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PHOTOGRAPHIC MATERIALS AND METHOD OF PRODUCING THE SAME

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11 Claims. (Cl. 96—66)

The present invention relates to antifogging and stabilizing agents for photographic silver halide emulsions and, more particularly, to light-sensitive silver halide materials containing as a stabilizing and antifogging agent a triazine each carbon atom of which is substituted by a heterocyclic thioether group.

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 emulsions, 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, all stabilizing and antifogging compounds heretofore used in this art have the disadvantage that upon addition to the emulsion thy cause a loss of speed and/or contrast of the emulsion.

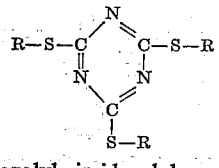
It is, accordingly, an object of this invention to produce a light-sensitive emulsion which is fast, stable, has a reduced tendency to fog and has good contrast.

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 contrast of the emulsion.

A still further object of this invention is to provide a light-sensitive emulsion containing a compound which stabilizes the emulsion against fogging and at the same time does not appreciably reduce the sensitivity to light of longer wave length effectd by the presence of sensitizing dyes.

Other objects and advantages of this invention will appear to those skilled in the art from the detailed description thereof given below.

The stabilizers and antifoggants contemplated for use herein may be typified by the following structural formula:



in which R is thiazolyl, imidazolyl, oxazolyl, benzothiazolyl, benzimidazolyl or benzoxazolyl.

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, solubilizd 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 antiabrasion 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 antifoggants of our invention are preferably added to the emulsion in an amount ranging from 1 milligram to 25 milligrams per 0.6 mol of silver halide and when used as a "coating final" they are preferably added in an amount ranging from 10 milligrams to 300 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 antifoggants of our invention may also be used in combination with known antifoggants and stabilizers. The antifoggants of our invntion can also be used in combination with sensitizers such as sulfur, metal and reduction sensitizers as well as with accelerators such as the polyoxyethylenes (see U.S.P. 1,970,578) and their derivatives and polyvinyl-pyrrolidone.

The novl antifoggants 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 antifoggants and stabilizers of the present invention are prepared by the dropwise addition to an organic solvent solution of cyanuric chloride of a 2-mercapto-benzothiazole, -benzimidazole, -benzoxazole, -thiazole, -imidazole or -oxazole while the latter is dissolved in an aqueous low boiling organic solvent such as acetone, butyl acetate or the like in the presence of an acid binding agent such as potassium hydroxide, sodium hydroxide, sodium carbonate or the like. After commingling the reactants, the mixture is stirred at a temperature of from 50–80° C. and then chilled and filtered. The resulting solid may be purified by washing with acetone and recrystallized from benzene.

The following examples illustrate a method of preparing one of the compounds falling under the general formula given above and the manner of using the compound in conjunction with light-sensitive photographic silver halide emulsion. It is to be understood, however, that these examples are given by way of illustration only and not by way of limitation.

Example I

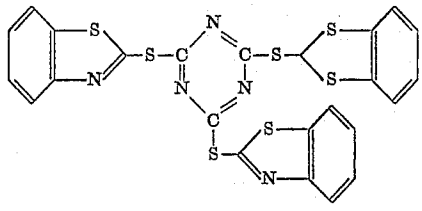
A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was prepared in a conventional manner and brought up to its maximum light sensitivity. It was then readied for coating, finals were added such as sensitizing dyes and hardening agents. A 1% solution of 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine was prepared and added in varying amounts to samples of the emulsion as an antifoggant 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
p-(n-methyloamino)phenol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	,8
Water to make liter.	1

The results obtained were as follows:

Quantity of Compound Used, mg.	Relative Speed	Fog at 12'	Oven Fog at 6' Development
0	105	0.42	0.76
2.5	100	.37	.51
5.0	100	.36	.51
10.0	100	.25	.38

The compound 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine used above has the following chemical structure:



The method used by us in preparing this compound is as follows:

To a stirred solution containing 8.4 grams of (.05 mol) 2-mercaptobenzothiazole, 150 ml. of acetone, 8 ml. of H_2O, and 3.3 grams of potassium hydroxide (.05 mol) was added dropwise a solution containing 3.1 gram (.017 mol) of cyanuric chloride in 100 ml. of acetone. The addition was carried out at room temperature. The stirred reaction mixture was heated to 60° C. for 5 hours, and then chilled and filtered. The solid was washed with 20 ml. of acetone, then with water until free of the inorganic salts. After crystallization from benzene, the pale yellow product melted at 210–211° C. (uncorrected). Yield—5 grams. Calcd. for $C_{24}H_{12}N_6S_6$.

