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2,935,404

FOG REDUCTION IN PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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10 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 bis-(s-triazolopyrimidine) disulfides for such purpose.

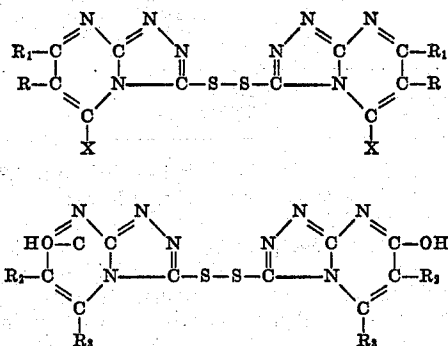
It is recognized that light sensitive emulsions such as gelatino silver halide emulsions have a tendency to fog. The fog may be caused in a number of ways as, for example, by excessive ripening of the emulsion, by storage of the light sensitive element at elevated temperatures and humidity or by prolonged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

I have now found that the bis-(s-thiazolo [4,3-a] pyrimidine) disulfides are excellent stabilizers and antifogants 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 bis-(s-triazolo[4,3-a]pyrimidine)disulfides, the use of which is contemplated herein, may be represented by the following formulae:

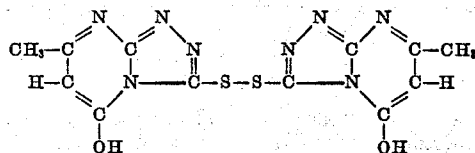


wherein R is hydrogen, alkyl, e.g., methyl, ethyl, propyl, isopropyl, butyl, amyl and the like; alicyclic, e.g., cyclopentyl, cyclohexyl and the like; aryl, e.g., phenyl, naphthyl, diphenyl and the like; or a heterocyclic radical, e.g., pyridyl, furyl, pyrrol, pyrazolyl and R1 is amino, hydroxy, carbalkoxy, e.g., carbethoxy, carbopropoxy and the like; or an alkyl, alicyclic, aryl or heterocyclic radi-

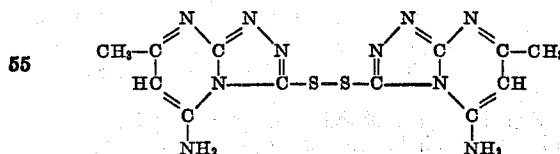
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cal of the same value as R; and R and R1 together represent the atoms necessary to complete a 5-membered or 6-membered alicyclic or heterocyclic ring structure, e.g., cyclopentyl, cyclohexyl and the like; aryl e.g., phenyl, naphthyl, diphenyl; pyridyl, furyl, pyrrol, pyrazolyl and the like. R2 is hydrogen or a carbalkoxy group e.g., carbomethoxy, carbethoxy, carbopropoxy group and R3 is either hydrogen, methyl or phenyl and X is an amino or hydroxy group.

The general formula assigned to these products is based on the findings of E. J. Birr and W. Walther published in *Chemische Berichte*, volume 86, pages 1401-3 (1953). However, it is to be understood that the compounds employed in the present invention are compounds obtained by the processes outlined below, whatever their chemical structure may ultimately prove to be. Examples of compounds falling within the ambit of such general formula which we have found to be effective are:



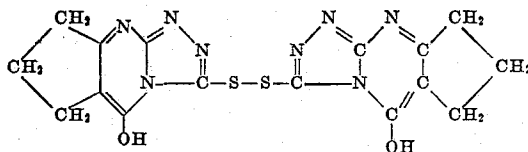
- bis-(4 - hydroxy - 6 - methyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis - (4 - hydroxy - 6 - phenyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis - (4 - 6 - dihydroxy - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis - (4 - hydroxy - 6 - amino - s - triazolo[4,3 - a]pyrimidine)sulfide
- bis - (4 - hydroxy - 6 - carbethoxy - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis - (4 - hydroxy - 6 - (β - pyridyl) - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - hydroxy - 6 - cyclohexyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - hydroxy - 5 - cyclohexyl - 6 - methyl - s - triazolo[4,3-a]pyrimidine)disulfide
- bis(4 - hydroxy - 5 - (α - furyl) - 6 - methyl - s - triazolo[4,3-a]pyrimidine)disulfide
- bis(4 - hydroxy - 5 - phenyl - 6 - methyl - s - triazolo[4,3-a]pyrimidine)disulfide
- bis(4 - hydroxy - 6 - (α - furyl) - s - triazolo[4,3-a]pyrimidine)disulfide
- bis(4 - hydroxy - 6 - benzyl - s - triazolo[4,3 - a]pyrimidine)disulfide



