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2,728,664

PHOTOGRAPHIC EMULSIONS CONTAINING
MERCURY SALTS

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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 simple mercuric or mercurous salt of an inorganic or organic acid.

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 salts which may be used for the purpose of our invention include mercury halides, e. g., mercuric chloride, mercurous chloride, mercuric bromide, mercurous bromide, mercuric iodide and mercurous iodide, mercuric nitrate, mercurous nitrate, mercurous sulfate, and mercuric acetate, and the corresponding complexes formed with an excess of acid anion, e. g., $K_2Hg(CN)_4$ and K_2HgBr_4 .

A solution of the mercury salt which we employ, when added in suitable concentration before coating to unsensitized or optically sensitized silver halide emulsions, does not appreciably affect the sensitivity when measurements

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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. The mercury salt may be added to the emulsion in solution in any convenient solvent, such as water or alcohol.

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, (3) the second digestion or after-ripening to obtain increased sensitivity. (Mees, *The Theory of the Photographic Process*, 1942.) The fog-inhibiting agents may be added at any stage, e. g., after the final digestion. The most useful concentration range of fog inhibitor is from about 0.05 to 0.25 mg. of fog inhibitor per gram mole of silver halide in the emulsion. This amount will vary, e. g., depending on the silver halide used.

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

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

The emulsions may 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 antifoggant and stabilizing action was determined by incubation of the emulsions for one week. The results of aging tests are tabulated below and compare speed, gamma and fog of the emulsions with and without the stabilizing compound. A high speed orthochromatic bromiodide emulsion was used and it was treated as described in the following examples.

Example 1

To 1 liter of a gelatino-silver bromiodide emulsion containing 0.24 mole of silver halide per liter, optically sensitized with 20 mg. of 3,3'-diethyl-9-methylthiacarbocyanine bromide per liter, containing 10 cc. of 8% saponin solution, there were added the amounts of mercuric salts in alcohol solution, shown in the following table. The emulsion was coated on glass plates and the coated plates together with other plates coated at the same time and with the same emulsion to which no mercuric salt had been added were exposed on an Eastman type IIB Sensitometer and developed for five minutes at 68° F. in a developer of the following formula:

N-methyl-p-aminophenol sulfate..... 2.5
Sodium sulfite (desiccated)..... 30

Grams

Upon testing the fresh and incubated samples for speed, gamma and fog, the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		250	1.46	.09	265	1.46	.12
(I) Triethylene tetramine.....	36	295	1.63	.11	315	1.48	.20
I-mercuric chloride.....	0.12	295	1.54	.09	400	1.36	.14

Hydroquinone..... 2.5
Sodium metaborate..... 10
Potassium bromide..... 0.5
Water to 1 liter.

The plates with and without the mercuric salts were held at 120° F. and 20 percent relative humidity for one week and were then exposed and developed as indicated. The results of tests for speed, gamma and fog were as follows, speed being measured as 10/i, where i is the inertia:

Compound	mg./mole	Fresh Coating			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		540	1.62	.08	500	1.55	.13
Coating containing mercuric chloride.....	0.21	450	1.82	.08	460	1.51	.04
Coating containing mercuric iodide.....	0.08	500	1.73	.08	560	1.55	.08

Example 4

A medium speed gelatino-silver bromoiodide emulsion was digested with 20 mg. per mole of silver halide of allylthiourea and divided into portions to which were added the mercury compounds shown in the following table. These portions were coated on cellulose acetate film support, exposed on a Ib Sensitometer, and developed for 4 minutes in a developer having the same composition as that used in Example 3. Upon testing for speed, gamma and fog before and after incubation for 4 weeks

at 120° F., the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		255	1.24	.09	210	1.09	.50
Mercuric chloride.....	.078	220	1.20	.07	225	1.15	.26
Mercuric bromide.....	.078	235	1.24	.09	195	1.09	.40
Mercuric iodide.....	.078	210	1.28	.10	245	1.08	.33
Mercuric nitrate.....	.0195	255	1.25	.08	215	1.12	.34
Do.....	.039	265	1.23	.09	225	1.10	.36

Example 2

To portions of a gelatino-silver bromoiodide emulsion containing 0.24 mole of silver halide per liter, digested with a sulfur sensitizer such as disclosed in Sheppard U. S. Patent 1,574,944, and potassium chloroaurate, and optically sensitized with a mixture of cyanine and merocyanine dyes, there were added varying amounts of mercurous sulfate, and the emulsions were coated and treated as described in Example 1. Upon testing for speed, gamma and fog, the following results were obtained:

Compound	mg./mole	Fresh Coating			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		1,320	0.82	.09	1,260	0.87	.20
Mercurous sulfate.....	0.08	1,500	0.74	.09	1,550	0.78	.14
Do.....	0.8	1,260	0.79	.08	1,200	0.80	.08
Do.....	4.0	550	0.68	.06	460	0.66	.05

It can be seen that when larger amounts, say 4 mg. per mole, are used, the speed is considerably reduced.

Example 3

A medium speed gelatino-silver bromoiodide emulsion was sensitized with a mixture of gold and sulfur compounds as in Example 2, and divided into two portions. To one portion there was added the reduction sensitizer triethylene tetramine (U. S. Patent 2,518,698), and to a portion of the emulsion sensitized in this way there was added mercuric chloride. Each of the emulsions was incubated for three days at 120° F. and 20 per cent relative humidity, exposed on a Ib Sensitometer and developed in the following solution:

N-methyl-p-aminophenol sulfate..... 2.2
Hydroquinone..... 8.8
Sodium sulfite (desiccated)..... 96
Sodium carbonate, monohydrate..... 56
Potassium bromide..... 5
Water to 1 liter.

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 film 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 salt, such as silver bromide, silver iodide, silver chloride or mixed silver halides. 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.

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

What we claim is:

1. A silver halide emulsion substantially free from increase in fog and loss of speed upon storage, containing as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in the emulsion, of a mercury salt selected from the class consisting of mercuric chloride, mercurous chloride, mercuric bromide, mercurous bromide, mercuric iodide, mercurous iodide, mercuric nitrate, mercurous nitrate, mercurous sulfate, mercuric acetate, $K_2Hg(CN)_4$ and K_2HgBr_4 .

2. A silver halide emulsion substantially free from increase in fog and loss of speed upon storage, containing as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in the emulsion, of mercuric chloride.

3. A silver halide emulsion substantially free from increase in fog and loss of speed upon storage, containing as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in the emulsion, of mercuric iodide.

4. The method of reducing fog and loss of speed upon storage of a silver halide emulsion, which comprises in-

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corporating in said emulsion at any stage prior to coating, as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in said emulsion, of a mercury salt selected from the class consisting of mercuric chloride, mercurous chloride, mercuric bromide, mercurous bromide, mercuric iodide, mercurous iodide, mercuric nitrate, mercurous nitrate, mercurous sulfate, mercuric acetate, $K_2Hg(CN)_4$ and K_2HgBr_4 .

5. 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, as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in said emulsion, of mercuric chloride.

6. 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, as the only heavy metal salt other than silver halide, an appreciable and fog-inhibiting amount, but not more than about 0.25 mg. per mole of silver halide in said emulsion, of mercuric iodide.

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