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2,728,663

PHOTOGRAPHIC EMULSIONS CONTAINING MOLECULAR COMPOUNDS OF MERCURIC SALTS WITH AMINES

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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 molecular compound of a mercuric salt with an amine or with a salt of an amine.

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 usually does not appreciably affect the sensitometric values for sensitivity and fog when measurements are made soon after coating. However, when sensitometric meas-

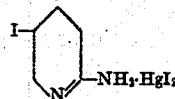
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urements are made after appreciable intervals of time under tropical or dry conditions of storage at elevated temperatures, these compounds do stabilize photographic speed and maintain fog at a low level.

The following compounds may be used according to our invention:

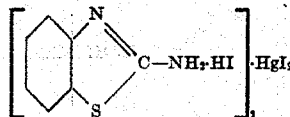
Molecular compounds of mercuric salts with amines or salts of amines

10 1.



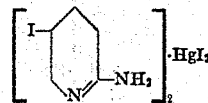
2-amino-5-iodopyridine mercuric iodide

15 2.



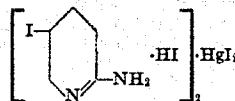
Bis(2-aminobenzothiazole hydroiodide) mercuric iodide

20 3.



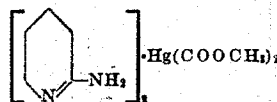
Bis(2-amino-5-iodopyridine) mercuric iodide

25 4.



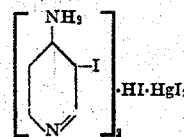
Bis(2-amino-5-iodopyridine hydroiodide) mercuric iodide

30 5.



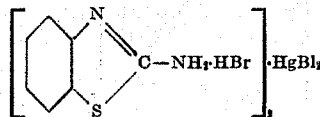
Bis(2-aminopyridine) mercuric acetate

35 6.



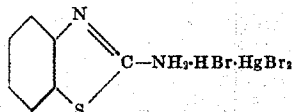
Bis(4-amino-3-iodopyridine) hydroiodide mercuric iodide

40 7.



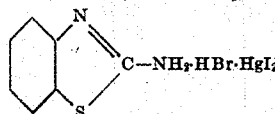
Bis(2-aminobenzothiazole hydrobromide) mercuric chloride

45 8.



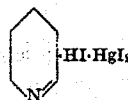
2-aminobenzothiazole hydrobromide mercuric bromide

50 9.



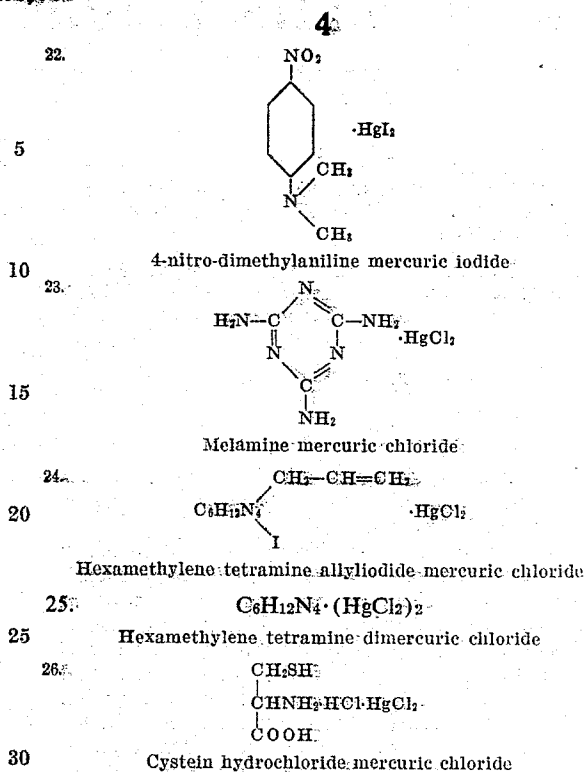
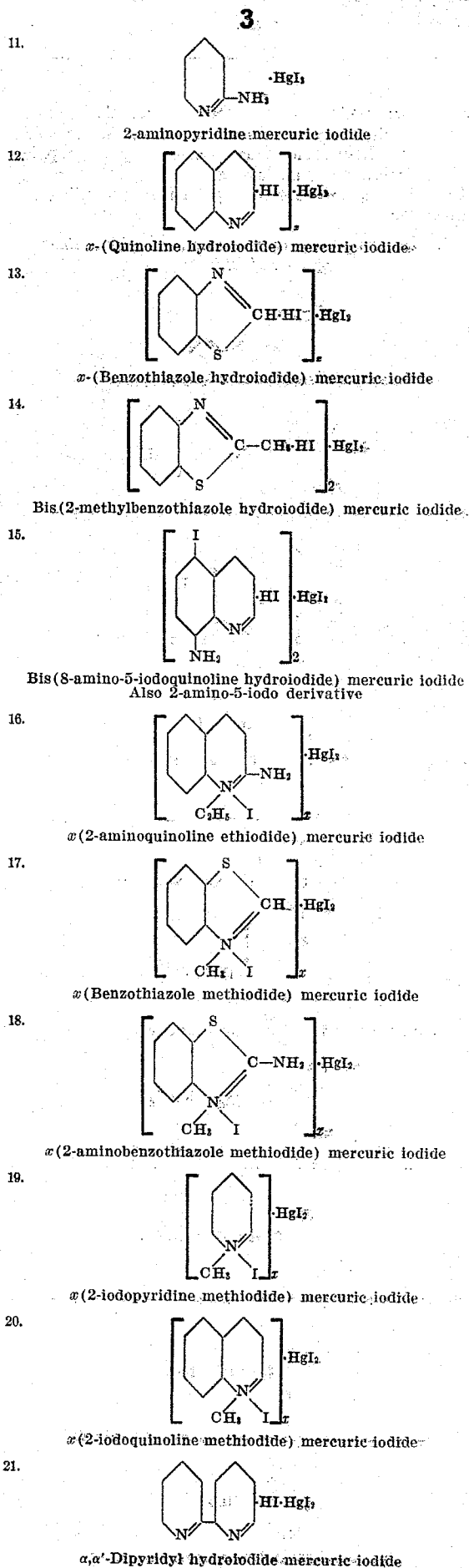
2-aminobenzothiazole hydrobromide mercuric iodide

