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2,939,789

FOG REDUCTION IN PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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12 Claims. (Cl. 96—66)

The present invention relates to the use of antifogging and stabilizing agents for photographic silver halide emulsions and, more particularly, to the employment of azolylmercaptoalkanediones for such purpose.

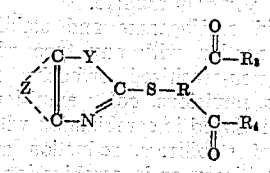
It is recognized that light-sensitive emulsions such as gelatine silver halide emulsions have a tendency to fog. The fog may be caused in a number of ways as, for example, by excessive ripening of the emulsion, by storage of the light-sensitive element at elevated temperatures and humidity or by prolonged development of the exposed emulsion.

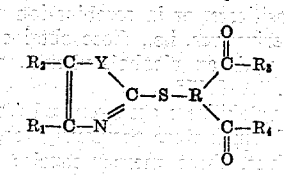
A great number of antifogging and stabilizing agents have been recommended in the literature for the purpose of preventing the formation of fog in light-sensitive silver halide emulsions. Although these compounds have the ability to control fog during manufacture, as well as during storage, they also have distinct shortcomings. For instance, they lower the sensitivity of the emulsion either immediately or under storage conditions, thus causing speed regression.

We have now found that azolylmercaptoalkanediones are excellent stabilizers and antifoggants for silver halide emulsions, having the ability to maintain the sensitivity and fog at or close to initial optimum values under keeping conditions of high temperature and humidity.

The use of such compounds to inhibit fog and to stabilize silver halide emulsions either by location of the same in the emulsion, in layers adjacent to the emulsion or in processing baths for the emulsion, constitutes the purposes and objects of the present invention.

The azolylmercaptoalkanediones, the use of which is contemplated herein, may be represented by the following formulae:

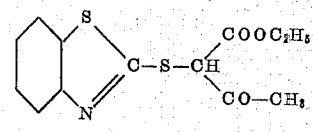




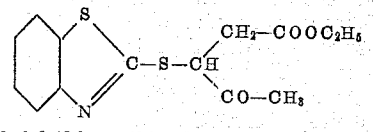
wherein Y is an imino group, or an oxygen, selenium or sulfur atom, R is a lower alkylene group of less than three carbon atoms, e.g., methylene, ethylene, or propylene, R_1 and R_2 are hydrogen atoms or alkyl radicals, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, dodecyl and the like; an acyl radical, e.g., acetyl propionyl and the like; a carboxyalkoxy radical, e.g. carboxymethoxy, carboxyethoxy, carboxypropoxy, R_3 is an alkyl group, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert.-butyl, amyl, hexyl, octyl or decyl group, or an alkoxy group, e.g., methoxy, ethoxy, propoxy, isopropoxy, amyloxy, heptyloxy and nonyloxy

group, R_4 is an alkyl or alkoxy group having the same values as given for R_3, and Z represents the atoms necessary to complete a fused-on aromatic ring system such as a benzo or naphtho ring.

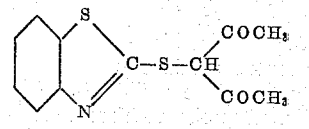
Examples of compounds falling within the ambit of such general formulae which we have found to be effective are:



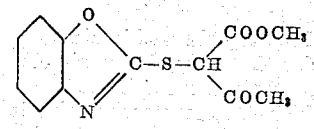
Ethyl-α-(2-benzothiazolylmercapto)-acetoacetate



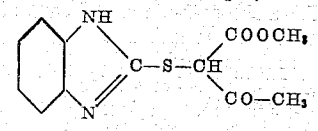
Ethyl-β-(2-benzothiazolylmercapto)-levulinate



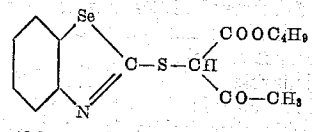
3-(2-benzothiazolylmercapto)-2,4-pentanedione



