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3,761,277

SILVER HALIDE EMULSION CONTAINING A SULPHO SUBSTITUTED DISULPHIDE AS STABILIZER

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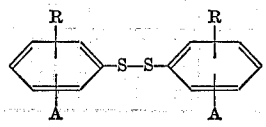
Int. Cl. G03c 1/34
U.S. Cl. 96—109 15 Claims

ABSTRACT OF THE DISCLOSURE

Light-sensitive silver halide emulsions are provided which comprise a disulphide compound of the formula:



wherein:

A is a sulpho group or a sulpho group carrying substituent, the sulpho group being in acid or salt form, and
R is hydrogen or a substitutent.

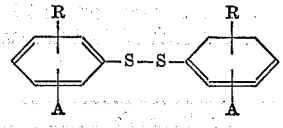
The emulsion has improved stability and fogging characteristics.

This invention relates to photographic materials, more particularly to light-sensitive silver halide emulsions comprising compounds having fog-inhibiting or stabilizing properties.

It is well known that light-sensitive silver halide materials comprising gelatin silver halide emulsion layers are subject to fogging. Fogging in general and chemical fogging in particular may be defined as the formation of a uniform deposit of silver on development which is dependent on a whole series of circumstances and factors namely on the nature of the emulsions, on their age, on the conditions under which they have been stored, on the development conditions, etc. For particular development conditions the fog tends to be higher when the time of storage and the temperature and relative humidity of the atmosphere in which the emulsions are stored are increased. Fog also increases with the degree of development and by rapid development at elevated temperatures.

Several compounds have been described in the prior art for reducing fog in light-sensitive silver halide emulsions. Many of these compounds, however, have the disadvantage of causing decreased sensitivity resulting in loss of speed and/or gradation of the emulsion when developed.

It has now been found that compounds corresponding to the following general formula:



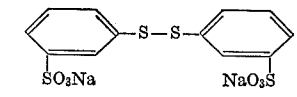
wherein:

A stands for a sulpho group or a sulpho group carrying substituent for example sulphobenzoylamine, the sulpho group being in acid or salt form, and
R stands for hydrogen or a substitutent such as alkyl, halogen, alkoxy and sulpho in acid or salt form,

exert a fog-inhibiting action on light-sensitive photographic emulsions without giving rise to an objectionable desensitization thereof, and are particularly suitable to reduce fog-formation in photographic colour emulsions comprising colour forming couplers.

The compounds having the structures listed below are representatives of those falling within the scope of the above general formula.

(1)



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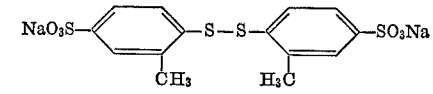

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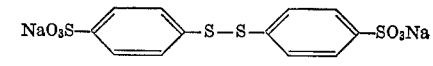

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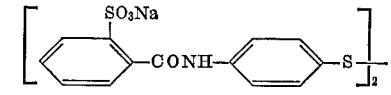


Compounds 1, 2 and 3 can be prepared according to the method described by H. A. Smith, G. Doughthy and G. Gorin in J. Org. Chem., 29, (1964), 1484.

Compound 4 was prepared as follows:

7.44 g. (0.03 mole) of 4,4'-dithiodianiline and 16.5 g. (0.09 mole) of o-sulphobenzoic anhydride were boiled for 11 hours in 150 ml. of pyridine. The solution was concentrated by evaporation whereupon the residue was dissolved in water and neutralized with sodium carbonate. The solution was again concentrated by evaporation and the pyridine residues were removed. The residue was recrystallized from 100 ml. of water. Yield: 8 g. (40%). Melting point: >260° C.

The compounds according to the present invention are generally incorporated into the silver halide emulsion layer of the light-sensitive material. The way in which the compounds of use according to the invention are added to the emulsions is not critical and the addition can be made during no matter what step of emulsion preparation, they can be added before or after the emulsion has been optically sensitized, preferably just before coating of the emulsion on a suitable support such as for example paper, glass or film.

Instead of incorporating the compounds of the invention into the emulsion layer they can also be incorporated into another water-permeable colloid layer of the photographic material, e.g. a gelatin antistress layer or intermediate layer, which is in water-permeable relationship with the said emulsion layer.

The compounds of use according to the present invention may be incorporated into any type of light-sensitive material comprising a silver halide emulsion e.g. an X-ray or other nonspectrally sensitized emulsion, a silver halide emulsion of use in diffusion transfer processes for the production of silver images, an orthochromatic, panchromatic and infrared-sensitive emulsion etc. They may be incorporated into high speed negative material as well as into rather low speed positive materials. Various silver salts may be used as light-sensitive salt e.g. silver bromide, silver iodide, silver chloride, or mixed silver halides e.g. silver chlorobromide or silver-bromo-iodide.

