

1

2

3,161,520
**FOG REDUCTION IN PHOTOGRAPHIC SILVER
 HALIDE EMULSIONS**

Emil B. Rauch, Port Dickinson, and Fritz Dersch, Binghampton, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Dec. 11, 1962, Ser. No. 243,745
 15 Claims. (Cl. 96-109)

This invention relates to photographic materials and to methods of preparing them. More particularly, this invention relates to light-sensitive silver halide emulsions containing as a stabilizing and antifogging agent a 3-hydroxymethylazolethione.

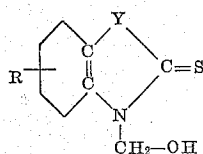
It is well known in the photographic art that light-sensitive emulsions, such as gelatino-silver halide emulsions, have a tendency to fog. Fog is usually caused by a prolonged ripening of the emulsion, by prolonged storage especially at elevated temperatures and humidity, and by prolonged development. To overcome this undesirable property, it has been the practice in this art to add certain chemical compounds to the emulsions to increase their stability and to reduce their tendency to fog. However, the stabilizing and antifogging compounds heretofore used in this art have the disadvantage that upon addition to the emulsion they cause a loss of speed and/or contrast of the emulsion.

It is, accordingly, an object of this invention to produce a light-sensitive emulsion which is fast, stable, has a reduced tendency to fog and has good contrast.

A further object of this invention resides in a light-sensitive emulsion which contains a compound which stabilizes the emulsion against fogging and at the same time does not materially reduce the speed and/or the contrast of the emulsion.

We have discovered that 3-hydroxymethylazolethiones when added to a light-sensitive silver halide emulsion, stabilize and inhibit the fogging of the emulsion.

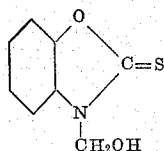
The azolethiones, the use of which is contemplated herein, may be represented by the following formula:



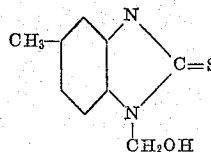
wherein R is a hydrogen atom, a halide atom, e.g., chlorine or bromine; a lower alkyl radical, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl; a carboxy group; a lower alkoxy group, e.g., methoxy, ethoxy, propoxy; and Y is an oxygen or sulfur atom.

The following specific compounds are examples of compounds belonging to the class of compounds having the general formula given above which we have found suitable for use as stabilizing and antifogging agents:

3-hydroxymethyl-benzoxazole-2-thione



3-hydroxymethyl-6-methylbenzoxazole-2-thione



3-hydroxymethyl-5-methoxy-benzoxazole-2-thione

3-hydroxymethyl-5-chloro-benzoxazole-2-thione

3-hydroxymethyl-5-methyl-benzothiazole-2-thione

3-hydroxymethyl-6-methyl-benzothiazole-2-thione

3-hydroxymethyl-7-methyl-benzothiazole-2-thione

3-hydroxymethyl-6-tert.butyl-benzothiazole-2-thione

3-hydroxymethyl-5-chloro-benzothiazole-2-thione

3-hydroxymethyl-6-chloro-benzothiazole-2-thione

3-hydroxymethyl-5-bromo-benzothiazole-2-thione

3-hydroxymethyl-6-bromo-benzothiazole-2-thione

3-hydroxymethyl-4,6-dimethyl-benzothiazole-2-thione

3-hydroxymethyl-4,6-dimethyl-7-chloro-benzothiazole-2-thione

3-hydroxymethyl-4-methyl-6-chloro-benzothiazole-2-thione

4,6-dimethyl-5,7-dichloro-benzothiazole-2-thione

3-hydroxymethyl-5-chlorobenzoxazole-2-thione

3-hydroxymethyl-5-methoxybenzoxazole-2-thione

3-hydroxymethyl-5-methylbenzoxazole-2-thione

These compounds are prepared by reacting a 2-mercapto-substituted azole of the benzoxazole and benzothiazole series with formaldehyde in the presence of a suitable solvent such as methanol, ethanol, isopropanol and the like. The preparation of these compounds is described in more detail in *Berichte*, vol. 90, page 2246, and *Journal of the Chemical Society*, 1948, page 1717.