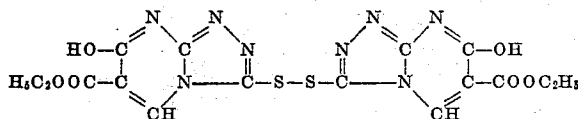
- bis(4 - amino - 6 - methyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - amino - 6 - phenyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - amino - 5 - ethyl - 6 - methyl - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - amino - 6 - phenyl - 5 - methyl - s - triazolo[4,3-a]pyrimidine)disulfide
- bis(4 - amino - 6 - (β - pyridyl) - s - triazolo[4,3 - a]pyrimidine)disulfide
- bis(4 - amino - 6 - cyclohexyl - s - triazolo[4,3 - a]pyrimidine)disulfide

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bis(4 - amino - 5 - cyclohexyl - 6 - methyl - s - triazolo [4,3-a]pyrimidine)disulfide



bis(4 - hydroxy - 5,6 - cyclopentano - s - triazolo[4,3-a] pyrimidine)disulfide
bis(4 - amino - 5,6 - cyclohexano - s - triazolo[4,3-a] pyrimidine)disulfide



bis(6 - hydroxy - 4 - carbethoxy - s - triazolo[4,3-a] pyrimidine)disulfide

bis(6-hydroxy-s-triazolo[4,3-a]pyrimidine)disulfide
bis(6 - hydroxy - 4 - phenyl - 5 - carbethoxy - s - triazolo[4,3-a]pyrimidine)-disulfide
bis(6 - hydroxy - 4 - methyl - 5 - carbomethoxy - s - triazolo[4,3-a] pyrimidine)-disulfide

The above compounds are best prepared by oxidizing the 3-mercapto-s-triazolo[4,3-a]pyrimidine derivative in aqueous solution and in a mildly alkaline medium (pH=8.0-9.0) with a mild oxidizing agent such as hydrogen peroxide or sodium or potassium persulfate. The 3-mercapto-s-triazolo pyrimidines are prepared by reacting 5-amino-3-mercapto-4,1,2-triazole with a β -keto ester, a malonic ester or a nitrile of a malonic ester as illustrated by United States Patent 2,444,605; with a β -immonitrile or a β -ketonitrile as illustrated by United States Patent 2,444,606; with a cyclic β -keto ester or a cyclic β -ketonitrile as illustrated by United States Patent 2,444,607; or with an alkoxymethylene malonic acid ester as illustrated by United States Patent 2,450,397. In general, the 2-mercapto-s-triazolo[4,3-a]pyrimidine is obtained by heating the mercapto-amino-triazole with the ester or nitrile in glacial acetic acid under reflux conditions as described in the foregoing patents. In some instances, the reaction can be carried out in the absence of the solvent by employing somewhat higher temperatures than those required when a solvent is used.

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 0.4 to 6.5 milligrams per mol of silver halide and when used as coating finals in a concentration 6 to 50 milligrams per mol of silver halide. 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

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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, boiltype 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).

The mercaptotriazolopyrimidines from which my stabilizers are prepared have previously been recommended as emulsion additives. However, these mercaptotriazolopyrimidines have the inherent disadvantage of many other mercapto type stabilizers: They reduce fog at the sacrifice of speed and contrast. 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 my 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 1

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 and finals were added such as sensitizing dyes, stabilizers and hardening agents. A 1 percent solution of bis-3(4-hydroxy - 6 - methyl - s - triazolo[4,3 - a]pyrimidine)-disulfide was added to the emulsion as an antifoggant. The emulsion samples weighed one kilogram and contained about 0.4 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 having 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	.22	95	.34
5.0-----	100	.16	105	.16

The bis - 3(4 - hydroxy - 6 - methyl - s - triazolo[4,3 - a]pyrimidine)disulfide was prepared as follows:

Four grams of 5 - amino - 3 - mercapto - 4,1,2 - triazole (Berichte, volume 54, page 2099) and 10 milliliters of ethyl acetoacetate were heated in 60 milliliters of glacial acetic acid under reflux for 9 hours. The 3-mercapto-4 - hydroxy - 6 - methyl - s - triazolo[4,3 - a]pyrimidine precipitated on cooling. The product melted at 281° C. after recrystallization.