The antifoggants of use according to the present invention are particularly suitable for use in silver halide materials intended for colour photography, for example, materials containing colour-forming couplers which, by reaction with the oxidation product of aromatic primary amino developing agents such as those of the p-phenylene diamine type, form dyestuffs. In these emulsions most of the known antifoggants are unsuccessful to reduce the

fog, which is largely due to the presence of the colour coupler, or give rise to a marked decrease in sensitivity. They were also found particularly suitable for use in colour radiographic material containing colour forming coupler compounds e.g. colour radiographic material as described in published Dutch patent application 6912843 and U.S. patent application Ser. No. 852,246.

The silver halides can be dispersed in the common hydrophilic colloids such as gelatin, casein, zein, polyvinyl alcohol, carboxymethylcellulose, alginic acid, etc. gelatin being, however, favoured.

The amount of compound according to the present invention employed in the light-sensitive silver halide material depends on the particular type of emulsion and the desired effect and can vary within very wide limits. The optimum amount to be added is best determined for each particular type of emulsion by trial. The most suitable concentration of compound according to the present invention is generally comprised between 0.005 millimole and 1 millimole, preferably between 0.01 millimole and 0.25 millimole per mole of silver halide.

The light-sensitive emulsions may be chemically as well as optically sensitized. They may be chemically sensitized by effecting the ripening in the presence of small amounts of sulphur containing compounds such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in our British patent specification 789,823 and small amounts of noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium.

Furthermore, the emulsions may also comprise compounds which sensitize the emulsion by development acceleration for example alkylene oxide polymers. These alkylene oxide polymers may be of various types. Various derivatives of alkylene oxides may be used to sensitize the silver halide emulsions e.g. alkylene oxide condensation products as described among others in U.S. patent specifications 2,531,832 and 2,533,990 in U.K. patent specifications 920,637, 940,051, 945,340 and 991,608 and in Belgian patent specification 648,710. Other compounds that sensitize the emulsion by development acceleration and that are suitable for use in combination with the compounds of use according to the invention are the quaternary ammonium compounds and onium derivatives of amino-N-oxides as described in U.K. patent specification 1,121,696.

In conjunction with light-sensitive materials comprising compounds according to the above general formula there may also be used known stabilizers for instance heterocyclic nitrogen containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-Δ_2-tetrazoline-5-thione, mercury compounds such as those described in Belgian patent specifications 524,121 and 677,337 and in U.K. Pat. Nos. 1,173,609 and 1,194,401 and compounds of the hydroxytriazolo-pyrimidine type (hydroxyazaindolizines) such as 5-methyl-7-hydroxy-s-triazolo[1,5-a] pyrimidine particularly in extreme storage and development circumstances.

Other addenda such as hardening agents, coating aids, plasticizers, colour couplers, developing agents and optical sensitizers can be incorporated into the emulsion in the usual way.

The following examples illustrate the stabilizing or fog-inhibiting action of the compounds according to the invention.

EXAMPLE 1

A conventional photographic gelatino silver bromoiodide emulsion (4.5 mole percent iodide) comprising per kg. an amount of silver halide equivalent to 50 g. of silver nitrate was divided into four portions. To three of these portions one of the compounds according to the invention was added in a concentration of ⅛ millimole per kg. of emulsion. Then the emulsions were coated on a conventional support and dried.

The values of speed, gradation and fog of the materials formed were determined shortly after preparation and after incubation for 5 days at 57° C. and 34% relative humidity. The values obtained are listed in the table below. The values I and II given for the speed are relative values corresponding with density 0.1 above fog and density 1 above fog respectively; the speed of the fresh comparison material comprising no compound according to the invention is given the value 100.

Development occurred at 20° C. for 5 min. in a developing solution having the following composition:

Water	cc	800
p-Monomethylaminophenol sulphate	g	1.5
Sodium sulphite (anhydrous)	g	50
Hydroquinone	g	6
Sodium carbonate (anhydrous)	g	32
Potassium bromide	g	2

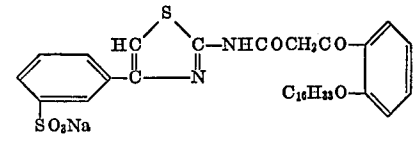
Fater to make 1000 cc.