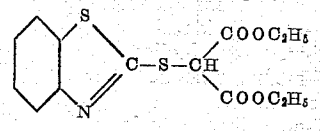
Methyl-α-(2-benzoxazolylmercapto)-acetoacetate



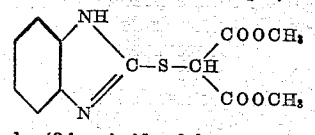
Methyl-α-(2-benzimidazolylmercapto)-acetoacetate



n-Butyl-α-(2-benzoselenazolylmercapto)acetoacetate



Diethyl-α-(2-benzothiazolylmercapto)malonate



Dimethyl-α-(2-benzimidazolylmercapto)malonate

These compounds are prepared by reacting a 2-mercapto-substituted azole of the imidazole, benzimidazole, oxazole, benzoxazole, selenazole, benzoselenazole, thiazole and benzothiazole series with a halogenated alkylene dicarbonyl compound in which the halogen is attached to a carbon atom adjacent to one carbonyl group and not more than one carbon atom removed from the other. The condensation is carried out in an alkaline medium with the removal of hydrogen halide. As representative of such azoles, the following are mentioned:

4-methyl-2-mercaptothiazole
4-ethyl-2-mercaptothiazole
4-propyl-2-mercaptothiazole
4-dodecyl-2-mercaptothiazole
4-butyl-2-mercaptothiazole

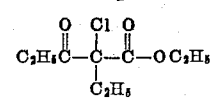
4-phenyl-2-mercaptothiazole
4-p-chlorophenyl-2-mercaptothiazole
4-p-methoxyphenyl-2-mercaptothiazole
4,5-propano-2-mercaptothiazole
4,5-dimethyl-2-mercaptothiazole
4,5-diphenyl-2-mercaptothiazole
4,5-diethyl-2-mercaptothiazole
5-carbomethoxy-4-methyl-2-mercaptothiazole
5-acetyl-4-methyl-2-mercaptothiazole
4-methyl-2-mercaptothiazoline
5-methyl-2-mercaptothiazoline
5,5-dimethyl-2-mercaptothiazoline
5-phenyl-2-mercaptothiazoline
5-methyl-2-mercaptothiazole
6-methyl-2-mercaptobenzothiazole
7-methyl-2-mercaptobenzothiazole
6-tert.-butyl-2-mercaptobenzothiazole
6-phenyl-2-mercaptobenzothiazole
5-hydroxy-2-mercaptobenzothiazole
5-chloro-2-mercaptobenzothiazole
5-bromo-2-mercaptobenzothiazole
6-chloro-2-mercaptobenzothiazole
6-bromo-2-mercaptobenzothiazole
6-nitro-2-mercaptobenzothiazole
5-amino-2-mercaptobenzothiazole
6-amino-2-mercaptobenzothiazole
6-acetamido-2-mercaptobenzothiazole
6-benzamido-2-mercaptobenzothiazole
6-dimethylamino-2-mercaptobenzothiazole
5-carboxyl-2-mercaptobenzothiazole
4,6-dimethyl-2-mercaptobenzothiazole
4-methyl-6-chloro-2-mercaptobenzothiazole
5,6-dichloro-2-mercaptobenzothiazole
4-carboxy-6-chloro-2-mercaptobenzothiazole
4,6-dimethyl-7-chloro-2-mercaptobenzothiazole
4,6-dimethyl-5,7-dichloro-2-mercaptobenzothiazole
4,5-benzo-2-mercaptobenzothiazole
6,7-benzo-2-mercaptobenzothiazole
2-mercapto-4,5,6,7-dibenzobenzothiazole
2-mercapto-5,6-naphthobenzothiazole
2-mercapto-5,6-benzobenzothiazole
2-mercapto-4,5-fluorenyl (1,2)-thiazole
6,7-benzo-2-mercaptobenzoselenazole
2-mercaptobenzoselenazole
2-mercaptoselenazole
2-mercaptobenzimidazole
2-mercapto-6-chlorobenzimidazole
2-mercapto-6-methylbenzimidazole
2-mercapto-1-methylimidazole
2-mercapto-6-methoxyquinoline
2-mercapto-6-methylquinoline
2-mercaptobenzoxazole
2-mercapto-5-phenylbenzoxazole
2-mercapto-5-methoxybenzoxazole
2-mercapto-5-methylbenzoxazole
2-mercapto-4,5-benzobenzoxazole
2-mercaptobenzoselenazole
2-mercapto-5-methoxybenzoselenazole
2-mercapto-5-methylbenzoselenazole

