution of 15 g. of $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{13}\text{H}$ in 50 cc. of dry benzene was added with 6.1 g. of



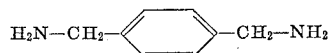
The mixture was refluxed for 8 hours and then the benzene was removed by distillation under reduced pressure

to obtain the compound (6) in the form of a slightly yellow transparent solution, n_D^{25} 1.4873.

SYNTHESIS EXAMPLE 4

5 Synthesis of the compound (12):

A solution of 13.6 g. of



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in dry benzene was gradually added with 26.2 g. of $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{NCO}$. The mixture was refluxed for 3 hours and was then cooled to deposit a crystalline mass. This mass was recovered by filtration and was recrystallized from methanol to obtain the compound (12), M.P. 207°–208° C.

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Other compounds than those mentioned above can also be synthesized according to the above-mentioned synthesis examples.

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The thus obtained compounds employed in the present invention may be added to emulsions at any stage during the second ripening. Most desirably, however, they are preferably added at the beginning of the second ripening. Silver halide emulsions containing these compounds are

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increased in gamma, photographic speed and maximum density and make is possible to obtain light-sensitive photographic materials having improved storability.

The above-mentioned compound useful in the present

invention may be added to a silver halide emulsion after

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dissolving the compound in water or in a water-miscible organic solvent such as methanol or ethanol. The amount of the compound to be added varies depending on the kind of the compound or of the silver halide emulsion employed, but is ordinarily in the range of 0.1 mg.–1000

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mg. per kg. of silver halide emulsion.

The compounds employed in the present invention are

applicable to all types of silver halide emulsions such as

silver chlorobromide emulsion, silver iodobromide emul-

sion, etc. Further the emulsions may have been subjected

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to gold sensitization or sulfur sensitization, and may have been incorporated with spectral sensitizers, polyalkylene oxide type sensitizers, various stabilizers, hardeners and coating aids.

The compounds employed in the present invention can

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be applied not only to monochromatic photographic emulsions but also to color photographic emulsions containing oil-soluble or water-soluble color couplers.

The silver halide photographic emulsions of the present

invention which are obtained in the above-mentioned

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manner are coated onto common supports such as, for example, glass, cellulose triacetate film bases, polyester film bases or baryta papers.

The present invention is illustrated in further detail

below with reference to examples, but the invention is

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not limited to these examples.

EXAMPLE 1

A silver halide emulsion comprising 2 mole percent of

silver iodide and 98 mole percent of silver bromide was

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subjected to second ripening by the use of a sulfur sensitizer and a gold sensitizer to prepare a silver iodobromide emulsion for high speed photographic negatives. This emulsion was divided into portions of 100 g. each, and the divided emulsions were individually incorporated with the present compounds set forth in Table 1 below. The thus treated emulsions were coated onto cellulose triacetate film bases and were then dried to prepare samples.

For comparison, the compound



disclosed in U.S. Pat. No. 3,021,215 was treated in the

same manner as above to prepare a control sample.

These samples were exposed to light by means of a

sensitometer KS-1 (manufactured and sold by Konishiroku Photo Industry Co., Ltd.) at 160 Lux-5400° K., and

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were then developed at 20° C. for 5 minutes with a developer having the following composition:

Metol	3	G.
Anhydrous sodium sulfite	50	5
Hydroquinone	6	
Sodium carbonate (monohydrate)	29.5	
Potassium bromide	1	
Water to make 1 liter.		

(The developer was used after dilution with water to 1:1.)

Thereafter, the samples were subjected to sensitometry 20 to obtain the results shown in Table 1.

TABLE 1

Incorporated compound	Amount (mg./100 g. emulsion)	Speed	Gamma	Maximum density	Fog
Compound (2)	50	120	0.95	2.25	0.06
Compound (8)	50	130	0.95	2.27	0.07
Compound (10)	50	125	1.00	2.30	0.07
Control sample	50	120	0.88	2.05	0.09
Non-incorporated sample		100	0.80	2.02	0.09

NOTE.—In the table, the speed is a relative value measured by assuming as 100 the speed of the non-incorporated sample.

As is clear from Table 1, light-sensitive photographic materials improved in speed, gamma and maximum density can be obtained by the use of the silver halide photographic emulsions in accordance with the present invention.

EXAMPLE 2

A neutral photographic emulsion for photographic negatives, which comprised 5 mole percent of silver iodide and 95 mole percent of silver bromide, was added with given amounts of a sulfur sensitizer and a gold sensitizer, and was then divided into portions of 100 g. each. The divided emulsions were individually incorporated with the present compounds set forth in Table 2 below. Each emulsion was maintained at 56° C. and was subjected to second ripening so as to attain the maximum density. Subsequently, 20 mg. per 100 g. of the emulsion of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were added, and then suitable amounts of a film hardener and a coating aid were added. The thus treated emulsions were uniformly coated onto cellulose triacetate film bases and were then dried to prepare samples. These samples were subjected to storage test, and were then subjected to sensitometry in the same manner as in Example 1 to obtain the results as set forth in Table 2.