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Pyridine hydroiodide mercuric iodide

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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 or noble metals such as gold or by various combinations of these as described more fully hereinafter.

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, we have found that few emulsions are likely to tolerate as much as 5 times this upper limit without serious desensitization.

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 Yutzky and Leermakers U. S. Patent 2,597,915. Suitable compounds are potassium chloroaurate, 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).

of silver halide per liter, and digested with a sulfur sensitizer such as disclosed in Sheppard U. S. Patent 1,574,944, and potassium chloroaurate. Upon development and testing for speed, gamma and fog, before and after incubation as in Example 1, the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		920	2.00	.14	1,260	1.49	.32
(2-amino-5-iodopyridine) ₂ ·2HI·HgI ₂	1.0	820	1.86	.14	1,180	1.67	.10
(4-amino-3-iodopyridine) ₂ ·HI·HgI ₂	1.0	800	1.81	.12	840	1.92	.06
(8-amino-5-iodoquinoline) ₂ ·2HI·HgI ₂	1.0	840	1.94	.15	1,120	1.48	.14
(2-amino-5-iodoquinoline) ₂ ·2HI·HgI ₂	1.0	860	1.76	.11	1,100	1.63	.11

The antifoggant and stabilizing action was determined by incubation of the emulsions for varying periods, usually about 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. Speed was measured as $10/i$, where i is the inertia.

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 methyl alcohol solution shown in the following table, the amount of mercuric salt being calculated per mole of silver halide. 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 *Ib* Sensitometer and developed for five minutes at 68° F. in a developer of the following formula:

	Grams
N-methyl paraminophenol sulfate.....	2.5
Sodium sulfite (desiccated).....	30
Hydroquinone.....	2.5
Sodium metaborate.....	10
Potassium bromide.....	0.5
Water to 1 liter.	

The plates with and without the mercuric compounds were held at 120° F. and 20% 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:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		540	1.62	.08	500	1.55	.13
(2-amino-5-iodo-pyridine) ₂ ·2HI·HgI ₂	1.0	470	1.68	.06	420	1.61	.08

EXAMPLE 2

Coatings were made as in Example 1 but using a gelatino-silver bromiodide emulsion, optically sensitized in the same way as in Example 1, containing 0.24 mole

EXAMPLE 3

A silver halide emulsion which had been chemically sensitized with a mixture of gold and sulfur sensitizers to which a reducing agent had been added, was tested with and without a mercury compound, in the following way:

One liter of a gelatino-silver bromiodide emulsion containing 0.24 mole of silver halide per liter was digested with a sulfur sensitizer such as disclosed in Sheppard U. S. Patent 1,574,944, and potassium chloroaurate, under conditions leading to the maximum speed in the final emulsion but without causing any appreciable fogging of the emulsion. A portion of the emulsion was then coated and dried.

