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STABILIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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9 Claims. (Cl. 96—109)

This invention relates to fog-inhibiting agents and stabilizers for photographic emulsions, and to photographic emulsions containing them.

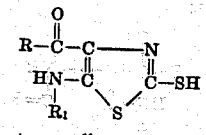
It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given; this is commonly called "fog," and sometimes called "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation; in this invention, we are not concerned with the latter.

Fog depends both on the emulsion and the conditions of development; for a given emulsion it increases with the degree of development. With constant development conditions, it tends to increase with time, temperature and relative humidity of storage conditions; it is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is, of course, desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is non-uniform. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide vapor, and strongly reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that an antifoggant protects against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

It is, accordingly, an object of our invention to provide a method for stabilizing photographic emulsions. A further object of our invention is to maintain the sensitivity and fog of silver halide emulsions at or close to initial optimum values under keeping conditions of high temperature and humidity. A further object is to provide photographic silver halide emulsions containing antifoggants or stabilizers. Other objects will become apparent from a consideration of the following description and examples.

The above objects are accomplished by adding to the photographic emulsion a compound selected from those represented by the following general formula:

(I)



wherein R represents an alkoxyl group, such as methoxyl, ethoxyl, etc. or an amino group and R_1 represents a hydrogen atom or a lower alkyl group, such as methyl, ethyl, etc.

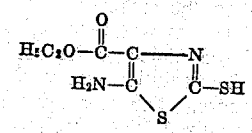
The fog inhibitors which we propose to use are added to the emulsion during the process of manufacture, to avoid loss of sensitivity and to inhibit the growth of fog with passage of time under non-ideal conditions of storage.

A solution of the compounds of the invention when added in suitable concentration, before coating, to unsensitized, chemically sensitized, or optically sensitized photographic emulsions does not appreciably affect the sensitometric values for sensitivity and fog when measurements are made soon after coating. When sensitometric measurements are made at appreciable intervals of time, at elevated temperatures and dry or somewhat humid conditions, these compounds do stabilize photographic speed and maintain fog at a low level.

The preparation of silver halide emulsions involves three separate operations: (1) the emulsification and digestion or ripening of the silver halide, (2) the freeing of the emulsion from excess soluble salts, usually by washing, and (3) the second digestion or after-ripening to obtain increased sensitivity. (Mees "The Theory of the Photographic Process," 1942.) We prefer to add the fog-inhibiting agents after the final digestion or after-ripening, although they can advantageously be added prior to digestion.

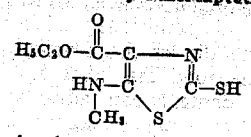
Listed below are a number of compounds coming within the scope of the above general formula, which we have found to be particularly advantageous in practicing our invention. These compounds belong to a group of compounds which we shall designate as aminothiazoles.

(1)



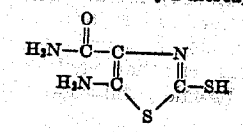
5-amino-4-carbethoxy-2-mercaptothiazole

(2)



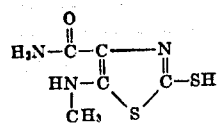
5-methylamino-4-carbethoxy-2-mercaptothiazole

(3)



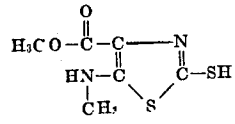
5-amino-4-carbamyl-2-mercaptothiazole

(4)



5-methylamino-4-carbamyl-2-mercaptothiazole

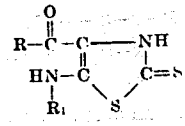
(5)



5-methylamino-4 carbomethoxy-2-mercaptothiazole

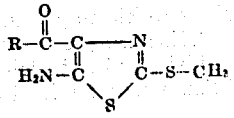
The above compounds can be prepared according to the methods of Cook et al., "Jour. Chem. Soc." (London), 1947, p. 1598, 1949, pps. 1064, 1441, 2329. The compounds of Formula I can alternatively be written in the following form:

(II)



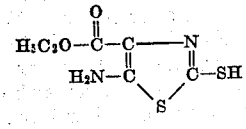
while the compounds of Formula I wherein R_1 is a methyl group can be written in the tautomeric form:

(III)



It is to be understood that our invention contemplates the above compounds in any of their tautomeric forms. An improved method for making compound 1 follows:

Example A.—5-amino-4-carbethoxy-2-mercaptothiazole



A solution of 35.5 g. of ethyl isonitrosocyanoacetate (prepared by the method of Conrad and Schulze, Ber., 42, 735 (1909)) in 300 ml. of absolute ethanol was shaken for a few minutes with a teaspoon of Raney nickel. This treatment is necessary to remove materials which poison the platinum oxide catalyst. The mixture was then filtered and the filtrate was hydrogenated over 0.5 g. of platinum oxide catalyst at room temperature and under 2–3 atmospheres' pressure of hydrogen for 22 to 24 hours. The catalyst was removed by filtration and the ethanolic solution of ethyl aminocyanoacetate (pure ethyl aminocyanoacetate prepared as a pale yellow liquid, B. P. 88–90° C. (1 mm.); n_D^{27} 1.4425) was boiled under reflux for one hour with 50 ml. of carbon disulfide. The resulting solution was concentrated in vacuo on the steam bath until crystallization occurred. The vacuum was then relieved and sufficient absolute ethanol was added to the boiling suspension to effect solution. The solution was clarified with charcoal and allowed to cool. The crystalline product was collected and recrystallized from absolute ethanol to afford 25 g. of white, granular crystals, M. P. 186–187° C.

The photographic emulsions used in practicing our invention are generally of the developing-out type; also, it is to be understood that photographic emulsions of varying halide content can advantageously be used. The antifoggant compounds used in our invention have been found particularly useful when employed in conjunction with gelatino-silver bromiodide emulsions, although they can also be advantageously employed for stabilizing other silver halide emulsions, such as gelatino-silver chloride, bromide, chlorobromide, chlorobromiodide, etc.

The emulsions can also be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U. S. Patent 1,574,944 and U. S. 1,623,499, and Sheppard and Brigham U. S. Patent 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U. S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U. S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller and Dodd U. S. Patent 2,399,083, or stabilized with gold salts as described in Damschroder U. S. Patent 2,597,856 and Yutzy and Leermakers U. S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U. S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U. S. Patent 2,518,698), polyamines such as spermine (Lowe and Allen U. S. Patent 2,521,925), or bis-(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U. S. Patent 2,521,926).

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U. S. application Serial No. 319,611 (now U. S. Patent No. 2,728,663, issued December 27, 1955), Carroll and Murray U. S. application Serial No. 319,612 (now U. S. Patent No. 2,728,664, issued December 27, 1955) and Leubner and Murray U. S. application Serial No. 319,613 (now U. S. Patent No. 2,728,665, issued December 27, 1955), all filed November 8, 1952.

The stabilizing combinations of aminothiazoles are effective in the presence or absence of optical sensitizing dyes. Since optical sensitizing may affect stability of emulsions with respect to sensitivity, fog and latent image changes, the action of the compounds of this invention is not completely independent of optical sensitizing or other emulsion variables. We have found, however, that both unsensitized emulsions and emulsions sensitized with cyanine or merocyanine dyes or both can be treated with aminothiazoles according to our invention.

The antifoggant and stabilizing action was determined by incubation of the emulsions for the times indicated in the following table at a temperature of 120° F. and constant relative humidity (obtained by placing the emulsions in closed containers, the ambient temperature being about 70° F. and relative humidity about 55 percent prior to sealing the containers).

The efficiency of the various antifoggants was determined by measuring the speed, gamma and fog of the incubated emulsions containing an antifoggant and comparing these measurements with those of the same batch of emulsion before incubation. Also similar measurements were made on a photographic emulsion containing no antifoggant, both before and after incubation.

The tests were made using high speed silver bromiodide emulsions (coated on cellulose acetate supports), which had been panchromatically sensitized. The emulsions were exposed in an Eastman Type I*b* sensitometer and developed for the times indicated in the table, using the developers indicated. The speed, gamma and fog for the emulsions were then measured as indicated above. While the same batch of emulsion was not employed in

all of the examples, the same batch was employed in the coatings of each individual example for purposes of comparison.

The optimum amount of fog-inhibting agent can be determined by making the customary tests employed in

Example	Compound No.	Conc., g./mol. AgX	Fresh Test			Incubation Test				Developer	
			Speed	Gamma	Fog	Time (Wks.)	Speed	Gamma	Fog	No.	Time (Minutes)
1. (a)	None		2,700	.72	.11	1	1,190	.67	.26	A	6.5
(b)	1	.0165	2,950	.75	.11	1	1,500	.73	.20	A	6.5
2. (a)	None		2,700	.72	.11	1	1,190	.67	.26	A	6.5
(b)	2	.165	2,600	.71	.11	1	1,440	.65	.19	A	6.5
3. (a)	None		2,250	.70	.09	2	865	.60	.28	A	6.5
(b)	3	.03	2,100	.65	.08	2	1,040	.58	.17	A	6.5
4. (a)	None		3,100	1.23	.10	2	2,300	1.04	.22	B	4
(b)	4	.0075	3,150	1.24	.09	2	2,050	1.04	.17	B	4
5. (a)	None		8,050	1.04	.12	1	6,000	.96	.21	C	5
(b)	1	.03	7,200	.98	.11	1	6,400	.95	.12	C	5
(c)	2	.03	7,900	1.00	.12	1	6,150	.97	.16	C	5
(d)	4	.03	7,900	.99	.12	1	6,250	.96	.16	C	5

In the above table, developer A had the following composition:

	Grams
Hydroquinone	1.3
N-methyl-p-aminophenol sulfate	1.5
Sodium sulfite (anhyd.)	75
Borax	4.5
Potassium bromide	0.4
Water to make 1 liter.	

developer B had the following composition:

N-methyl-p-aminophenol sulfate	2.0
Hydroquinone	8.0
Sodium sulfite (anhyd.)	90
Sodium carbonate monohydrate	52.5
Potassium bromide	5.0
Water to make 1 liter.	

and developer C had the following composition:

N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite	30.0
Sodium metaborate	10.0
Potassium bromide	0.5
Water to make 1 liter.	

As shown in the above Cook et al. references, the compounds of Formula I above wherein R_1 is an alkyl group can be prepared by simply intermixing an alkaline solution of a compound of Formula I wherein R_1 is a hydrogen atom with an alkyl salt, e. g., methyl sulphate, ethyl sulphate, etc. The desired compounds separate from the aqueous solutions. It is to be understood that it is the product (or products) of this reaction which are contemplated by Formula I above wherein R_1 is an alkyl group.

The results in the above table show that the compounds of our invention are not only useful as antifoggants, but that they also stabilize photographic emulsions against loss in speed in many instances.

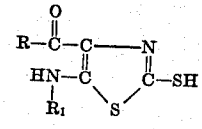
In a manner similar to that illustrated in the above example, other aminothiazoles selected from those represented by the above general Formula I can be incorporated in photographic emulsions for the purpose of stabilization. The fog-inhibiting agents useful in practicing our invention can be used in various kinds of photographic emulsions. In addition to being useful in ordinary non-sensitized emulsions, they can also be used in orthochromatic, panchromatic and X-ray emulsions. If used with sensitizing dyes, they can be added to the emulsion before or after the dyes are added. Suitable dispersing agents for the silver halide emulsions stabilized according to our invention comprise gelatin, or other colloids, such as collodion, albumen, cellulose organic derivatives, synthetic resins, etc.

emulsion making. Of course, the optimum amount for a given emulsion will vary depending on the presence of emulsion addenda, such as chemical sensitizers, optical sensitizers, etc. In general, we have found that from 0.001 to 5.0 g. of fog-inhibiting agent per mole of silver halide is sufficient for the purposes of our invention.

Instead of adding the fog-inhibiting agent directly to the photographic emulsion, it is sometimes desirable to incorporate the fog-inhibiting agent in a separate layer which is placed in contact with the silver halide emulsion layer which is to be stabilized. Under such conditions, of course, it is advisable to use a higher concentration of fog-inhibiting agent than indicated above.

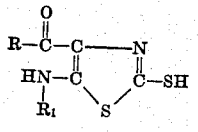
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion containing a compound selected from those represented by the following general formula:



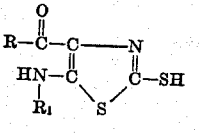
wherein R represents a member selected from the group consisting of an alkoxyl group and an amino group, and R_1 represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group.

2. A photographic gelatino-silver-halide developing-out emulsion containing a compound selected from those represented by the following general formula:



wherein R represents a member selected from the group consisting of an alkoxyl group and an amino group, and R_1 represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group.

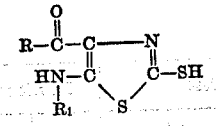
3. A photographic gelatino-silver-bromiodide developing-out emulsion containing a compound selected from those represented by the following general formula:



wherein R represents a member selected from the group consisting of an alkoxyl group and an amino group, and R_1 represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group.

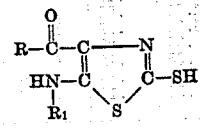
4. A photographic gelatino-silver-halide developing-

out emulsion containing a compound selected from those represented by the following general formula:



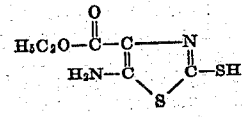
wherein R represents a member selected from the group consisting of an ethoxyl group and an amino group and R_1 represents a member selected from the group consisting of a hydrogen atom and a methyl group.

5. A photographic gelatino-silver-bromiodide developing-out emulsion containing a compound selected from those represented by the following general formula:

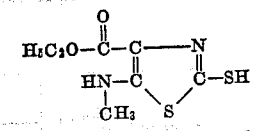


wherein R represents a member selected from the group consisting of an ethoxyl group and an amino group and R_1 represents a member selected from the group consisting of a hydrogen atom and a methyl group.

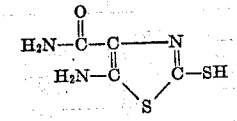
6. A photographic silver halide emulsion containing a compound represented by the following formula:



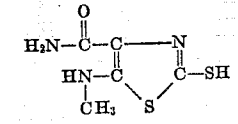
7. A photographic silver halide emulsion containing a compound represented by the following formula:



8. A photographic silver halide emulsion containing a compound represented by the following formula:



9. A photographic silver halide emulsion containing a compound represented by the following formula:



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