United States Patent Office 2,784,090 Patented Mar. 5, 1957

2,784,090

STABILIZATION OF EMULSIONS SENSITIZED WITH ONIUM COMPOUNDS

Burt H. Carroll, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application November 8, 1952, Serial No. 319,615

7 Claims. (Cl. 96—107)

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 film 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 known that the effective sensitivity of photographic silver halide emulsions may be increased by adding to them cationic surface active ammonium salts (Carroll U. S. Patent 2,271,623), cationic surface active sulfonium salts (Carroll and Allen U. S. Patent 2,275,727), onium salts comprising a quaternary ammonium or other onium salt group linked through its onium atom by a bivalent organic radical to the ammonium or other onium atom of a similar salt group (Carroll and Allen U. S. Patent 2,288,226) and certain other cyclammonium quaternary and non-quaternary salts (Carroll and Spence U. S. Patent 2,334,864). One disadvantage of the use of such compounds for chemically sensitizing silver halide emulsions is the tendency to increase fog in the emulsion upon storage, especially at elevated temperatures and humidities. The antifoggants previously available have not been entirely satisfactory for controlling this tendency since they desensitize the emulsion when added in sufficient amounts to stop the fog on incubation of the emulsion.

It is therefore an object of the present invention to provide a method for stabilizing photographic emulsions sensitized with certain onium compounds. A further object is to provide a means for reducing the fog produced upon keeping of emulsions so sensitized, especially emulsions stored under tropical or other adverse conditions. A still further object is to provide a means for stabilizing the speed and contrast of emulsions so sensitized. Other objects will appear from the following description of my invention.

These objects are accomplished in general by adding to the emulsion sensitized with the onium compounds, certain organic compounds of mercury in which the mercury atom has at least one ionizable bond, or simple water-soluble mercury salts of an inorganic or organic acid.

The onium compounds used to sensitize the emulsions are generally of two classes: (1) cationic surface active ammonium, phosphonium or sulfonium compounds, (2) non-surface active onium salts of the type of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups linked through the onium atom by a bivalent organic radical to the onium atom of another quaternary ammonium, quaternary phosphonium or ternary sulfonium salt group, and (3) non-surface-active cyclammonium quaternary salts in which the quaternary nitrogen atom is the nitrogen atom of a pyridine nucleus.

The cationic surface active onium compounds are described in U. S. Patents 2,271,623 and 2,275,727 referred to above and include compounds such as lauryl triethyl ammonium perchlorate, decyl pyridinium perchlorate and n-nonyl dimethyl sulfonium p-toluene sulfonate.

The polyonium salts containing a quaternary ammonium, quaternary phosphonium or ternary sulfonium salt group linked through the onium atom by a bivalent organic radical to the onium atom of another quaternary ammonium, quaternary phosphonium or ternary sulfonium salt group are described in U. S. Patent 2,288,226 referred to above. They include both cationic surface active onium compounds and non-surface active onium compounds both of which are included within the scope of the emulsions treated with antifoggants according to my invention. Typical compounds of this class which may be used to sensitize photographic emulsions are ethylene bis-(oxy-methyl pyridinium perchlorate), ethylene bis-(oxy-methyl triethyl phosphonium chloride), N,N'-trimethylene bis-(2-undecyl imidazolinium bromide), etc.

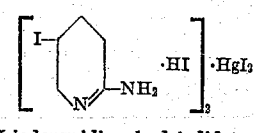
The non-surface-active cyclammonium quaternary salts of the pyridine type are described in U. S. Patent 2,334,864 referred to above.

The organic compounds of mercury used to stabilize emulsions sensitized with the onium compounds are of three types: (1) molecular compounds of mercuric salts with amines or salts of amines, (2) organic compounds of mercury in which the mercury atom is attached by a non-ionic or covalent bond to an organic nucleus, especially a heterocyclic organic nucleus and by an ionic or electrovalent bond to an anion, and (3) simple salts of mercury with organic or inorganic acids.

The principal purpose of my 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 I propose to use are added to the emulsion at any stage during the process of manufacture prior to coating the emulsion. 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.