After digestion to maximum speed there was added to the emulsion containing the sulfur and gold sensitizers a methanol solution of 0.01 g. of triethylene tetramine per mole of silver halide and the mixture digested for 20 minutes at 40° C., after which the emulsion was coated on a suitable film support. To other portions of emulsion digested with triethylene tetramine there was added prior to coating varying amounts of (2-amino-5-iodopyridine)₂·2HI·HgI₂. The resulting films were exposed on a *Ib* Sensitometer which gives intensity scale exposures to light of sunlight quality, and developed for 4 minutes at 20° C. in a developer of the following composition:

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

The coatings with and without the mercuric compounds were held for one week at 120° F. and 20% relative humidity and were then exposed and developed as indicated.

The following sensitometric results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		123	1.50	.03	112	1.21	.35
(I) Reduction sensitized with Triethylene tetramine.....	10	220	1.45	.04	98	1.23	.49
I+Hg compound.....	0.2	185	1.45	.05	133	1.18	.36
I+Hg compound.....	0.5	165	1.45	.04	133	1.26	.14

EXAMPLE 4

A positive-speed gelatino-silver bromiodide emulsion was prepared and digested with a sulfur sensitizer and a gold salt as in Example 3.

This emulsion was divided into three portions and one portion was digested for 30 minutes at 40° C. with 400 mg. of β,β' -diamino diethyl sulfide dihydrochloride per mole of silver halide.

To a portion of the latter there was added 0.4 mg. of (2-amino-5-iodopyridine) $_2 \cdot 2\text{HI} \cdot \text{HgI}_2$ per mole of silver halide, and all three portions were coated.

The resulting coatings were exposed on a *Ib* Sensitometer and developed for 5 minutes in a developer of the following composition:

	Grams
N-methyl-p-aminophenol sulfate.....	0.3
Sodium sulfite (desiccated).....	38
Hydroquinone.....	6
Sodium carbonate, monohydrate.....	22.5
Potassium bromide.....	0.9
Citric acid.....	0.7
Potassium metabisulfite.....	1.4
Water to 1 liter	

Other coatings were incubated as in Example 1. Upon testing for speed, gamma and fog the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		88	2.27	.03	96	1.82	.06
(I) Reduction sensitized with β,β' -diaminodiethyl sulfide di-HCl.....	400	115	2.30	.04	100	1.70	.74
I+Hg compound.....	0.4	98	2.43	.04	130	1.71	.55

EXAMPLE 5

A medium-speed gelatino-silver bromiodide emulsion was digested with 20 mg. per mole of silver halide of allyl-

thiourea and divided into two portions to one of which there was added 4-nitro-dimethylaniline hydroiodide mercuric iodide as shown in the following table. Each of these emulsions was coated on a cellulose acetate support and the coatings were exposed on a *Ib* Sensitometer and developed for four minutes in a developer of the same composition as that used in Example 3. Upon

testing for speed, gamma and fog, before and after in-

cubation 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
Mercury compound.....	.0195	265	1.20	.08	200	1.22	.28

EXAMPLE 6

A gelatino-silver bromiodide emulsion was chemically sensitized with sulfur and gold sensitizers as in Example 3 and was then digested to optimum speed and divided into portions to which were added the various mercury antifoggants shown in the following table. These portions were coated and exposed on a *Ib* Sensitometer and developed for five minutes in a developer of the following composition:

	Grams
N-methyl-p-aminophenol sulfate.....	2.5
Hydroquinone.....	2.5
Sodium sulfate (desiccated).....	30
Sodium metaborate.....	10
Potassium bromide.....	0.5
Water to 1 liter	

Upon testing for speed, gamma and fog, before and after incubation as in Example 1, the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....		1,500	0.86	.08	1,450	0.81	.19
Bis(2-aminobenzothiazole-HI)-HgI $_2$	0.24	1,800	0.80	.03	1,780	0.76	.10
(2-aminobenzothiazole-HBr)-HgBr $_2$	0.24	1,500	0.83	.07	1,750	0.76	.08
Pyridine HI-HgI $_2$	0.06	1,500	0.81	.06	1,120	0.82	.06
x(benzothiazolemethiodide)-HgI $_2$	0.96	1,400	0.79	.06	1,320	0.75	.07
x(2-aminobenzothiazole methiodide)HgI $_2$	0.96	1,480	0.80	.07	1,380	0.76	.07