TABLE 2

Incorporated compound	Amount (mg./100 g. emulsion)	Incubated at room temperature for 3 days			Incubated at 55° C. for 3 days			Incubated at 55° C. relative humidity 80% for 3 days		
		Speed	Maximum density	Fog	Speed	Maximum density	Fog	Speed	Maximum density	Fog
Compound (4)	1.0	125	2.35	0.05	125	2.32	0.07	130	2.30	0.07
Compound (7)	1.0	140	2.40	0.07	135	2.42	0.08	135	2.41	0.06
Compound (11)	1.0	115	2.30	0.04	120	2.32	0.05	115	2.30	0.05
Non-incorporated sample		100	2.02	0.08	105	2.08	0.08	100	2.05	0.07

(In the table, the speed is a relative value measured by assuming as 100 the speed of the non-incorporated sample.)

From the above table, it is clear that the silver halide photographic emulsions in accordance with the present invention give light-sensitive photographic materials which, even when stored under severe conditions, are less subject to formation of fog and free from any decrease in speed.

EXAMPLE 3

To a silver iodobromide color photographic emulsion containing 4 mole percent of silver iodide were added given amounts of chemical sensitizers according to sulfur sensitization and gold sensitization, and then the emulsion was divided into portions of 100 g. each. The thus divided emulsions were individually incorporated with the compounds as shown in Table 3.

After being subjected to second ripening so as to attain the optimum properties, each emulsion was charged with the same stabilizer as in Example 2. To this emulsion was

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then added as a magenta coupler a given amount of a dispersion prepared by dissolving at an elevated temperature 1 - (2,4,6 - trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamide) benzamide] - 5 - pyrazolone in a mixture comprising di-n-butyl phthalate and ethyl acetate, and then dispersing the solution in a gelatine solution by means of sodium alkylbenzenesulfonate. This emulsion was thoroughly stirred and was then adjusted to pH 6.8 to obtain a color photographic emulsion.

Emulsions obtained in the above manner were immediately coated uniformly onto cellulose triacetate film bases and were then dried to prepare samples. These samples were exposed in the same manner as in Example 1 and were then developed at 21° C. for 10 minutes with a color developer of the following composition:

N-Ethyl-N-β-methanesulfonamidoethyl - 3 - methyl- aminoaniline sulfate	2.5	G.
Anhydrous sodium sulfite	2.0	
Benzyl alcohol	3.8	
Sodium hexametaphosphate	2.0	
Sodium carbonate (monohydrate)	50.0	
Potassium bromide	1.0	
Caustic soda	0.6	
Water to make 1 liter.		

Thereafter, the samples were subjected to ordinary bleaching, fixing and water-washing treatments and then to sensitometry to obtain the results as shown in Table 3.

TABLE 3

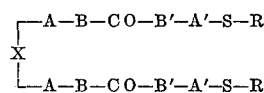
Incorporated compound	Amount (mg./100 g. emulsion)	Speed	Gamma	Fog
Compound (1)	1.5	125	0.85	0.03
Compound (3)	1.5	130	0.07	0.03
Non-incorporated sample		100	0.65	0.03

NOTE.—In the table, the speed is a relative value measured by assuming as 100 the white light speed of the non-incorporated sample.

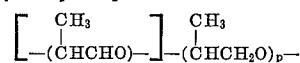
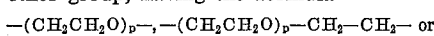
As is clear also from Table 3, the silver halide photographic emulsions according to the present invention give, even when used in combination with a magenta coupler, color photographic materials which are high in sensitivity and less in fog.

What we claim is:

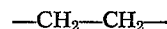
1. A light-sensitive silver halide photographic emulsion comprising, as a sensitizer, a sensitizing amount of a compound having the formula



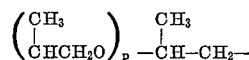
wherein A is a lower alkylene group, or a polyalkylene ether group, having the formula



and which is not bonded through an oxygen atom to B; A' is a lower alkylene group, or a polyalkylene ether group having the formula $-(\text{CH}_2\text{CH}_2\text{O})_p$



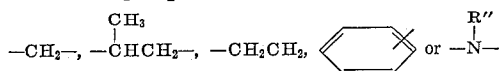
or



provided that A and A' are not both polyalkylene ether groups at the same time, and p is an integer of 2 to 30; B and B' are —NH— or —O— , provided that both are not —O— at the same time;

R is a lower alkyl group, a phenyl group, an aralkyl group or $\text{—(CH}_2)_q\text{—COOR'}$, wherein q is an integer of 1 to 3, and R' is a lower alkyl group; and

X is a divalent group of the formula —S— , —O— ,



wherein R'' is a lower alkyl group.

2. A light-sensitive silver halide photographic emulsion as claimed in claim 1, further comprising a color former.

3. A light-sensitive silver halide photographic emulsion as claimed in claim 1, further comprising at least one other known chemical and/or spectral sensitizer.

4. A light-sensitive silver halide photographic emulsion as claimed in claim 1, further comprising at least one

photographic additive selected from the group consisting of stabilizers and hardeners.

5. A light-sensitive silver halide photographic emulsion as claimed in claim 1, wherein the sensitizer is present in an amount of 0.1 to 1000 mg. per kg. of silver halide emulsion.

References Cited

UNITED STATES PATENTS

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	3,021,215	2/1962	Williams et al.	96—107
	3,046,129	7/1962	Graham et al.	96—107

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U.S. Cl. X.R.

96—109