TABLE

	Fresh material				Incubated material			
			Speed				Speed	
Compound added	Fog	Gradation	I	II	Fog	Gradation	I	II
None	0.11	1.61	100	100	0.69	1.61	93	103
Compound 1	0.05	1.71	60	73	0.11	1.76	118	111
Compound 2	0.07	1.57	69	71	0.19	1.53	136	107
Compound 3	0.05	1.76	60	73	0.07	1.82	97	108

EXAMPLE 2

To a negative blue-sensitive silver bromoiodide emulsion (5 mole percent of iodide) comprising per kg. 80 g. of gelatin, an amount of silver halide equivalent to 86 g. of silver nitrate, and a yellow forming colour coupler having the formula:



are added per kg.: 1.4 ml. of a 1% aqueous solution of compound 1 and 630 mg. of 5-methyl-7-hydroxy-s-triazolo [1,5-a]pyrimidine as well as common additives such as hardener and coating aids.

After having coated the emulsion on a film support and dried, the material formed is exposed through a grey wedge and then developed for 8 min. at 20° C. in a colour developing bath of the following composition:

Water	ml	900
Sodium hexametaphosphate	g	1
Anhydrous sodium sulphate	g	4
N,N-diethyl-p-phenylene diamine hydrochloride	g	2.7
Anhydrous sodium carbonate	g	25
Potassium bromide	g	2.2
Sodium carbonate	g	0.55

Water to makel litre

After treatment for 2 min. at 18–20° C. in an intermediate bath comprising 30 g. of sodium sulphate in 1 litre of water, the material is rinsed for 15 min. with water and treated in a bleach bath of the following composition:

	G.
Borax	20
Anhydrous potassium bromide	15
Anhydrous sodium bisulphate	4.2
Potassium hexacyanoferrate (III)	100

Water to make 1 litre.

After bleaching, the material is rinsed with water for 5 min. and fixed in an aqueous solution of 200 g. of sodium thiosulphate per litre.

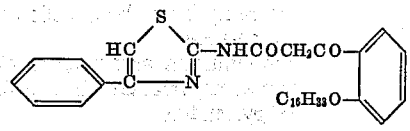
After a final rinsing for 15 min. the material showing a yellow wedge image is dried.

The processed material showed a yellow fog of 0.07 while a material comprising no compound 1 showed after processing a yellow fog of 0.17.

When processing was carried out after having stored the materials for 6 days at 57° C. and 34% of relative humidity the material comprising no compound 1 showed a yellow fog of 0.54 whereas the material comprising compound 1 showed a yellow fog of 0.23.

EXAMPLE 3

To a positive blue-sensitive gelatino silver chlorobromide (28 mole percent of chloride) emulsion comprising per kg. 76 g. of gelatin, an amount of silver halide equivalent to 72 g. of silver nitrate and a yellow forming colour coupler having the formula:



are added per kg.: one of the compounds of the invention as listed in the table below in the amounts given, 660 mg. of 5 - methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine as well as common additives such as hardeners and coating aids.

The emulsion is coated on a cellulose triacetate support and then overcoated with a gelatin antistress layer.

After exposure of the material formed, through a grey wedge having a constant of 0.15 the material is colour-processed using 2-amino-5-diethylamino-toluene hydrochloride as colour-developing agent.

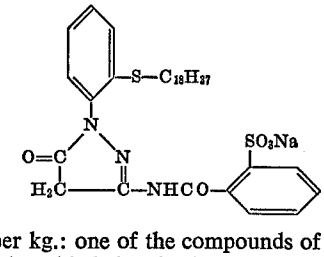
The results obtained with freshly prepared material and with material that has been stored for 6 days at 57° C. and 34% relative humidity are listed in the following table:

Compound added per kg. of emulsion	Fresh material		Stored material	
	Fog	Relative speed	Fog	Relative speed
None	0.11	100	0.18	83
4.5 ml. of a 1% aqueous solution of Compound 1	0.11	90	0.14	83
9 ml. of a 1% aqueous solution of Compound 1	0.10	83	0.13	79

The values given for the speed are relative values corresponding with density 1 above fog; the speed of the fresh material comprising no compound of the invention is given the value 100.

EXAMPLE 4

To a negative green-sensitized silver bromoiodide emulsion (5 mole percent of iodide) comprising per kg. 77 g. of gelatin, an amount of silver halide equivalent to 80 g. of silver nitrate and a magenta forming colour coupler having the following formula:



are added per kg.: one of the compounds of the invention as listed in the table below in the amounts given, 660 mg. of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine as well as common additives such as hardener and coating aids.

The emulsion is coated on a cellulose triacetate support and then overcoated with a gelatin antistress layer.

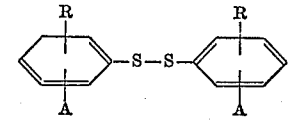
After exposure of the material formed through a grey wedge having a constant of 0.20 the material is colour processed. The values of the fog formed were determined after colour-development for 15 mins. and 20 mins. respectively in a colour developing bath comprising 2-amino-5-(N-ethyl-N-β-methylsulphonylaminoethyl)amino toluene sulphate as colour developing agent.