EXAMPLE 7

A medium-speed gelatino-silver bromiodide emulsion was sensitized with 20 mgs. of allyl thiourea per mole of silver halide and 1.75 mgs. of potassium chloroaurate per mole of silver halide and digested for 20 minutes at 70° C. To portions of this emulsion there were added varying amounts of 4-nitrodimethylaniline hydroiodide

mercuric iodide as shown in the following table. These emulsions were coated on a cellulose acetate support, exposed on a *Ib* Sensitometer and developed for 3 minutes in a developer having the same composition as that used in Example 3. Upon incubation and testing the samples as in Example 3, the following results were obtained:

Compound	mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control.....	-----	420	.79	.09	390	.56	.39
Mercury compound.....	.0275	290	.99	.09	430	.68	.18
Do.....	.055	450	.86	.08	360	.82	.16
Do.....	.0825	370	.87	.09	490	.66	.16

The compounds listed above were prepared as follows:

Compound 1.—2-amino-5-iodopyridine mercuric iodide

2.2 grams of 2-amino-5-iodopyridine and 4.5 grams of mercuric iodide in 50 cc. of ethyl alcohol were heated under refluxing condenser until the red mercuric iodide had disappeared. The solution was filtered hot and cooled to 10° C. in an ice bath. The tan colored crystals were filtered, washed once with 10 cc. of absolute ethyl alcohol and dried. The yield of the complex of M. P. 140–145° C. was 5.9 grams, which is 88% of the theoretical amount of 6.7 grams.

Compound 2.—Bis(2-aminobenzothiazole hydroiodide) mercuric iodide

To a solution of 22.7 g. (0.05 mole) of mercuric iodide and 25.6 g. of 50% hydroiodic acid in 100 cc. distilled water was added, with stirring, 15 g. (0.1 mole) of 2-aminobenzothiazole. The mixture was heated on the steam bath for 30 minutes. During this time an oil separated. This oil was dissolved by slowly adding absolute ethyl alcohol. The solution was treated with a small amount of Norit (decolorizing carbon) and filtered hot. Upon cooling, the new compound crystallized. The crystallization was finished by the addition of a small amount of water, and the product was filtered and dried. There was obtained 48.6 g. (48% of the theoretical amount of 100.8 g.) of the product which had a M. P. of 164–166° C.

Compound 3.—Bis(2-amino-5-iodopyridine) mercuric iodide

This compound was prepared by the the same method as used to prepare Compound 1, using double the amount of 2-amino-5-iodopyridine.

Compound 4.—Bis(2-amino-5-iodopyridine hydroiodide) mercuric iodide

90.8 grams of mercuric iodide were dissolved in a solution of 101 grams of 57% hydriodic acid, which had been freshly distilled from hypophosphorous acid, dissolved in 1100 cc. of distilled water. This solution was filtered into a 4-liter beaker and to it was added with stirring a filtered solution of 88 grams of mercury-free 2-amino-5-iodopyridine dissolved in 1100 cc. of absolute ethyl alcohol. This was cooled with stirring to 0° C. in an ice salt bath, and filtered. There were obtained 189 grams, M. P. 183–185° C., of tan-colored product. This is 67.7% of the theoretical amount of 279 grams.

Compound 5.—Bis(2-aminopyridine) mercuric acetate

2-aminopyridine (1.84 g.) was dissolved in water (16 cc.), and mercuric acetate (2.56 g.) was added and the whole heated for 2 minutes. The white powder was collected and washed thoroughly with ethanol after which it had M. P. 166–167°.

Compound 6.—Bis(4-amino-3-iodopyridine) hydroiodide mercuric iodide

This compound was made by the same method as that used for Compound 4, using 4-amino-3-iodopyridine instead of 2-amino-5-iodopyridine.

Compound 7.—Bis(2-aminobenzothiazole 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 colorless aggregates, M. P. 162–164°, from ethanol.

Compound 8.—2-aminobenzothiazole hydrobromide mercuric bromide

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 crystallized. It (3.2 g.) formed flat, colorless needles, M. P. 168–170°, from ethanol.

Compound 9.—2-aminobenzothiazole hydrobromide mercuric iodide

2-aminobenzthiazole hydrobromide (2.3 g.), mercuric iodide (2.27 g.) and ethanol (10 cc.) were heated for 20 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.