Four grams of the mercapto compound were dissolved in 60 milliliters of water which had been made slightly alkaline by the addition of 1.0 gram of sodium hydroxide. A solution of potassium persulfate ($K_2S_2O_8$) in 150 milliliters of water was added drop-wise during 25 minutes. The temperature rose to 27° C. at the start. The yellowish-white precipitate which was formed was filtered (yield

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3.76 g.). It was dissolved in aqueous sodium hydroxide and the resultant solution was treated with charcoal and filtered. Upon adding acetic acid to the filtrate, a white crystalline material was obtained, which melted at 290° C. under decomposition.

Example II

The procedure was the same as in Example I excepting that the bis-3-(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide was replaced by an equivalent quantity of bis-3-(4,6-dihydroxy-s-triazolo[4,3-a]pyrimidine)-disulfide. Results similar to those obtained in Example I were secured in this instance.

This compound was prepared by reacting 1 mol of 5-amino-3-mercapto-4,1,2-triazole with 1 mol of ethyl malonate in a solution of glacial acetic acid, and oxidizing the resultant 3-mercapto-4,6-dihydroxy-4,1,2-triazolo[4,3-a]pyrimidine with potassium persulfate as described in Example I.

Example III

The procedure was the same as in Example I except that the bis-3-(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide was replaced by an equivalent quantity of bis-3-(4-amino-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide. The results were similar to these of Example I. This compound was prepared by reacting 1 mol of 5-amino-3-mercapto-4,1,2-triazole with 1 mol of acetoacetonitrile in boiling glacial acetic acid. The resultant mercaptotriazolopyrimidine was then oxidized with potassium persulfate as described in Example I.

Example IV

A solution containing 30 grams of gelatin and 100 mg. of bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide per liter of water was coated on a subbed film-base in a manner known to the art. After 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 applied gelatin layer. After drying, film samples were exposed and processed as described in Example I. The samples exhibited a relative speed of 100 and a fog of 0.12 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 0.20.

Example V

The procedure was the same as in Example IV excepting that the bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide was replaced by an equivalent quantity of bis(4,6-dihydroxy-s-triazolo[4,3-a]pyrimidine)-disulfide. The results were similar to those obtained in Example IV.

Example VI

The antifogging action of bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide was compared with that of 4-hydroxy-6-methyl-3-mercapto-s-triazolo[4,3-a]pyrimidine. The following results were obtained.

Quantity of Compound	Compound (type)	Relative Speed after 6 Day Oven Test at 50° C.	Oven Fog at 6' Development
0.0.....		100	0.48
1.0 mg.....	disulfide.....	100	0.38
2.5 mg.....	disulfide.....	100	0.35
1.0 mg.....	mercapto.....	88	0.40
2.5 mg.....	mercapto.....	85	0.35

It is evident from this table that the bis(triazolopyrimidine)-disulfide reduces the fog without loss of speed to a greater extent than mercapto triazolo pyrimidine which, in addition to its poorer antifogging performance, causes serious loss of speed.

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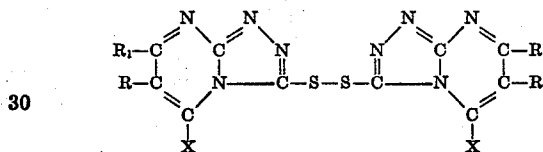
Example VII

Exposed samples of a photographic film were developed for twelve minutes at 65° C. in a standard metol-hydroquinone developer. Two tests were made, one with the normal developing solution and one with a developer containing 20 mgs. of bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide per liter of developer. Sensitometric strips, developed in the normal developer (control) for twelve minutes, showed a fog of .28 whereas those strips which were developed in the developer containing the antifoggant had a fog of .20.