N: calcd., 14.58%; found, 14.53%
S: calcd., 33.33%; found, 33.14%

Example II

Exposed samples of a photographic film were developed for twelve minutes at 65° F. in a standard p-(N-methylamino)phenol hydroquinone developer. Two tests were made, one with the normal developing solution and one with a developer containing 100 mgs. of 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine per one 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 .20.

Example III

The procedure is the same as in Example I excepting that the antifoggant and stabilizer is 2,4,6-tri (benzoxazolyl-2-thio)-S-triazine. The results obtained with this compound are similar to those of Example I.

This compound is prepared by the same method as that used in Example I excepting that the 2-mercaptobenzothiazole is replaced by .05 mol of 2-mercaptobenzoxazole.

Example IV

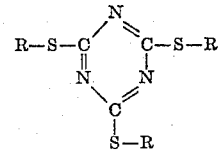
The procedure is the same as in Example II excepting that the antifoggant and stabilizer employed is 2,4,6-tri (imidazolyl-2-thio)-S-triazine or 2,4,6-tri (thiazolyl-2-thio)-S-triazine.

These compounds are prepared in the same manner as the compound of Example I, excepting that 2-mercaptoimidazole or 2-mercapto-thiazole is used in lieu of the 2-mercapto-benzothiazole.

Modifications of the invention will occur to persons skilled in the art. We, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims.

We claim:

1. A light-sensitive material comprising a base and a light-sensitive silver halide emulsion thereon, said material containing an antifoggant and stabilizing compound having the following chemical formula:



wherein R is selected from the group consisting of thiazolyl, imidazolyl, oxazolyl, benzothiazolyl, benzimidazolyl and benzoxazolyl.

2. A light-sensitive silver halide emulsion containing 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine as an antifoggant and stabilizer.

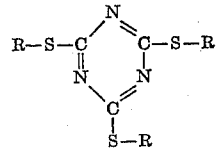
3. A light-sensitive silver halide material as recited in claim 1 wherein the antifoggant and stabilizing compound is present in the emulsion and in the ratio of 1 to 300 milligrams per 0.6 mol of silver halide.

4. A light-sensitive silver halide emulsion as recited in claim 2 wherein the antifoggant and stabilizing compound is present in the emulsion in the ratio of 1 to 25 milligrams per 0.6 mol of silver halide.

5. A light-sensitive silver halide material as recited in claim 1 wherein the antifoggant and stabilizing compound is present in the emulsion and in the ratio of 10 to 300 milligrams per 0.6 mol of silver halide.

6. A light-sensitive photographic element as recited in claim 1 wherein the antifoggant and stabilizing compound is 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine.

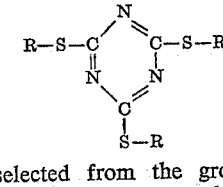
7. In a process of developing an exposed silver halide emulsion, the step which comprises developing said emulsion with a p-(N-methylamino)phenol-hydroquinone developing solution in the presence of an antifogging and stabilizing compound having the following chemical formula:



wherein R is selected from the group consisting of thiazolyl, imidazolyl, oxazolyl, benzothiazolyl, benzimidazolyl and benzoxazolyl.

8. A process as recited in claim 7 wherein the antifogging and stabilizing compound is 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine.

9. A p-(N-methylamino)phenol-hydroquinone developing solution containing a compound having the following chemical formula:



wherein R is selected from the group consisting of thiazolyl, imidazolyl, oxazolyl, benzothiazolyl, benzoimidazolyl and benzoxazolyl.

10. A p-(N-methylamino)phenol-hydroquinone developing solution containing 2,4,6-tri (benzothiazolyl-2-thio)-S-triazine.

11. A p-(N-methylamino)phenol-hydroquinone developing solution containing 100 milligrams of 2,4,6-tri-(benzothiazolyl-2-thio)-S-triazine per liter of solution.

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