As representatives of azoles used in the reaction, the following are mentioned:

2-mercaptobenzothiazole

5-methyl-2-mercaptobenzothiazole

6-methyl-2-mercaptobenzothiazole

7-methyl-2-mercaptobenzothiazole

6-tert.butyl-2-mercaptobenzothiazole

5-methoxy-2-mercaptobenzothiazole

5-chloro-2-mercaptobenzothiazole

5-bromo-2-mercaptobenzothiazole

6-chloro-2-mercaptobenzothiazole

6-bromo-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

2-mercaptobenzoxazole

2-mercapto-5-chlorobenzoxazole

2-mercapto-5-methoxybenzoxazole

2-mercapto-5-methylbenzoxazole

The antifogging agents of our invention may be added to the emulsion at any stage during its process of production. Thus, they may be added as a "ripening final" or as a "coating final." When added as a "ripening final," they are added during the ripening or sensitivity increasing stage of the emulsion making process. Such addition may be made before, during or after the addition of the soluble silver salt to the soluble halide in the presence of a suitable colloid, such as gelatin, polyvinyl alcohol, solubilized casein or albumin. When added as a "coating final," the antifogging agent of our invention is added to the emulsion just prior to coating it on a suitable support such as glass, paper, or film at a time when the emulsion has nearly attained its maximum sensitivity.

In some instances, it is advantageous to apply the antifogging and stabilizing compounds of our invention in a separate layer such as an undercoating layer or in an anti-abrasion gelatin surface. Sometimes it is desirable to incorporate the compounds in one or all processing baths or in the pre- and post-baths.

When used as a "ripening final," the antifogants of our invention are preferably added to the emulsion in an amount ranging from 0.1 milligram to 20 milligrams per 0.6 mol of silver halide and when used as a "coating final," it is preferably added in an amount ranging from 0.5 milligram to 50 milligrams per 0.6 mol of silver halide. The optimum amount to be added depends primarily on the type of emulsion and should be determined individually in each case.

The stabilizers and antifogants of our invention may also be used in combination with known antifogants and stabilizers. The antifogants of our invention can also be used in combination with sensitizers such as sulfur, metal and reduction sensitizers as well as with speed-increasing agents and accelerators such as the reaction products of long-chain alcohols and ethylene oxide (see U.S.P. 1,970,578) and their derivatives and polyvinylpyrrolidone.

The novel antifogants of our invention may be used with various types of photographic emulsions, such as non-sensitized orthochromatic, panchromatic and X-ray emulsions, paper emulsions and color emulsions.

The following specific examples are given as an illustration of the manner in which the antifogants of our invention can be used. It is to be understood, however, that these examples are given by way of illustration and not by way of limitation.

Example I

A silver halide emulsion in gelatin containing 2 percent silver iodide and 98 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 and hardening agents. A 0.1 percent solution of 3-hydroxymethylbenzothiazole-2-thione prepared according to the method described in the Journal of the Chemical Society, 1948, page 1717, was added in varying amounts to samples of the emulsion as an antifogant and stabilizer. Each emulsion sample contained about 0.6 mol of silver halide. 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 |
|---------------------------------------|-------|
| Metal | 1.5 |
| Sodium sulfite (anhydrous) | 45 |
| Sodium bisulfite | 1 |
| Hydroquinone | 6 |
| Sodium carbonate (monohydrated) | .8 |
| Water to make 1 liter. | |

The developed samples were short-stopped, fixed, washed and dried. The results obtained were as follows:

| Quantity of Compound Used | Relative Speed | Fog at 12' Development | Oven Fog at 6' Development |
|---------------------------|----------------|------------------------|----------------------------|
| 0 | 100 | .36 | .20 |
| 1 mg | 100 | .28 | .18 |
| 2.5 mg | 100 | .26 | .17 |
| 5 mg | 95 | .24 | .16 |

Example II

The procedure followed was identical to Example I, except that in place of 3-hydroxymethylbenzothiazole-2-thione the compound used was 3-hydroxymethylbenzoxazole-2-thione prepared according to the method described in Berichte, vol. 90, page 2250.

The results obtained were as follows:

| Quantity of Compound Used | Relative Speed | Fog at 12' Development | Oven Fog at 6' Development |
|---------------------------|----------------|------------------------|----------------------------|
| 0 | 100 | .36 | .20 |
| 1 mg | 100 | .27 | .17 |
| 2.5 mg | 100 | .26 | .16 |
| 5 mg | 95 | .25 | .15 |

Example III

The procedure followed was identified to Example I, but in place of 3-hydroxymethylbenzothiazole-2-thione, the compound used was 5-chloro-3-hydroxymethylbenzothiazole-2-thione which had been prepared in analogy to the method described in J.C.S., 1948, 1717, except that 5-chloro-2-mercaptobenzothiazole was used as the starting material in place of 2-mercaptobenzothiazole.