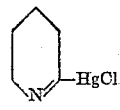
A solution of the mercury compound which I employ when added in suitable concentration before coating to unsensitized or optically sensitized silver halide emulsions does not appreciably affect the sensitivity and fog when measurements are made soon after coating. However, when sensitometric measurements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

Any of the mercuric compounds disclosed in Allen, Byers and Murray U. S. Patent 2,728,663, may be used to stabilize the emulsions according to my invention. The following is typical:



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

Any of the compounds disclosed in Leubner and Murray U. S. Patent 2,728,665 may also be used. The following is typical:



2-pyridyl mercuric chloride

Any of the compounds disclosed in Carroll and Murray U. S. Patent 2,728,664 may also be used. These compounds include mercuric chloride, mercurous chloride, mercuric bromide, mercurous bromide, mercuric iodide, mercurous iodide, mercuric acetate, mercuric nitrate, mercurous sulfate, etc.

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 photographic emulsions which I use are of the developing-out type and best results have been obtained with gelatino-silver bromoiodide emulsions. However, emulsions of varying halide content may be used.

The emulsions may be chemically sensitized by any of the accepted procedures, in addition to or in combination with the sensitizing with onium compounds. The emulsion 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 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 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 chloroaurite, 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 sensitizing and stabilizing combinations of onium compounds and mercuric compounds 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. I have found, however, that both unsensitized emulsions and emulsions sensitized with cyanine or merocyanine dyes or both may be treated with the onium compounds and mercuric compounds according to my invention.

The most useful concentration of the mercuric compound in the emulsion is from about 0.05 mg. to 1.0 mg. per gram mole of silver halide in the emulsion. Although higher amounts may be used, I have found that no emulsion is likely to tolerate as much as five times this upper limit without serious desensitization. Optimum concentrations are about 1 mg. per gram mole of silver halide for the molecular compounds of mercuric salts with amines or salts of amines, about 0.1 mg. per gram mole of silver halide for the organic compounds of mercury in which the mercury atom is attached by a non-ionic bond to an organic nucleus and by an ionic bond to an anion, and from 0.05 mg. to 0.5 mg. for the simple mercuric salts such as mercuric chloride and mercuric iodide.

The stabilizing action was determined by incubation of the emulsions for varying periods of time at 120° F. and 20% relative humidity. The result of aging tests are tabulated below and compare speed, gamma and fog of the emulsions with and without the stabilizing compound.

Example 1

A medium speed gelatino-silver bromoiodide emulsion containing 0.24 mole of silver halide per liter was digested with a sulfur compound such as disclosed in Sheppard U. S. Patent 1,574,944 and potassium chloroaurate and divided into two portions. To one portion of this emulsion there was added the reduction sensitizer triethylene tetramine (U. S. Patent 2,518,698), and to another portion was added a mixture of triethylene tetramine and ethylene bis(oxy-methyl pyridinium perchlorate). To separate portions of the emulsion sensitized in this way there were added the mercuric compounds shown in the table below. Each of these emulsions was coated and the coatings were exposed on a Ib sensitometer and developed for three minutes in a developer of the following composition:

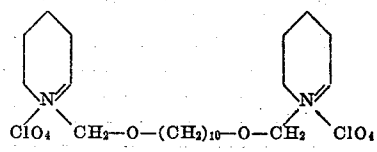
	Grams
N-methyl-p-aminophenal sulfate	2.2
Hydroquinone	8.8
Sodium sulfite (desiccated)	96
Sodium carbonate, monohydrate	56
Potassium bromide	5
Water to 1 liter	

The coatings with and without the various addenda were held at 120° F. and 20% relative humidity for three days 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 3 days' Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control		235	1.85	.11	240	1.82	.11
Triethylene tetramine	36	310	1.67	.09	315	1.62	.11
I {Triethylene tetramine / Ethylene bis (oxy-methyl pyridinium perchlorate)	36 / 480	470	1.57	.21	500	1.50	.21
I + (2-Amino-5-iodo-pyridine)$_2$·HI·HgI$_2$	0.3	400	1.63	.19	500	1.48	.18
I + Mercuric chloride	0.06	440	1.55	.21	530	1.42	.20
I + Pyridyl mercuric chloride	0.3	420	1.60	.16	440	1.54	.16

Example 2

A medium speed gelatino-silver bromoiodide 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. A portion of this emulsion was sensitized with 33 mgs. per mole of silver halide of decamethylene-bis-(oxymethyl pyridinium perchlorate):

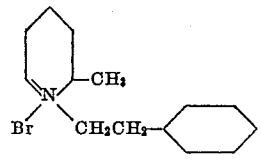


To portions of the emulsion sensitized in this way there were added the mercury compounds shown in the following table. Each of the emulsions was coated on a cellulose acetate support, exposed on a Ib sensitometer and developed for 3 minutes in a developer having the same composition as that used in Example 1. Upon incubation of each of the coatings for one week at 120° F. and testing both sets for speed, gamma and fog, the following results were obtained:

Compound	Mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control		530	0.68	0.07	740	0.72	0.18
(I) With decamethylene bis-(oxymethyl pyridinium perchlorate)	33	650	.76	.12	740	.72	.28
I+2-chloromercurithiophene	.275	520	.81	.12	860	.70	.16
Do	.550	380	.89	.12	760	.59	.09
I+8-chloromercuriquinoline	.825	560	.76	.12	760	.68	.17

Example 3

A medium speed gelatino-silver bromoiodide emulsion made in the same way as in Example 2 was sensitized with α-picolinium-β-phenyl-ethobromide:



instead of the pyridinium salt used in Example 2. Portions of the emulsion were treated and tested exactly as described in Example 2, with the following results:

Compound	Mg./mole	Fresh Test			After Incubation		
		Speed	Gamma	Fog	Speed	Gamma	Fog
Control		610	0.61	0.07	630	0.71	0.10
(I) With α-picolinium-β-phenyl-ethobromide	4,000	660	.73	.08	1,500	.58	.21
I+8-chloro-mercuriquinoline	.825	560	.73	.08	1,550	.51	.12
I+mercuric iodide	.083	740	.65	.08	1,780	.54	.18
I+mercuric nitrate	.083	630	.67	.07	1,650	.54	.17

Instead of incorporation in the silver halide emulsion the fog inhibitors of my 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 I 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 stabilizers and onium 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 I contemplate as included within my invention all modifications and equivalents falling within the scope of the appended claims.

I claim:

1. A light-sensitive silver halide emulsion sensitized with an onium compound selected from the class consisting of (1) cationic surface-active onium compounds of the class consisting of ammonium, phosphonium and sulfonium compounds, (2) non-surface active onium salts of the class consisting of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups linked through the onium atom by a bivalent organic radical to the onium atom of another onium salt group of the class consisting of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups, and (3) non-surface active cyclammonium quaternary salts in which the quaternary nitrogen atom is the nitrogen atom of a pyridine nucleus, said emulsion containing from .05 to 1 mg. per gram mole of silver halide in the emulsion of a mercury compound selected from the class consisting of (1) a molecular addition compound of a mercury salt with a nitrogen compound of the class consisting of heterocyclic nitrogen compounds in which at least three bonds of the heterocyclic nitrogen atom are attached to carbon, amine-substituted mononuclear aromatic compounds in which three bonds of the amino nitrogen atom are attached to carbon, their halogen acid salts, and the halogen acid salts of aliphatic amines containing at least three carbon atoms, (2) organic compounds of mercury in which the mercury atom is attached by a non-ionic mercury to carbon bond to a cyclic organic nucleus and by an ionic bond to an anion, and (3) simple salts of mercury with organic and inorganic acids.

2. A light-sensitive silver halide emulsion sensitized with ethylene bis-(oxymethyl pyridinium perchlorate), said emulsion containing a small amount of bis-(2-amino-5-iodopyridine hydriodide) mercuric iodide.

3. A light-sensitive sulfur-sensitized silver halide emulsion sensitized with an onium compound selected from the class consisting of (1) cationic surface-active onium compounds of the class consisting of ammonium, phosphonium and sulfonium compounds, (2) non-surface active onium salts of the class consisting of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups linked through the onium atom

by a bivalent organic radical to the onium atom of another onium salt group of the class consisting of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups, and (3) non-surface active cycl-ammonium quaternary salts in which the quaternary nitrogen atom is the nitrogen atom of a pyridine nucleus, said emulsion containing from .05 to 1 mg. per gram mole of silver halide in the emulsion of a mercury compound selected from the class consisting of (1) a molecular addition compound of a mercury salt with a nitrogen compound of the class consisting of heterocyclic nitrogen compounds in which at least three bonds of the heterocyclic nitrogen atom are attached to carbon, amine-substituted mononuclear aromatic compounds in which three bonds of the amino nitrogen atom are attached to carbon, their halogen acid salts, and the halogen acid salts of aliphatic amines containing at least three carbon atoms, (2) organic compounds of mercury in which the mercury atom is attached by a non-ionic mercury to carbon bond to a cyclic organic nucleus and by an ionic bond to an anion, and (3) simple salts of mercury with organic and inorganic acids.

4. The emulsion of claim 3 which is additionally chemically sensitized with gold salts.

5. The emulsion of claim 3 which is additionally chemically sensitized with reduction sensitizers.

6. The emulsion of claim 3 which is additionally chemically sensitized with both gold salts and reduction sensitizers.

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

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