Compound 10.—Pyridine hydroiodide mercuric iodide

Pyridine (0.8 g.), hydriodic acid (s. g. 1.97) (2 cc.), mercuric iodide (4.5 g.) and ethanol were heated gently with swirling. The iodide dissolved rapidly. Gradual cooling caused the whole to solidify. It (5.8 g.) after washing with a little ethanol was obtained as pale yellow flakes, M. P. 174°, from ethanol or acetic acid.

Compound 11.—2-aminopyridine mercuric iodide

Mercuric iodide, 4.54 g., and 2-aminopyridine, 2 g., and chloroform, 15 cc. were heated under a refluxing condenser until the red color of the mercuric iodide had disappeared. The solution was filtered, concentrated to incipient crystallization and cooled. The pale yellow crystalline product was filtered and dried. There was obtained 2.2 g. of 2-aminopyridine mercuric iodide, melting at 130–131° C.

Compound 12.—x(Quinoline hydroiodide) mercuric iodide

Quinoline (1.3 cc.), ethanol (10 cc.), hydriodic acid (s. g. 1.97) (2 cc.) and mercuric iodide (4.5 g.) were warmed gently to dissolve. The product oiled out on cooling, then it solidified. It (5.0 g.) after an ethanol wash formed yellow crystals, M. P. 162°, from ethanol.

Compound 13.—x(Benzothiazole hydroiodide) mercuric iodide

Benzothiazole (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 crystallized on chilling. It (6.5 g.), formed colorless blades, M. P. 93–96°, from ethanol.

Compound 14.—Bis(2-methylbenzothiazole hydroiodide) 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.

11

Compound 15.—*Bis(8-amino-5-iodoquinoline hydroiodide) mercuric iodide*

This compound was made by the same method as that used for Compound 4, using 8-amino-5-iodoquinoline instead of 2-amino-5-iodopyridine.

Compound 16.—*x(2-aminoquinoline ethiodide) mercuric iodide*

2-aminoquinoline ethiodide (3.0 g.) mercuric iodide (4.5 g.) and ethanol (100 cc.) were refluxed to dissolve. The crystals (7.2 g.) were collected after chilling and formed heavy yellow prisms, M. P. 186–188° from ethanol.

Compound 17.—*x(Benzothiazole methiodide) mercuric iodide*

This compound was prepared by the method used to prepare Compound 18, using the simple 3-methyl benzthiazoline instead of the 2-imino derivative.

Compound 18.—*x(2-aminobenzothiazole 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.

Compound 19.—*x(2-iodopyridine methiodide) mercuric iodide*

2-iodopyridine methiodide (3.5 g.), mercuric iodide (4.5 g.) and ethanol (20 cc.) were refluxed for 15 minutes. It (7.1 g.) formed a yellow powder, M. P. 178–179°, from much ethanol.

Compound 20.—*x(2-iodoquinoline methiodide) mercuric iodide*

2-iodoquinoline methiodide (4.0 g.), mercuric iodide (4.5 g.) and ethanol (20 cc.) were refluxed for 15 minutes. The heavy yellow precipitate (6.5 g.) formed yellow needles, M. P. 154–155°, from much ethanol.

Compound 21.—*α,α'-Dipyridyl hydroiodide mercuric iodide*

This compound was made by the same method as that used for Compound 4, using α,α'-dipyridyl instead of 2-amino-5-iodopyridine.

Compound 22.—*4-nitro-dimethylaniline mercuric iodide*

To a solution of 3.3 grams of 4-nitrodimethylaniline in 100 cc. of absolute ethyl alcohol there was added 4.5 grams of HgI₂, and the mixture heated under reflux until the red color disappeared. The solution was filtered hot, cooled and again filtered. The solution was concentrated to one-fourth volume and cooled, whereupon the product crystallized out as crystals having a melting point of 150–155° C.

Compound 23.—*Melamine mercuric chloride*

A solution of 27 g. mercuric chloride in 100 cc. absolute ethyl alcohol was added to a slurry of 12.6 g. of melamine in 500 cc. absolute ethyl alcohol. The mixture was refluxed on a steam bath for 24 hours. While hot, the white solid was filtered, washed with 50 cc. absolute ethyl alcohol and dried. The yield of melamine mercuric chloride was quantitative and the solid had a M. P. of 295° C.

Compound 24.—*Hexamethylene tetramine allyliodide mercuric chloride*

This compound was prepared by the same method as Compound 25, using hexamethylene tetramine alloiodide instead of the simple hexamethylene tetramine.

