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ANTIFOGGANTS AND STABILIZERS FOR PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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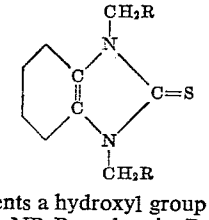
This invention relates to the stabilization of photographic materials. More particularly, this invention relates to light-sensitive photographic silver halide emulsions containing 1,3-disubstituted - 2 - benzimidazolinethiones as stabilizing and antifogging agents, and to methods of producing photographic emulsions containing them.

It is well known in the photographic art that light-sensitive emulsions such as gelatin-silver halide emulsions have an inherent tendency to fog. Conditions under which fogging occurs are: prolonged ripening of the emulsions, storage over prolonged periods of time especially under conditions of elevated temperature and by prolonged developing. These troublesome properties of photographic emulsions have long harassed the art and numerous remedies have been proposed to overcome them. Thus, it is the practice to add certain chemical compounds such as benzimidazole and its derivatives, particularly 2-mercaptobenzimidazole, to photographic emulsions to increase their stability and reduce their tendency to fog. However, such compounds, referred to in the art as stabilizing and/or antifogging agents, as used heretofore, often are characterized by deleterious side reactions which adversely affect the light-sensitive emulsion. In many instances, the incorporation of stabilizing and/or antifogging agents of the prior art cause an excessive loss of speed and/or contrast of the emulsion. In some cases, optical sensitization or dye sensitizing may be adversely affected, a condition which is probably attributed to displacement of the sensitizing dye from the silver halide grain surface by the stabilizing agent.

It has now been discovered that 1,3-disubstituted-2-benzimidazolinethiones are eminently suitable as antifoggants and/or stabilizers for light-sensitive silver halide emulsions and, furthermore, are capable of performing their function without interfering or deleteriously affecting the speed and/or contrast, optical sensitization or dye sensitization of the emulsion in which they are incorporated.

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

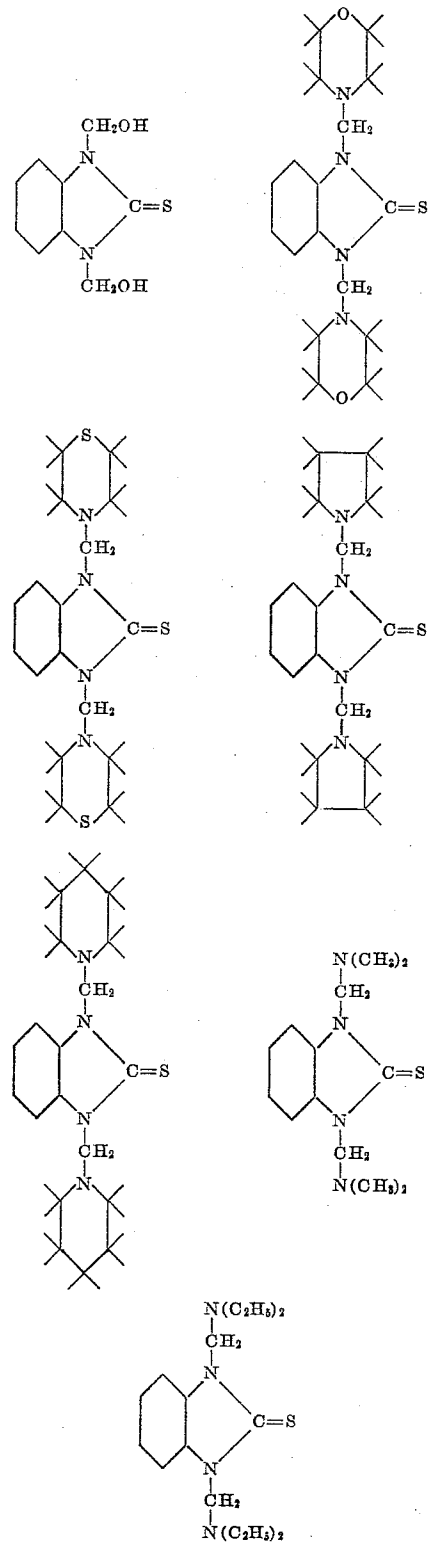
The 1,3-disubstituted-2-benzimidazolinethiones, the use of which is contemplated herein as stabilizers or antifoggants, may be represented by the following general formula:



wherein R represents a hydroxyl group or an amino group of the formula $—NR_1R_2$, wherein R_1 and R_2 represent hydrogen, an alkyl group, i.e., methyl, ethyl, propyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, etc., a lower aralkyl group, wherein the aryl rings can be a monocyclic

or bicyclic aromatic nucleus, i.e., benzyl, phenethyl, naphthylmethyl, naphthylethyl, etc., or R_1 and R_2 can complete a heterocyclic ring structure of the pyrrolidine, piperidine, morpholine and thiazine series.

Examples of compounds which fall within the scope of the above formula and which are effective as antifoggants or stabilizers for the purpose of practicing the invention are typified in the following formulate:



The 1,3-disubstituted-2-benzimidazolinethiones of the type employed herein are described in the chemical literature. For instance, representative members of the aforesaid class of compounds can be synthesized according to the method of H. Zinner et al., Berichte 90, page 2852 (1957). The method described therein is an adaptation of the Mannich reaction in which a 2-benzimidazolinethione, formalin and an amine are reacted to give the 1,3-bis-aminomethylbenzimidazolinethione. The reaction is normally carried out in a lower alcoholic solvent at elevated temperatures such as those prevailing at the boiling point of the particular solvent employed. If the 1,3-bis-hydroxymethylbenzimidazolinethione is the desired product, this can be obtained by the reaction of the corresponding 2-benzimidazolinethione and formaldehyde in aqueous solution under reflux.

Secondary amines which can be used to form the 1,3-disubstituted-2-benzimidazolinethiones include secondary alkylamines, i.e., dimethylamine, methylethylamine, diethylamine, dipropylamine, methylbutylamine, dibutylamine, propylbutylamine, amylpropylamine, methylhexylamine, methylheptylamine, methyloctylamine, ethylnonylamine, methyldecylamine, propylundecylamine, etc. and heterocyclic amines of the pyrrolidine series, piperidine series, morpholine series, thiazine series and diazine series.

The antifogging and/or stabilizing agents of our invention can be incorporated or contacted with a silver halide photographic emulsion at any of the various stages during its processing. Thus, they may be added as "ripening finals" or as "coating finals." "Ripening finals" are added during the ripening or sensitivity increasing stage of the emulsion-making process and 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, albumin, carboxymethyl cellulose, zein or the like. When added as "coating finals," the compounds of the present invention are combined with the emulsion just prior to coating and when maximum sensitivity has almost been achieved. Such emulsions can then be coated on the usual supports familiar to the art as exemplified by glass, paper, metal, or film base such as cellulose triacetate, polyterephthalate esters, etc.

In some instances, it may be desirable to apply the antifogging and stabilizing compounds in separate layers adjacent to the emulsion as, for instance, in a separate undercoating layer or in the antiabrasion gelatin surface. Under different circumstances, the desired result may best be attained by adding the antifoggant and/or stabilizer to one or perhaps all of the processing baths for the involved emulsion.

When used as "ripening finals," the aforesaid 1,3-disubstituted-2-benzimidazolinethiones of our invention are advantageously used in concentrations of 0.1 to 25 mg. per 0.6 mole of silver halide. In the case of "coating finals," the concentration can be varied from 1 to 30 mg. per 0.6 mole of silver halide. As the concentration depends primarily on the type of emulsion employed, it is advisable to determine the optimum quantities of antifoggant and/or stabilizer in each instance.

Of the various types of emulsions which can be stabilized with our antifoggants and/or stabilizers, the nonsensitized orthochromatic, panchromatic, X-ray, paper and color emulsions are typical.

