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ANTIFOGGANTS AND STABILIZERS FOR PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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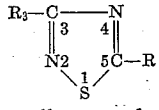
This invention relates to the stabilization of photographic materials. More particularly, this invention relates to light-sensitive photographic silver halide emulsions containing mercapto-1,2,4-thiadiazoles as stabilizing and antifogging agents, and to methods of producing photographic emulsions containing them.

It is well-known in the photographic art that light-sensitive emulsions such as gelatin-silver halide emulsions have a 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 humidity, 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, have the disadvantage that upon addition to the emulsion an excessive loss of speed and/or contrast of the emulsion occurs as an undesirable side reaction.

It has now been discovered that mercapto-1,2,4-thiadiazoles are eminently suitable as antifoggants or stabilizers for light-sensitive silver halide emulsions and, furthermore, are capable of performing their function without seriously affecting the speed and/or contrast of the emulsion with which they are associated.

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.

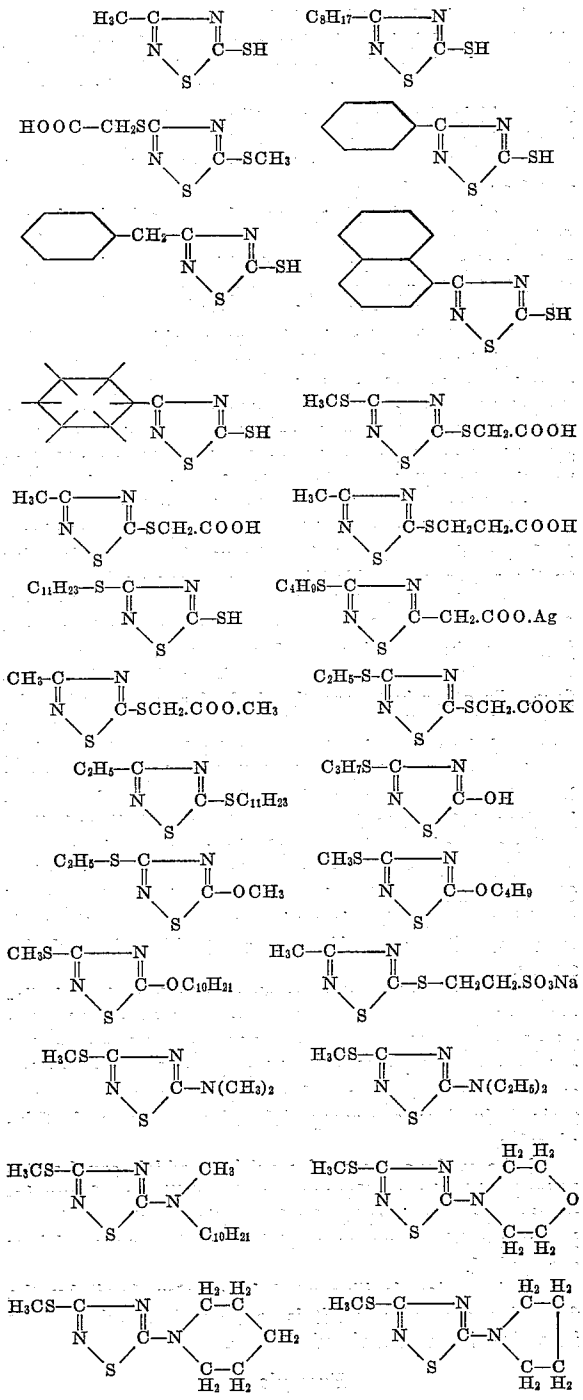
The mercapto-1,2,4-thiadiazoles, the use of which is contemplated herein as stabilizers or antifoggants, may be represented by the following structural formula:



wherein R is hydroxy, alkoxy such as methoxy, ethoxy, propoxy, butoxy, amoxy, hexoxy, heptoxy, octoxy, nonoxy, decoxy, undecoxy, etc.; —NR_1R_2 wherein R_1 and R_2 represent hydrogen, alkyl, e.g., methyl, ethyl, n-propyl, n-butyl, iso-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, and together, R_1 and R_2 can complete a heterocyclic ring system such as morpholine, piperidine, pyrrolidine, etc.; carboxy lower alkyl, e.g., carboxymethyl, carboxyethyl, carboxypropyl, etc., and the salts and esters thereof; sulfo lower alkyl, e.g., sulfomethyl, sulfoethyl, etc., and the salts and esters thereof; a mercapto group, alkylmercapto, e.g., methylmercapto, ethylmercapto, n-propylmercapto, n-butylmercapto, n-amylmercapto, n-hexylmercapto, n-heptylmercapto, n-octylmercapto, n-nonylmercapto, n-hexylmercapto, n-undecylmercapto, etc.; carboxy lower alkylmercapto, e.g., carboxymethylmercapto, carboxyethylmercapto, carboxypropylmercapto, etc., and the salts and esters thereof, and R_3 is alkyl as above for R_1 and R_2, arloweralkyl, e.g.,

benzyl, phenethyl, naphthyl, naphthylmethyl, naphthylethyl, etc.; an aryl group of the benzene and naphthalene series, alkylmercapto as above for R, at least one of said R and R_3 always being a mercapto group.

Examples of compounds which fall within the scope of the above formula and which are effective as antifoggants or stabilizers are typified in the following formulae:



The mercapto-1,2,4-thiadiazoles of the type employed herein may be prepared according to methods described by J. Goerdeler, H. Groschoff and U. Sommerlad in Ber., 90, pp. 182–187 (1957), and Ber., 90, pp. 892–901 (1957). In general, these methods comprise reacting an amidine hydrohalide salt or a thiuronium salt with perchloromethylmercaptan in the presence of sodium

hydroxide to produce a 5-chloro-1,2,4-thiadiazole which, in turn, can be reacted with a wide variety of reagents and transformed into the numerous thiadiazole compounds previously listed.

Thus, 5-hydroxy-1,2,4-thiadiazole can be readily produced by acid hydrolysis of the corresponding 5-chloro base. Treatment of the 5-chlorothiadiazole with thiourea in the presence of base, yields the corresponding 5-mercapto derivative, whereas reaction with amines produces a 5-amino-1,2,4-thiadiazole. The 5-hydroxy and 5-mercapto derivatives can be further transformed by methods well-known in the art into their corresponding ethers and thioethers. If it is desired to produce carboxyalkylmercapto derivatives, these may be obtained by refluxing the 5-mercapto-1,2,4-thiadiazole with prerequisite halo fatty acid in the presence of sodium hydroxide. The so obtained carboxyalkylmercapto-1,2,4-thiadiazole can then be converted into the ester, if so desired, or into an alkali metal or ammonium salt.

The aforementioned compounds are effective in reducing the fog of silver halide photographic emulsions and may be added or contacted with the emulsion at any stage 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, 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 attained. Such emulsions are coated on the usual supports familiar to the art as exemplified by glass, paper or film.

In some instances, it is advantageous to apply the antifogging and stabilizing compounds in separate layers adjacent to the emulsion as, for example, in a separate undercoating layer or in the anti-abrasion gelatin surface. In other instances, the desired result may best be achieved by adding the antifoggant and stabilizer to one or all of the processing baths for the involved emulsion.

When used as "ripening finals," the thiadiazoles of our invention are advantageously used in concentrations ranging from 0.1 mg. to 5 mg. per 0.4 mole of silver halide. In the case of "coating finals," the concentrations range from 0.5 mg. to 50 mg. per 0.4 mole of silver halide. Since the concentration depends primarily on the type of emulsion employed, it is advisable to determine the optimum quantities of antifoggant or stabilizer in each instance.

Especially good results are obtained when the thiadiazoles of the present invention are used in combination with known antifoggants and stabilizers. Other emulsion adjuncts, namely, sulfur sensitizers, metal and reduction sensitizers, accelerators such as the polyoxyethylenes and their derivatives, are compatible with the aforesaid thiadiazoles.

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

The invention is illustrated in greater detail 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 was prepared in a conventional manner and brought up to its maximum light-sensitivity. The silver halide used to form the emulsion consisted of 2% silver iodide and 98% silver bromide. The emulsion was then prepared for coating, after which the finals such as sensitizing dyes and hardening agents were added. A 0.10% methyl alcoholic solution of 5-mercapto-3-methyl-1,2,4-thiadiazole was prepared and added in varying amounts to samples of the emulsion as antifoggant and stabilizer. Each sample contained about 0.4 mole of silver halide. The so prepared emulsion samples were each coated on a suitable cellulose ester such as cellulose triacetate base and dried. These coated film samples were then exposed in a type IIB Sensitometer and developed in a developer of the following composition:

	G.
Metol	1.5
Sodium sulfite, anhydrous	45.0
Sodium bisulfite	1.0
Hydroquinone	3.0
Sodium carbonate, monohydrated	6.0
Potassium bromide	0.8

Water to make 1.0 liter.

The results obtained were as follows:

Quantity of Antifoggant Compound Added, mg.	Relative Speed at 3 Minute Development	Fog at 12 Minute Development	Oven Fog at 6 Minute Development
0	100	.30	.66
2.5	90	.26	.30
5.0	90	.24	.30

The 5-mercapto-3-methyl-1,2,4-thiadiazole was prepared according to the procedure given in Ber., 90, 186 (1957).

Example II

This example was carried out in a manner similar to Example I except that a conventional antifoggant and stabilizer was present in the emulsion, in addition to the 5-mercapto-3-methyl-1,2,4-thiadiazole of the antifoggant of the preceding example. The results obtained were as follows:

Quantity of Antifoggant Compound Added, mg.	Relative Speed at 3 Minute Development	Fog at 12 Minute Development	Oven Fog at 6 Minute Development
0	100	.30	.26
1	90	.26	.21

Example III

In this example, a similar procedure and a similar emulsion was used as in Examples I and II. However, 5-carboxymethylmercapto-3-methyl-1,2,4-thiadiazole was substituted for the 5-mercapto-3-methyl-1,2,4-thiadiazole of the two preceding examples. A conventional antifogging agent was also used, as in Example II, together with the antifogging agent of our invention. The results obtained were as follows:

Quantity of Antifoggant Compound Added, mg.	Relative Speed at 3 Minute Development	Fog at 12 Minute Development	Oven Fog at 6 Minute Development
0	150	.20	.16
10	125	.13	.12
50	125	.14	.10

The 5-carboxymethylmercapto - 3 - methyl-1,2,4-thiadiazole used in this example was prepared as follows:

3.96 grams of 5-mercapto-3-methyl-1,2,4-thiadiazole, 4.17 g. of bromoacetic acid and 2.5 g. of sodium hydroxide were mixed with 30 ml. of H_2O and heated under reflux for three hours. The reaction mixture was then cooled and acidified with concentrated hydrochloric acid until Congo red paper turned blue, then chilled and filtered. The solid residue was dissolved in ethanol, treated

with charcoal and recrystallized from a water-ethanol solution.

Example IV

Several samples of conventional photographic film were exposed in a Type IIB Sensitometer and then divided into two groups. One group of samples was developed for twelve minutes at 65° F. in a standard metol-hydroquinone developer. The other group of samples was developed for the same length of time and at the same temperature as the first group in a standard metol-hydroquinone developer to which has been added 20 mg. of 5-mercapto-3-methyl-1,2,4-thiadiazole per liter of developer. It was found that the samples developed in the standard developer showed a fog of .30, whereas the samples developed in the developer containing the novel antifogging agent of our invention showed a fog of .20.

Example V

The procedure of Example I was repeated excepting that the stabilizer in this case was 5-mercapto-3-phenyl-1,2,4-thiadiazole. The preparation of the thiadiazole is given in Ber., 90, 182–187 (1957).

Example VI

The procedure was the same as presented in Example I except that the stabilizer used therein was replaced by 3-methyl-mercapto - 5 - carboxymethylmercapto-1,2,4-thiadiazole.

The latter compound was prepared by refluxing 5-chloro-3-methylmercapto-1,2,4-thiadiazole (Ber. 90, 892–901 (1957)) with a haloacetic acid in the presence of an alkali.

Example VII

The procedure was the same as in Example I except that the stabilizer, as used therein, was replaced by 5-carboxymethyl-3-ethylmercapto-1,2,4-thiadiazole.

The latter compound was prepared by reacting 5-chloro-3-mercapto-1,2,4-thiadiazole with malonic ester in the presence of alkali followed by acid hydrolysis. This procedure is given in the previously cited Berichte references.

Example VIII

The procedure was the same as in Example I except that the stabilizer, as used therein, was replaced by 5-mercapto-3-phenyl-1,2,4-thiadiazole.

The latter compound was prepared from the method disclosed in the above Berichte references.

Example IX

The procedure was the same as given in Example I except that 5-heptylmercapto-3-cyclohexyl-1,2,4-thiadiazole was substituted for the stabilizer of said Example I.

Example X

The same procedure was followed as outlined in Example I except that the antifoggant in this instance was 5-diethylamino-3-methylmercapto-1,2,4-thiadiazole.

Quantity of Antifoggant Compound Added, mg.	Relative Speed at 4 Minute Development	Fog at 12 Minute Development	Oven Test	
			Speed at 4 Minute Development	Fog
0	100	.20	50	.13
150	100	.18	100	.13

The photographic emulsion employed in compiling the above table is a type well-known to the art and contained 4% silver iodide and 96% silver bromide.

Example XI

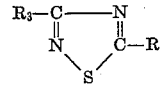
In this example, 5-diethylamino-3-methylmercapto-1,2,4-thiadiazole was also used as the antifoggant except that the photographic emulsion consisted of 2% silver iodide and 98% silver bromide. The results are presented in table form below.

Quantity of Antifoggant Compound Added, mg.	Relative Speed at 3 Minute Development	Fog at 12 Minute Development	Oven Test	
			Speed at 6 Minute Development	Fog
0	100	.65	100	.53
45	100	.45	100	.45
100	100	.30	100	.40

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

We claim:

1. A photographic material comprising a base and a light-sensitive silver halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a mercapto-1,2,4-thiadiazole of the following general formula:

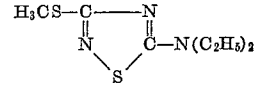


wherein R is selected from the class consisting of an alkoxy group of from 1 to 11 carbon atoms, a hydroxy group, a carboxy lower alkyl group and the alkali metal, ammonium and silver salts and lower alkyl esters thereof, a sulfo lower alkyl group and the alkali metal and ammonium salts thereof, an —SR_4 grouping wherein R_4 is selected from the class consisting of hydrogen, an alkyl group of from 1 to 11 carbon atoms and a carboxy lower alkyl group and the alkali metal and ammonium salts and lower alkyl esters thereof, a radical of the formula —NR_1R_2 wherein R_1 and R_2 are each selected from the class consisting of an alkyl group of from 1 to 10 carbon atoms and taken together can complete a heterocyclic ring selected from the class consisting of morpholine, piperidine and pyrrolidine; R_3 is selected from the class consisting of an alkyl group of from 1 to 8 carbon atoms, an —SR_4 grouping wherein R_4 is selected from the class consisting of hydrogen, an alkyl group of from 1 to 11 carbon atoms and a carboxy lower alkyl group and the alkali metal and ammonium salts and the lower alkyl esters thereof, an aralkyl group of the benzene and naphthalene series wherein the alkyl chain contains from 1 to 2 carbon atoms and at least one of said R and R_3 always being a —SR_4 grouping.

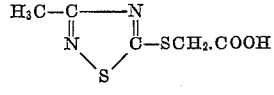
2. The product as defined in claim 1 wherein said mercapto-1,2,4-thiadiazole is located in the silver halide emulsion.

3. The product as defined in claim 1 wherein said mercapto-1,2,4-thiadiazole is located in a layer adjacent to said silver halide emulsion layer.

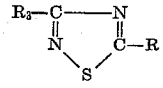
4. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion carried thereby, said photographic material containing, in fog inhibiting amounts, the compound of the formula:



5. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion carried thereby, said photographic material containing, in fog inhibiting amounts, a compound of the formula:

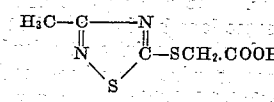


6. The process of reducing and minimizing fog in light-sensitive silver halide materials comprising a base having a light-sensitive silver halide emulsion thereon which comprises exposing said emuslion and developing the same in the presence of a compound of the following general formula:

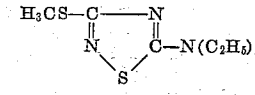


wherein R is selected from the class consisting of an alkoxy group of from 1 to 11 carbon atoms, a hydroxy group, a carboxy lower alkyl group and the alkali metal, ammonium and silver salts and lower alkyl esters thereof, a sulfo lower alkyl group and the alkali metal and ammonium salts thereof, an $-SR_4$ grouping wherein R_4 is selected from the class consisting of hydrogen, an alkyl group of from 1 to 11 carbon atoms and a carboxy lower alkyl group and the alkali metal and ammonium salts and lower alkyl esters thereof, a radical of the formula $-NR_1R_2$ wherein R_1 and R_2 are each selected from the class consisting of an alkyl group of from 1 to 10 carbon atoms and taken together can complete a heterocyclic ring selected from the class consisting of morpholine, piperidine, and pyrrolidine; R_3 is selected from the class consisting of an alkyl group of from 1 to 8 carbon atoms, an $-SR_4$ grouping wherein R_4 is selected from the class consisting of hydrogen, an alkyl group of from 1 to 11 carbon atoms and a carboxy lower alkyl group and the alkali metal and ammonium salts and the lower alkyl esters thereof, an aralkyl group of the benzene and naphthalene series wherein the alkyl chain contains from 1 to 2 carbon atoms and at least one of said R and R_3 always being a $-SR_4$ grouping.

7. The process as defined in claim 6 wherein the antifoggant is a compound of the following formula:



8. The process as defined in claim 6 wherein the antifoggant is a compound of the following formula:



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