The results are as follows:

Compound added per kg. of emulsion	Fog produced after development for—	
	15 min.	20 min.
None	0.12	0.19
5 ml. of a 1% aqueous solution of Compound 3	0.07	0.09
2.5 ml. of a 1% aqueous solution of Compound 3	0.07	0.09
1.25 ml. of a 1% aqueous solution of Compound 3	0.08	0.12

What we claim is:

1. A light-sensitive silver halide emulsion comprising as an antifogging and stabilizing agent a disulphide compound corresponding to the following general formula:



wherein:

A stands for a sulpho group or a sulpho group carrying substitutent, the sulpho group being in acid or salt form, and

R stands for hydrogen, alkyl, halogen, alkoxy, or a sulpho group in the acid or salt form;

said disulphide compound being present in an amount sufficient to inhibit fogging or improve the stability of said emulsion, said amount being from about 0.005 to 1 millimole per mole of silver halide.

2. A photographic silver halide emulsion according to claim **1**, wherein said emulsion also comprises a polyoxyalkylene development acceleration.

3. A photographic silver halide emulsion according to claim **1**, wherein said disulphide compound is present in a ratio of 0.01 millimole to 0.25 millimole per mole of silver halide.

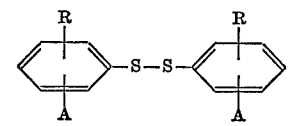
4. A light-sensitive silver halide emulsion according to claim **1**, wherein said antifogging and stabilizing agent is bis(m-sulphophenyl)disulphide in acid or salt form.

5. A light-sensitive silver halide emulsion according to claim **1**, wherein said antifogging and stabilizing agent is bis(p-sulphophenyl)disulphide in acid or salt form.

6. A light-sensitive silver halide emulsion according to claim **1**, wherein said antifogging and stabilizing agent is bis(p-sulpho-o-tolyl)disulphide in acid or salt form.

7. A light-sensitive silver halide emulsion according to claim **1**, wherein said antifogging and stabilizing agent is bis[p-(o-sulphobenzoylamino)phenyl]disulphide in acid or salt form.

8. A photographic element comprising a support coated with water-permeable colloid layers including at least one light-sensitive silver halide emulsion layer, wherein one of said layers comprises an antifoggant or stabilizer corresponding to the following general formula:



wherein:

A stands for a sulpho group or a sulpho group carrying substitutent, the sulpho group being in acid or salt form, and

R stands for hydrogen, alkyl, halogen, alkoxy, or a sulpho group in the acid or salt form;

said antifoggant or stabilizer being present in an amount sufficient to inhibit fogging or improve the stability of said emulsion, said amount being from about 0.005 to 1 millimole per mole of silver halide.

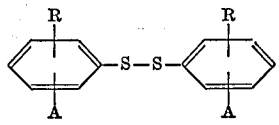
9. A photographic element according to claim **8**, wherein said element also comprises a hydroxytriazolo-pyrimidine stabilizer.

10. A photographic element according to claim 9, wherein said hydroxytriazolopyrimidine is 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine.

11. A photopraghic element according to claim 8, wherein said element also comprises a polyoxyalkylene development accelerator.

12. A photographic element according to claim 8, wherein said element comprises one or more light-sensitive silver halide emulsion layers containing a colour coupler, which on colour development by means of an aromatic primary amino colour developing agent forms a dye image.

13. A light-sensitive silver halide emulsion useful in colour photography comprising a colour-forming coupler and as an antifogging and stabilizing agent a disulphide compound corresponding to the following general formula:



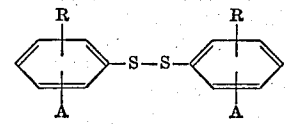
wherein:

A stands for a sulpho group or a sulpho group carrying substitutent, the sulpho group being in acid or salt form, and

R stands for hydrogen, alkyl, halogen, alkoxy, or a sulpho group in the acid or salt form;

said disulphide compound being present in an amount sufficient to inhibit fogging or improve the stability of said emulsion, said amount being from about 0.005 to 1 millimole per mole of silver halide.

14. A light-sensitive silver halide emulsion comprising a hydroxytriazolopyrimidine stabilizer and as an antifogging and stabilizing agent a disulphide compound corresponding to the following general formula:



wherein:

A stands for a sulpho group or a sulpho group carrying substituent, the sulpho group being in acid or salt form, and

R stands for hydrogen, alkyl, halogen, alkoxy, or a sulpho group in the acid or salt form;

said disulphide compound being present in an amount sufficient to inhibit fogging or improve the stability of said emulsion, said amount being from about 0.005 to 1 millimole per mole of silver halide.

15. A light-sensitive emulsion according to claim 14, wherein said hydroxytriazolopyrimidine is 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine.

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96—69, 74, 100