12

Compound 25.—*Hexamethylene tetramine dimercuric chloride*

A filtered solution of 14 g. (0.1 mole) of hexamethylene tetramine in 475 cc. absolute ethyl alcohol was added all at once with vigorous stirring to a filtered solution of 54 g. (0.2 mole) mercuric chloride in 175 cc. of absolute ethyl alcohol. There was an immediate precipitation of a white solid. The mixture was permitted to stand at room temperature for three hours. After it was filtered, the mixture was washed once with 50 cc. absolute ethyl alcohol and dried. The yield of hexamethylene dimercuric chloride which decomposed at 235° C. was almost quantitative.

Compound 26.—*Cystein hydrochloride mercuric chloride*

This compound was prepared by the same method as Compound 23, using cystein hydrochloride instead of melamine.

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 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.

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 mercury salt with a nitrogen compound of the class consisting of (1) heterocyclic nitrogen compounds in which at least 3 bonds of the heterocyclic nitrogen atom are attached to carbon, (2) amine-substituted mononuclear aromatic compounds in which 3 bonds of the amino-nitrogen atom are attached to carbon, (3) their halogen acid salts, and (4) the halogen acid salts of aliphatic amines containing at least 3 carbon atoms.

2. A light-sensitive silver halide emulsion containing a small amount of a molecular addition compound of a mercury salt with a halogen acid salt of a heterocyclic nitrogen compound in which at least 3 bonds of the heterocyclic nitrogen atom are attached to carbon.

3. A light-sensitive silver halide emulsion containing a small amount of a molecular addition compound of a mercury salt with a halogen acid salt of a primary amine substituted heterocyclic nitrogen compound in which at least 3 bonds of the heterocyclic nitrogen atom are attached to carbon.

4. A light-sensitive silver halide emulsion containing a small amount of a double salt of a pyridine hydrohalide and a mercuric salt.

5. A light-sensitive silver halide emulsion containing a small amount of a double salt of a pyridine hydroiodide and a mercuric halide.

6. A light-sensitive silver halide emulsion containing a small amount of a double salt of a 5-iodopyridine hydroiodide and a mercuric halide.

7. A light-sensitive silver halide emulsion containing a

small amount of bis(2-amino-5-iodopyridine hydroiodide) mercuric iodide.

8. A light-sensitive silver halide emulsion containing a small amount of bis (4-amino-3-iodopyridine) hydroiodide mercuric iodide.

9. A light-sensitive silver halide emulsion containing a small amount of pyridine hydroiodide mercuric iodide.

10. A light-sensitive silver halide emulsion containing a small amount of bis(8-amino-5-iodoquinoline hydroiodide) mercuric iodide.

11. A light-sensitive silver halide emulsion containing a small amount of 4-nitro-dimethylaniline hydroiodide mercuric iodide.

12. A light-sensitive sulfur-sensitized silver halide emulsion containing a small amount of a molecular addition compound of a mercury salt with a nitrogen compound of the class consisting of (1) heterocyclic nitrogen compounds in which at least 3 bonds of the heterocyclic nitrogen atom are attached to carbon, (2) amine-substituted mononuclear aromatic compounds in which 3 bonds of the amino-nitrogen atom are attached to carbon, (3) their halogen acid salts, and (4) the halogen acid salts of aliphatic amines containing at least 3 carbon atoms.

13. The emulsion of claim 12 which is additionally chemically sensitized with gold salts.

14. A light-sensitive sulfur sensitized silver halide emulsion additionally chemically sensitized with gold salts and containing a small amount of a double salt of a pyridine hydrohalide and a mercuric salt.

15. The emulsion of claim 12 which is additionally chemically sensitized with reduction sensitizers.

16. A light-sensitive sulfur sensitized silver halide emulsion additionally chemically sensitized with reduction sensitizers and containing a small amount of a double salt of a pyridine hydrohalide and a mercuric salt.

17. The emulsion of claim 1 which is chemically sensitized with reduction sensitizers.

18. The emulsion of claim 12 which is additionally chemically sensitized with both gold salts and reduction sensitizers.

19. 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 small amount of a molecular addition of a mercury salt with a nitrogen compound of the class consisting of (1) heterocyclic nitrogen compounds in which at least 3 bonds of the heterocyclic nitrogen atom are attached to carbon, (2) amine-substituted mononuclear aromatic compounds in which 3 bonds of the amino-nitrogen atom are attached to carbon, (3) their halogen acid salts, and (4) the halogen acid salts of aliphatic amines containing at least 3 carbon atoms.

20. 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 double salt of a 5-iodopyridine hydroiodide and a mercuric halide.

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