As representative of such halogenated alkylene dicarbonyl compounds, the following are mentioned:

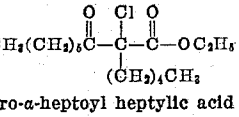
Methyl α-chloroacetoacetate
Ethyl α-bromoacetoacetate
3-chloro-2,4-pentanedione
Dimethyl α-chloromalonate
Diethyl α-bromomalonate
Ethyl β-bromolevulinate
Ethyl α-chloro acetoacetate
Ethyl α-chloro α-propionyl propionate
α-Chloro butyl acetic ester
$CH_3CH_2CH_2COCHClCOOR$



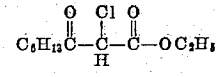
α-Chloropropionyl acetic acid ester



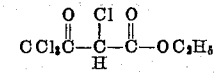
α-Chloro-α-butyryl butyric acid ester



α-Chloro-α-heptoyl heptylic acid ester



α-Chloroheptoacetic ester



Ethyl-α-chlorotrichloro acetoacetate

Beneficial effects and fog reduction are obtained when aqueous or alcoholic solutions of the aforementioned compounds are incorporated in the silver halide emulsions as "ripening finals" or as "coating finals." "Ripening finals" are added during the ripening or the sensitivity increasing stage of the emulsion making process. Such additions may be made before, during or after the decomposition of the soluble silver salt such as silver nitrate by means of a soluble halide such as potassium bromide, sodium chloride or the like in the presence of a colloidal carrier such as gelatin, PVA, solubilized casein or albumen.

"Coating finals" are added to the emulsion just prior to coating on a suitable support such as glass, paper or film at a time when the emulsion has nearly obtained its maximum sensitivity.

When used as ripening finals, the antifoggants are best employed in a concentration of 1 to 10 milligrams per 0.4 mol of silver halide (2.5 to 25 milligrams per mol) and when used as coating finals in a concentration of 10 to 150 milligrams per 0.4 mol of silver halide (25 to 375 milligrams per mol). The concentration used depends on the type of emulsion employed and it is advisable to determine the optimum concentration from case to case. In some instances, it is advantageous to apply the antifoggant and stabilizers in layers adjacent to the emulsion, that is, in a separate undercoating layer or in the anti-abrasion gelatin surface. In other instances, the desired result may be obtained by addition of the antifoggant and stabilizer to one of several processing baths such as developer, fixer or the like.

The aforesaid antifoggants and stabilizers may be utilized in connection with any type of photographic emulsion, e.g., non-sensitized, orthochromatic, panchromatic, boil-type emulsions, color emulsions or the like. They may be employed in combination with other known antifoggants and stabilizers, reduction and metal and noble metal sensitizers, or in combination with hydroxypolyethenoxy derivatives, i.e., those obtained by reacting ethylene oxide with an alcohol, phenol, amine or the like (see U.S.P. 1,970,578).

Although our stabilizers are prepared from mercaptoazoles, some of which were previously recommended as emulsion additives, these mercaptoazoles have the inherent disadvantage of being extremely powerful desensitizers, thus reducing fog while sacrificing most of the speed and contrast. In many instances, these losses do not stop with the manufacturing operation, but progress during the storage of the light-sensitive material thus reducing the shelf-life of the commercial product. The compounds of our invention are free from these disadvantages.

The invention is illustrated by the following examples, but it is to be understood that the invention is not restricted thereto.