Although the aforesaid 1,3-disubstituted-2-benzimidazolinethiones are effective by themselves, they may be used in combination with the various other adjuncts that are commonly added to photographic emulsions such as sulfur sensitizers, reduction and metal sensitizers, noble metal sensitizers or accelerators such as polyoxyethylenes and their derivatives or polyvinylpyrrolidone.

As previously pointed out, our stabilizers and/or antifoggants do not interfere with the optical sensitization of

the silver halide emulsions by displacing the sensitizing dye from the silver halide grain surface.

The following examples are given to illustrate the manner in which the antifoggants and/or stabilizers of our invention can be used. It is to be understood, however, that these examples are illustrative only and in no way are to be construed as limiting the invention.

Example I

A gelatin-silver halide emulsion 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, stabilizers and hardening agents. A 0.1% solution of 1,3-bis[(1-piperidyl)methyl]-2-benzimidazolinethione in methanol was prepared and added to the emulsion as an antifoggant and stabilizer. The emulsion samples contained about 0.6 mole 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:

	G.
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	0.8
Water to make 1 liter.	

The results obtained are summarized in the following table:

Quantity of Compound Added	Relative Speed	Fog at 12 Minute Development	Oven Speed	Oven Fog at 4 Minute Development
0	100	.38	100	.41
2.5 mg	100	.31	100	.35

The 1,3 - bis[(1-piperidyl)methyl]-2-benzimidazolinethione, used as described above, was prepared according to the method of H. Zinner et al. given in the aforementioned Ber. 90, p. 2852 (1957) and was carried out as follows:

15 grams of 2-benzimidazolinethione was suspended in 100 ml. of methanol to which was then added 22 ml. of piperidine and 23 ml. of a 35% aqueous formaldehyde solution. The resulting mixture evolved heat and a clear solution was formed. On cooling, a crystalline product came down which was crystallized from petroleum ether. The melting point of the pure compound was 124–125° C.

Example II

The same procedure was followed as given in Example I except that the stabilizer used was 1,3-bis[(4-morpholinyl)methyl]-2-benzimidazolinethione. The results were substantially the same as obtained in Example I.

Example III

The same procedure was followed as given in Example I except that the stabilizer was 1,3-bis(hydroxymethyl)-2-benzimidazolinethione. The results are summarized in the following table:

Quantity of Compound Added	Relative Speed	Fog at 12 Minute Development	Oven Speed	Oven Fog at 4 Minute Development
0	100	.38	100	.41
2.5 mg	100	.28	100	.36

The preparation of the 1,3-bis(hydroxymethyl)-2-

benzimidazolinethione was carried out according to the Zinner method as disclosed above.

Example IV

The same procedure was followed as given in Example I except that the stabilizer was 1,3-bis(N,N-diethylaminomethyl)-2-benzimidazolinethione. The results are summarized in the following table:

Quantity of Compound Added	Relative Speed	Fog at 12 Minute Development	Oven Speed	Oven Fog at 4 Minute Development
0	100	.38	100	.41
2.5 mg	100	.27	100	.35

The 1,3-bis(N,N-diethylaminomethyl)-2-benzimidazolinethione was obtained using the Zinner method given above.

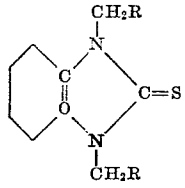
Example V

The same procedure was carried out as given in Example I except that a conventional stabilizer was also present in the photographic emulsion. The results are summarized in the following table:

Quantity of Compound Added	Relative Speed	Fog at 12 Minute Development	Oven Speed	Oven Fog at 4 Minute Development
0	100	.38	100	.25
2.5 mg	100	.32	100	.23

We claim:

1. A light-sensitive silver halide emulsion containing an antifogging and stabilizing compound having the following chemical structure:



wherein R is selected from the group consisting of an OH group, a $—NR_1R_2$ group, wherein R_1 and R_2 are selected from the class consisting of hydrogen, an alkyl group, an aromatic group selected from the class consisting of benzene and naphthalene, an aralkyl group selected from the class consisting of phenethyl and naphthyl, a heterocyclic radical selected from the class consisting of pyrrolidino, piperidino, thiazino, diazino and morpholino.

2. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is 1,3-bis[(4-morpholinyl)methyl]-2-benzimidazolinethione.

3. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is 1,3-bis[(1-piperidyl)methyl]-2-benzimidazolinethione.

4. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is 1,3-bis(hydroxymethyl)-2-benzimidazolinethione.

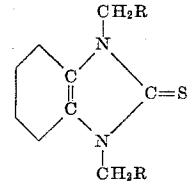
5. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is 1,3-bis(diethylaminomethyl)-2-benzimidazolinethione.

6. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is present in the emulsion in the ratio of 0.1 to 30 mg. per 0.6 mole of silver halide.

7. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is present in the emulsion in the ratio of 0.1 to 25 mg. per 0.6 mole of silver halide.

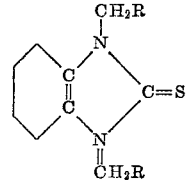
8. A light-sensitive silver halide emulsion as recited in claim 1 wherein the antifogging and stabilizing compound is present in the emulsion in the ratio of 0.1 to 30 mg. per 0.6 mole of silver halide.

9. A light-sensitive photographic element comprising a base and a coating of gelatino-silver halide emulsion thereon, said emulsion containing an antifogging and stabilizing compound having the following chemical structure:



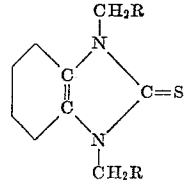
wherein R is selected from the group consisting of an OH group, a $—NR_1R_2$ group, wherein R_1 and R_2 are each selected from the class consisting of hydrogen, an alkyl group, an aromatic group selected from the class consisting of benzene and naphthalene, an aralkyl group selected from the class consisting of phenethyl and naphthylethyl and heterocyclic radicals selected from the class consisting of pyrrolidino, piperidino, thiazino, diazino and morpholino.

10. 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 an antifogging and stabilizing compound having the following chemical structure:



wherein R is selected from the group consisting of an OH group and an amino group $—NR_1R_2$, wherein R_1 and R_2 are each selected from the group consisting of hydrogen, an alkyl group, an aromatic group selected from the class consisting of benzene and naphthalene, an aralkyl group selected from the class consisting of phenethyl and naphthylethyl, a heterocyclic radical selected from the class consisting of pyrrolidino, piperidino, thiazino, diazino and morpholino.

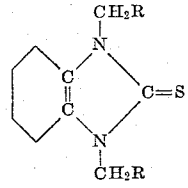
11. A process of forming a silver halide photographic emulsion having a reduced tendency to fog which comprises forming the emulsions, ripening the emulsion and during said ripening adding thereto a compound having the following chemical structure:



wherein R is selected from the group consisting of an OH group and an amino group $—NR_1R_2$, wherein R_1 and R_2 are each selected from the group consisting of hydrogen, an alkyl group, an aromatic group selected from the class consisting of benzene and naphthalene, an aralkyl group selected from the class consisting of phenethyl and naphthylethyl, a heterocyclic radical selected from the class consisting of pyrrolidino, piperidino, thiazino, diazino and morpholino.

12. A process of forming a silver halide light-sensitive

photographic element having a reduced tendency to fog which comprises forming an emulsion, ripening said emulsion, adding to said emulsion just prior to the coating of same, a compound having the following chemical structure:



wherein R is selected from the group consisting of an OH group and an amino group —NR_1R_2, wherein R_1 and R_2 are each selected from the group consisting of

hydrogen, an alkyl group, an aromatic group selected from the class consisting of benzene and naphthalene, an aralkyl group selected from the class consisting of phenethyl and naphthylethyl, a heterocyclic radical selected from the class consisting of pyrrolidino, piperidino, thiazino, diazino and morpholino and coating the so obtained emulsion on a base.

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