The results obtained were as follows:

| Quantity of Compound Used | Relative Speed | Fog at 12' Development | Oven Fog at 6' Development |
|---------------------------|----------------|------------------------|----------------------------|
| 0 | 100 | .20 | .23 |
| 5 mg | 100 | .25 | .21 |
| 10 mg | 100 | .23 | .18 |

Example IV

Example I was repeated except that 6-methyl-3-hydroxymethylbenzothiazole-2-thione was used in place of 3-hydroxymethylbenzothiazole-2-thione. The results obtained were essentially the same as those reported in Example I.

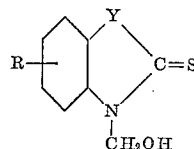
The synthesis of this compound was carried out in analogy to the process described in J.C.S., 1948, 1717, except that 6-methyl-2-mercaptobenzothiazole was used as the starting material in place of 2-mercaptobenzothiazole.

Our invention is not limited to the detailed description contained herein, but includes all modifications that fall within the scope of the appended claims.

This application is a continuation-in-part of our co-pending application Serial No. 765,339, filed October 6, 1958, now U.S. Patent 3,081,170.

What we claim is:

1. A light-sensitive silver halide emulsion containing as an antifogant a compound selected from the group of those having the following general chemical formula:



wherein R is selected from the group consisting of hydrogen, halogen, lower alkyl, lower alkoxy and carboxy; and Y is a member selected from the group consisting of oxygen and sulfur.

2. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifogant is 3-hydroxymethylbenzothiazole-2-thione.

3. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifogant is 3-hydroxymethylbenzoxazole-2-thione.

4. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifogant is 5-chloro-3-hydroxymethylbenzothiazole-2-thione.

5. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifogant is 6-methyl-3-hydroxymethylbenzoxazole-2-thione.

6. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifogant is 5-chloro-3-hydroxymethylbenzoxazole-2-thione.

5

7. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifoggant is present in the emulsion in the ratio of 0.1 to 50 milligrams per 0.6 mol of silver halide.

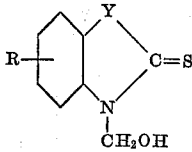
8. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifoggant is present in the emulsion in the ratio of 0.1 to 20 milligrams per 0.6 mol of silver halide.

9. A light-sensitive silver halide emulsion as recited in claim 1, wherein the antifoggant is present in the emulsion in the ratio of 0.5 to 50 milligrams per 0.6 mol of silver halide.

10. A light-sensitive silver halide emulsion as recited in claim 1, wherein said emulsion is a panchromatic emulsion.

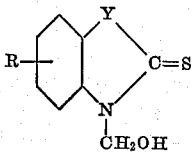
11. A light-sensitive silver halide emulsion as recited in claim 1, containing the reaction product of a long chain alcohol and ethylene oxide as an accelerator.

12. A light-sensitive photographic element comprising a base and a coating of gelatino-silver halide emulsion thereon, said emulsion containing as an antifogging and stabilizing agent, a compound selected from the group having the following formula:



wherein R is selected from the group consisting of hydrogen, halogen, lower alkyl, lower alkoxy; and Y is a member selected from the group consisting of oxygen and sulfur.

13. A light-sensitive structure comprising a base, a layer of light-sensitive silver halide emulsion thereon, and a separate layer adjacent said first-mentioned layer containing as an antifogging and stabilizing agent compound, a compound selected from the group having the following general chemical structure:

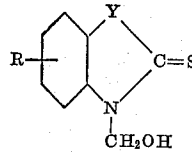


wherein R is selected from the group consisting of hydro-

6

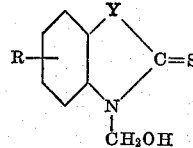
gen, halogen, lower alkyl, lower alkoxy and carboxy-alkoxy; and Y is a member selected from the group consisting of oxygen and sulfur.

14. A process of forming a photographic silver halide emulsion having a reduced tendency to fog which comprises forming the emulsion, ripening the emulsion and during said ripening adding thereto a compound selected from the group having the following general formula:



wherein R is selected from the group consisting of hydrogen, halogen, lower alkyl, lower alkoxy and carboxy and Y is a member selected from the group consisting of oxygen and sulfur.

15. A process of forming a light-sensitive photographic element having a reduced tendency to fog which comprises forming a silver halide emulsion, ripening said emulsion, coating said emulsion on a base and adding to said emulsion just prior to the coating thereof on the base a compound selected from the group having the following general formula:



wherein R is selected from the group consisting of hydrogen, halogen, lower alkoxy and carboxy; and Y is a member selected from the group consisting of oxygen and sulfur.

References Cited in the file of this patent

UNITED STATES PATENTS

| | | |
|-----------|--------------------|---------------|
| 2,870,015 | Allen et al. _____ | Jan. 20, 1959 |
| 3,026,201 | Rauch et al. _____ | Mar. 20, 1962 |