Example I

A silver halide emulsion in gelatin containing 4 percent silver iodide and 96 percent silver bromide was prepared in a conventional manner and brought up to its maximum light sensitivity. It was then readied for coating, finals were added such as sensitizing dyes, stabilizers and hardening agents. A 1.0 percent solution of methyl α-(2-benzothiazolylmercapto)-aceto-acetate was added to the emulsion as an antifoggant. The emulsion samples weighed one kilogram and contained about 0.4 mol of silver halide. The gelatin strength was on the order of 60 grams per kilogram of liquid emulsions. The so prepared emulsion samples were coated on a suitable cellulose ester base and dried. Samples of these film coatings were then exposed in a Type IIB Sensitometer and developed in a developer of the following composition:

	Grams
Metol (p-methylaminophenol sulfate)	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	0.8
Water to make 1 liter.	

Quantity of Compound added	Relative Speed	Fog at 12′ Development	Speed after Oven test	(6 days at 50° C.) Oven fog at 6′ Development
0	100	.23	100	.15
25 mg	100	.19	105	.11

The methyl α-(2-benzothiazolylmercapto)-acetoacetate was prepared as follows:

A solution of potassium 2-mercaptobenzothiazole was prepared by mixing 25 grams of 2-mercaptobenzthiazole with 8.4 grams of potassium hydroxide in 50 milliliters of acetone and 6 milliliters of water. 21 grams of methyl α-chloroacetoacetate were added at room temperature under stirring. The reaction was exothermic, the temperature rising to 50° C. in five minutes. The reaction mixture was then reacted on a steam bath for four hours with stirring. The potassium chloride was removed by filtration and the acetone removed by vacuum distillation. The solid residue was washed with water and crystallized from ethanol. The yield was 14 grams. The melting point of the compound was 104–105° C.

Example II

The procedure was the same as in Example I excepting that the methyl α-(2-benzothiazolylmercapto)-acetoacetate was replaced by an equivalent quantity of methyl α-(2-benzimidazolylmercapto)-acetoacetate. Results similar to those obtained in Example I were secured in this instance. This compound was prepared according to the procedure described in Example I, using 25 grams of 2-mercaptobenzoimidazole in place of 25 grams of 2-mercaptobenzothiazole. The yield was 16 grams; the melting point was 150° C.

Example III

The procedure was the same as in Example I except that the methyl α-(2-benzothiazolylmercapto)-acetoacetate was replaced by an equivalent quantity of 3-(2-benzothiazolylmercapto)-2,4-pentanedione, prepared according to the procedure described in Example 4 of United States Patent 2,772,277.

The results were similar to those of Example I.

Example IV

A gelatino silver halide emulsion containing 64 percent of silver bromide and 36 percent of silver chloride and also containing 50 milligrams of ethyl α-(2-benzothiazolylmercapto)-acetoacetate per liter was coated on film-base in a manner known to the art. After the coating was performed, a silver halide emulsion in gelatin containing 4 percent silver iodide and 96 percent of silver bromide was coated on top of the previously coated emulsion, commonly called the undercoating. After drying, film samples were exposed and processed as described in Example III. The samples exhibited a relative speed of 100 and a fog of 0.15 compared with a type coating of the same emulsion having an undercoating similar to that described above, but lacking the antifoggant and having a speed of 100 and a fog of 0.25.

Example V

The procedure was the same as in Example IV excepting that the lower silver chlorobromide emulsion layer was replaced by a plain gelatin layer prepared from a gelatin solution containing 200 milligrams of ethyl α(2-benzoxazolylmercapto)-acetoacetate and 30 grams of gelatin per liter. The results were similar to those obtained in Example IV. This compound was prepared by reacting 25 grams of 2-mercaptobenzoxazole with 21 grams of ethyl α-chloroacetoacetate following the procedure described in Example I.

Example VI

Exposed samples of a photographic film were developed for twelve minutes at 65° F. in a standard metol-hydroquinone developer. Two tests were made, one with the normal developing solution and one with a developer containing 100 milligrams of methyl α-(2-benzothiazolyl-mercapto)-acetoacetate per liter of developer. Sensitometric strips, developed in the normal developer (control) for twelve minutes, showed a fog of .30 whereas those strips which were developed in the developer containing the antifoggant had a fog of .24.