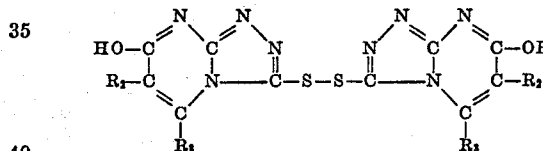
Various modifications of the invention will occur to persons skilled in the art. Thus, it is understood that in lieu of using the particular antifoggants of the examples, any of the antifoggants listed in the application may be employed with equivalent results. I, therefore, do not intend to be limited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

I 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 a compound selected from the group consisting of those having the following formulae:



and



wherein R is a member selected from the class consisting of hydrogen, alkyl, alicyclic, aryl, pyridyl and furyl groups, R₁ is a member selected from the class consisting of amino, hydroxy, carbalkoxy, alkyl, alicyclic, aryl, pyridyl and furyl groups, R₂ is a member selected from the class consisting of hydrogen and carbalkoxy groups, R₃ is a member of the class consisting of hydrogen, methyl and phenyl groups, and X is a member selected from the class consisting of amino and hydroxy groups.

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 halide emulsion thereon, said emulsion containing as an antifoggant the compound, bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide.

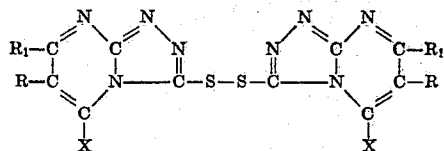
5. A light sensitive photographic material comprising a base with a light sensitive silver halide emulsion thereon, said emulsion containing as an antifoggant the compound, bis(4,6-dihydroxy-s-triazolo[4,3-a]pyrimidine)-disulfide.

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, bis(4-amino-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide.

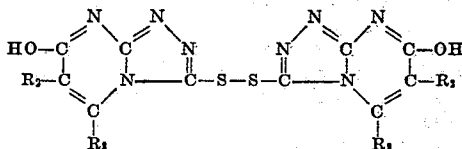
7. The process of minimizing and preventing fog in light sensitive silver halide materials comprising a base having a light sensitive silver halide emulsion thereon, which comprises exposing said emulsion to light and developing the same in the presence of an antifoggant and

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stabilizer selected from the class consisting of those having the following formulae:



and



wherein R is a member selected from the class consisting of hydrogen, alkyl, alicyclic, aryl, pyridyl and furyl groups, R₁ is a member selected from the class consisting of amino, hydroxy, carbalkoxy, alkyl, alicyclic, aryl, pyri-

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dyl and furyl groups, R₂ is a member selected from the class consisting of hydrogen and carbalkoxy groups, R₃ is a member of the class consisting of hydrogen, methyl and phenyl groups, and X is a member selected from the class consisting of amino and hydroxy groups.

5 The process as defined in claim 7 wherein the anti-foggant is bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide.

8. The process as defined in claim 7 wherein the anti-foggant is bis(4-hydroxy-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide.

9. The process as defined in claim 7 wherein the anti-foggant is bis(4,6-dihydroxy-s-triazolo[4,3-a]pyrimidine)-disulfide.

10. The process as defined in claim 7 wherein the anti-foggant is bis(4-amino-6-methyl-s-triazolo[4,3-a]pyrimidine)-disulfide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

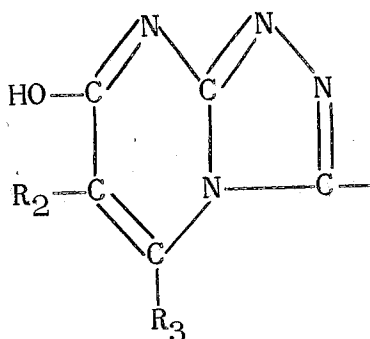
Patent No. 2,935,404

May 3, 1960

Fritz H. Dersch

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 58 to 64, the left-hand portion of the formula should appear as shown below instead of as in the patent:



Signed and sealed this 18th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents