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2,728,667

MOLECULAR COMPOUNDS OF MERCURY SALTS WITH BENZOTHAZOLES AS FOG INHIBITORS IN A SILVER HALIDE EMULSION

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8 Claims. (Cl. 95-7)

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

It is known that photographic emulsions, particularly ultra-sensitive emulsions or those containing optical sensitizers exhibit a tendency to form a deposit of silver in the emulsion upon development. This deposit extends more or less uniformly over the entire emulsion and is known as fog. Photographic fog is of two types: local and general. Local fog is formed by exposure of the film or plate at undesired points as by a light leak in the camera. General fog is formed in a number of ways. It may be caused by the conditions of high temperature or humidity or unusually long time of storage. The nature of the emulsion may also produce chemical fog as well as the conditions of development of the emulsion as by development for protracted periods of time or at temperatures above normal. We are primarily concerned with fog and sensitivity changes in photographic films produced by storage under adverse conditions of temperature and humidity or for prolonged periods of time before exposure and development.

General fog and loss of sensitivity of the emulsion are especially likely to occur when the sensitive material is stored under conditions other than ideal, that is, under conditions of high temperature and humidity, as in tropical regions.

It is an object of the invention to provide novel anti-fogging or fog-inhibiting compounds for emulsions. A further object is to provide anti-fogging agents which stabilize the initial sensitivity of the emulsion. A still further object is to provide anti-fogging agents which improve the keeping of the emulsion in tropical regions. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in a silver halide emulsion a molecular compound of a mercury salt with a benzothiazole or benzothiazole derivative.

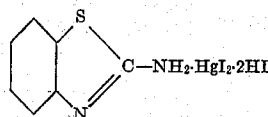
The principal purpose of our invention is to provide a means for maintaining the sensitivity and fog of silver halide emulsions at or close to initial optimum values under keeping conditions of high temperature and humidity. The fog inhibitors which we propose to use are added to the emulsion at any stage during the process of manufacture prior to coating the emulsion to avoid loss of sensitivity and to inhibit the growth of incubation or keeping fog with passage of time under non-ideal conditions of storage. The mercury fog inhibitor may be added to the emulsion in solution in any convenient solvent not injurious to the emulsion such as water, lower alcohols and ketones.

A solution of the mercuric compound which we employ when added in suitable concentration before coating to unsensitized or optically sensitized silver halide emulsions does not appreciably affect the sensitometric values for sensitivity and fog when measurements are made soon after coating. However, when sensitometric measurements are made after appreciable intervals of time under tropical or dry conditions of storage at elevated temperatures, these compounds do stabilize photographic speed and maintain fog at a low level.

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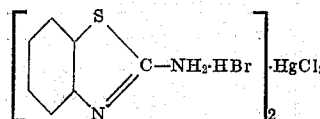
The following compounds may be used according to our invention:

(1)



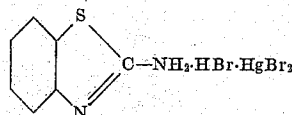
2-aminobenzothiazole mercuric iodide dihydroiodide

(2)



Bis-(2-aminobenzothiazole hydrobromide) mercuric chloride

(3)

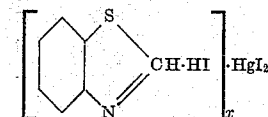


2-aminobenzothiazole hydrobromide mercuric bromide

(4)

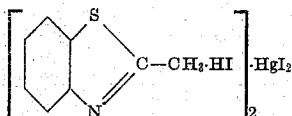
2-aminobenzothiazole hydrobromide mercuric iodide

(5)



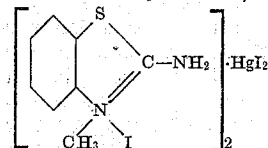
x-(Benzothiazole hydroiodide) mercuric iodide

(6)



Bis-(2-methylbenzothiazole hydroiodide) mercuric iodide

(7)



x-(2-aminobenzothiazole methiodide) mercuric iodide

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 aqueous soluble salts usually by washing, (3) the second digestion or after-ripening to obtain increased sensitivity (Mees, *The Theory of the Photographic Process*, 1942, page 3). The fog inhibiting agents may be added at any stage, e. g., after the final digestion.

The mercury compounds are useful generally in photographic silver halide developing out emulsions. They may be used in emulsions chemically sensitized with sulfur compounds, reducing agents such as stannous salts or polyamines, or noble metals such as gold, palladium or platinum or by various combinations of these.

The most useful concentration of fog inhibitor is from about 0.05 to 1.0 mg. of fog inhibitor per mole of silver halide in the emulsion. Although higher amounts may be used, it is generally undesirable to use more than five times this upper limit since desensitization of the emulsion may result.

The antifoggant and stabilizing action was determined by incubation of the emulsions for one week at 120° F. and 42% relative humidity. The results of aging tests are tabulated in the following example and compare fog of the emulsions initially and after incubation, for emulsions with and without the stabilizing compound.

Example

A fast negative gelatino-silver halide emulsion was used for incorporation of the mercury compounds, in each

case the mercury compound being incorporated in the emulsion in the amount in milligrams per mole of silver halide in the emulsion as indicated in the following table. Samples of the emulsion with and without the mercury compound were exposed for $\frac{1}{50}$ second in an intensity scale sensitometer and developed for 5 minutes in a developer of the following composition:

	Grams
N-methyl p-aminophenol sulfate -----	2.2
Sodium sulfite, desiccated -----	72
Hydroquinone -----	8.8
Sodium carbonate, desiccated -----	48
Potassium bromide -----	4
Water to 1 liter.	

Samples of each of the coatings were stored for 7 days in an atmosphere of 42% relative humidity at 120° F. and were then exposed and developed in the same way. The following table shows the results of tests for fog before and after incubation. The various control samples shown in the table indicate that different samples of the original emulsion were used and slightly different initial fog was therefore obtained.

Compound	mg./mole	Fog	
		Initial	After Incubation
Control -----		0.35	1.25
1 -----	0.85	0.20	0.28
Control -----		0.35	1.20
2 -----	0.85	0.28	0.72
3 -----	0.85	0.29	0.74
4 -----	0.85	0.33	0.73
5 -----	1.425	0.16	0.81
6 -----	1.7	0.30	1.23
Control -----		0.30	1.80
7 -----	1.7	0.09	1.19

¹ Desensitized 0.1 log units.

Instead of incorporation in the silver halide emulsion, the fog-inhibitors of our invention may be incorporated in a colloid layer such as a gelatin layer on one or both sides of the support or they may be incorporated in a processing bath such as a developer or pre-bath.

The fog-inhibiting agents which we have described may be used in various kinds of photographic emulsions. In addition to being useful in ordinary non-sensitized emulsions they may also be used in orthochromatic, panchromatic and X-ray emulsions. If used with sensitizing dyes, they may be added to the emulsion before or after the dyes are added. Various silver salts may be used as the sensitive salts, such as silver bromide, silver iodide, silver chloride and mixtures of these. The mercury compounds may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers, or emulsions to be developed by solutions containing couplers.

The dispersing agents may be gelatin or other colloid such as collodion, albumen, cellulose derivatives or synthetic resins.

The compounds which we use were prepared as follows:

(2-aminobenzthiazole) mercuric iodide.—2-aminobenzthiazole (3.0 g.), mercuric iodide (2.25 g.) and ethanol (30 cc.) were heated for 1 hour on a steam bath to give a clear solution. On chilling pale green needles (1.3 g.) separated. They were well washed with ethanol and had M. P. 165°. (Found: S, 5.25; I, 42.45. $C_7H_6N_2Si_2Hg$ requires S, 5.3; I, 42.1 percent).

Bis-(2-aminobenzthiazole hydrobromide) mercuric chloride.—2-aminobenzthiazole hydrobromide (2.3 g.), mercuric chloride (1.35 g.) and ethanol (10 cc.) were boiled to dissolve and allowed to cool. Glassy aggregates (3.3 g.) separated. They formed colourless aggregates, M. P. 162–164°, from ethanol.

(2-aminobenzthiazole hydrobromide) mercuric bro-

mid.—2-aminobenzthiazole hydrobromide (2.3 g.), mercuric bromide (1.8 g.) and ethanol (10 cc.) were warmed gently for 2 minutes until dissolved. The addition of water precipitated an oil which soon crystallised. It (3.2 g.) formed flat, colourless needles, M. P. 168–170°, from ethanol.

(2-aminobenzthiazole hydrobromide) mercuric iodide.—2-aminobenzthiazole hydrobromide (2.3 g.), mercuric iodide (2.27 g.) and ethanol (10 cc.) were heated for 2 minutes to dissolve then poured into water. The yellow oil crystallized rapidly. It (3.5 g.) formed yellow needles, M. P. 158°, from glacial acetic acid.

(Benzthiazole hydriodide) mercuric iodide.—Benzthiazole (1.3 cc.), ethanol (10 cc.), hydriodic acid S. G. 1.97 (2 cc.) and mercuric iodide (4.5 g.) were warmed gently together to dissolve. The product oiled out, then crystallised on chilling. It (6.5 g.) formed colourless blades, M. P. 93–96°, from ethanol.

Bis-(2-methylbenzthiazole hydriodide) mercuric iodide.—2-methylbenzthiazole (1.4 cc.), ethanol (10 cc.), hydriodic acid, S. G. 1.97 (2 cc.) and mercuric iodide (4.5 g.) were heated to dissolve. The product then crystallized from the hot solution. It (5.7 g.) formed pale yellow needles, M. P. 178° (softens at ca. 158°), from ethanol.

(2-aminobenzthiazole methiodide) mercuric iodide.—2-imino-3-methylbenzthiazoline (1.65 g.), mercuric iodide (4.54 g.), hydriodic acid, S. G. 1.97 (2 cc.) and ethanol (10 cc.) were heated for 2 minutes on a steam bath. The iodide dissolved as a crystalline precipitate formed. It (5.5 g.) was collected after chilling, washed with ethanol and obtained as pale yellow crystals, M. P. 202–205°, from ethanol.

It will be understood that we contemplate as included within our invention all modifications and equivalents falling within the scope of the appended claims.

We claim:

1. A light-sensitive silver halide emulsion containing a small amount of a molecular addition compound of a mercuric halide with a benzothiazole selected from the group consisting of amino benzothiazoles and benzothiazole hydrohalides.

2. A light-sensitive silver halide emulsion containing a small amount of a molecular addition compound of a mercuric halide with 2-amino benzothiazole.

3. A light-sensitive silver halide emulsion containing a small amount of a molecular addition compound of mercuric iodide with 2-amino benzothiazole.

4. A light-sensitive silver halide emulsion containing a small amount of 2-amino benzothiazole mercuric iodide dihydroiodide.

5. A light-sensitive silver halide emulsion containing a small amount of bis-(2-amino benzothiazole hydrobromide) mercuric chloride.

6. A light-sensitive silver halide emulsion containing a small amount of 2-amino benzothiazole hydrobromide mercuric bromide.

7. A light-sensitive silver halide emulsion containing a small amount of bis-(2-methyl benzothiazole hydroiodide) mercuric iodide.

8. The method of reducing fog and loss of speed upon storage of a silver halide emulsion, which comprises incorporating in said emulsion at any stage prior to coating, a molecular addition compound of a mercuric halide with a benzothiazole selected from the group consisting of amino benzothiazoles and benzothiazole hydrohalides.

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