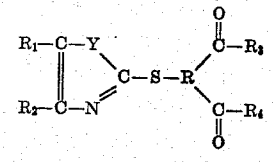
Example VII

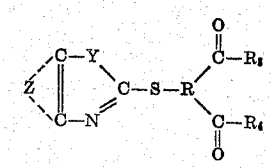
Example VI was repeated except that 100 milligrams of methyl α-(2-benzimidazolylmercapto)-acetoacetate were used in place of 100 milligrams of methyl α-(2-benzothiazolylmercapto)-acetoacetate. The results were similar to those obtained in Example VI.

Various modifications of the invention will occur to persons skilled in the art. Thus, it is understood that in lieu of using the particular antifoggants of the examples, any of the antifoggants listed in the application may be employed with equivalent results. We, therefore, do not intend to be limited in the patent granted except as necessitated by the prior art and the appended claims.

We claim:

1. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion, said light-sensitive material containing as an antifoggant, in an antifogging amount, a compound selected from the group consisting of those having the following formulae:





wherein R is an alkylene group of less than three carbon atoms; R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, acyl and carboxyalkoxy radicals; R_3 and R_4 are members selected from the group consisting of alkyl and alkoxy radicals, Y is a member selected

from the group consisting of imino radicals and oxygen, selenium and sulfur atoms and Z represents the atoms necessary to complete a fused-on aromatic ring system selected from the class consisting of benzo and naphtho rings.

2. The article as defined in claim 1 wherein the antifoggant is located in the silver halide emulsion.

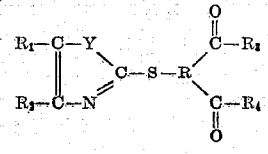
3. The article as defined in claim 1 wherein the antifoggant is located in a layer adjacent to said silver halide emulsion layer.

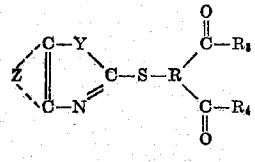
4. A light-sensitive photographic material comprising a base with a light-sensitive silver halide emulsion thereon, said emulsion containing as an antifoggant the compound methyl α-(2-benzothiazolymercapto)-acetoacetate.

5. A light-sensitive photographic material comprising a base with a light-sensitive silver halide emulsion thereon, said emulsion containing as an antifoggant the compound methyl α-(2-benzimidazolymercapto)-acetoacetate.

6. A light-sensitive photographic material comprising a base with a light-sensitive silver halide emulsion thereon, said emulsion containing as an antifoggant the compound 3-(2-benzothiazolylmercapto)-2,4-pentanedione.

7. The process of minimizing and preventing fog in light-sensitive silver halide materials comprising a base having a light-sensitive silver halide emulsion thereon, which comprises exposing said emulsion to light and developing the same in the presence of an antifoggant in an antifogging amount, selected from the class consisting of those having the following formulae:





wherein R is an alkylene group of less than three carbon atoms; R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, acyl and carboxyalkoxy radicals; R_3 and R_4 are members selected from the group consisting of alkyl and alkoxy radicals; Y is a member selected from the group consisting of imino radicals and oxygen, selenium and sulfur atoms and Z represents the atoms necessary to complete a fused-on aromatic ring system selected from the class consisting of benzo and naphtho rings.

8. The process as defined in claim 7 wherein the antifoggant is methyl α-(2-benzothiazolylmercapto)-acetoacetate.

9. The process as defined in claim 7 wherein the antifoggant is methyl α-(2-benzimidazolylmercapto)-acetoacetate.

10. The process as defined in claim 7 wherein the antifoggant is 3-(2-benzothiazolylmercapto)-2,4-pentanedione.

11. A light sensitive photographic material as defined by claim 2 wherein the amount of antifoggant ranges from 2.5 to 25 milligrams per mole of silver halide.

12. A light sensitive photographic material as defined by claim 3 wherein the amount of antifoggant ranges from 25 to 375 milligrams per mole of silver halide.

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