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FOG INHIBITOR FOR PHOTOGRAPHIC EMULSIONS

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6 Claims. (Cl. 95-7)

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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. 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 under which the film or plate is stored such as 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 salt having the structure RuX_3 where X is a halogen atom such as chlorine, bromine or iodine, for example, ruthenium chloride, $RuCl_3$, ruthenium bromide, $RuBr_3$ and ruthenium iodide, RuI_3 .

The 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. The fog inhibitors which we propose to use are added to the emulsion during the process of

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manufacture 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.

A solution of ruthenium chloride when added in suitable concentration before coating to unsensitized 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 after appreciable intervals of time under tropical or dry conditions of storage at elevated temperatures, however, this compound does 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, (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 may be added before digestion. The most useful concentration range of fog inhibitor is from .260 to 3.90 gm. of fog inhibitor per kilogram of silver nitrate used in making the emulsion and converted to silver halide. This amount will vary, e. g. depending on the silver halide used.

The anti-foggant and stabilizing action was determined by incubation of the emulsions under simulated tropical conditions and also by incubation in dry heat at 120° F. for various lengths of time. The results of these aging tests are tabulated here and compare speed, gamma, and fog of the emulsions with and without the anti-foggant and stabilizing compound. For the tests from which the following tabulation was made, was used a high-speed bromiodide emulsion exposed on an Eastman type IIB sensitometer and developed for five minutes at 68° F. in a developer of the following composition:

	Grams
Monomethyl paraminophenol sulfate	2.5
Sodium sulfite (desiccated)	30
Hydroquinone	2.5
Sodium metaborate	10
Potassium bromide	0.5
Water to one liter	

The results for ruthenium chloride are as follows: silver iodide, silver chloride and mixtures of these.

Sample No.	Gms. of Compound per Kg. AgNO ₃ (Converted to AgX) in Emulsion	Original			6 days 120° C.		
		10/i speed	Gamma	Fog	10/i speed	Gamma	Fog
1-----	0.0	1,900	1.46	.11	1,150	1.75	.32
2-----	0.0	1,780	1.52	.12	840	1.65	.34
3-----	0.258	1,550	1.44	.11	1,020	1.14	.26
4-----	1.031	1,400	1.50	.08	960	1.31	.25
5-----	1.031	1,300	1.33	.14	660	1.19	.32

Sample No.	9 days 120° F.			2 wks. tropical			4 wks. tropical		
	10/i speed	Gamma	Fog	10/i speed	Gamma	Fog	10/i speed	Gamma	Fog
1-----	1,350	1.43	.33	780	1.16	.64	-----	-----	-----
2-----	680	1.67	.28	225	1.35	.63	275	.86	.82
3-----	900	1.37	.30	480	1.34	.30	710	1.07	.34
4-----	900	1.37	.26	650	1.22	.22	680	1.14	.26
5-----	440	1.36	.43	350	1.19	.22	460	1.01	.30

¹ Different batches RuCl₃.

One of the chief advantages of our invention is the extent of stabilization action over a wide range of climatic conditions.

The fog-inhibiting compounds of the invention are unique in the respect that they represent a group of a very limited number of simple salts of metals of the platinum group which are effective in inhibiting fog in photographic emulsion. Another compound of this limited group Pd(NO₃)₂ is disclosed in the copending U. S. application Serial No. 792,844, filed December 19, 1947, in the names of Smith and Stauffer, now Patent No. 2,472,627, issued June 7, 1949.

The compounds when employed for use in emulsions are dissolved in water at a convenient concentration and added to a melted gelatino dye silver halide photographic emulsion in quantities ranging up to about 3.90 grams per kilogram of silver nitrate converted to silver halide. The emulsion is coated on a suitable support such as glass, film, or other, and dried in the conventional manner.

We also contemplate as a part of our invention those cases where it is desirable to coat the anti-foggant in a colloid layer, such as gelatin, on either or both sides of or also in the silver halide emulsion layer so that the anti-foggant is in at least one of the layers. In these cases we use the same or a slightly greater ratio of rare metal salt to silver halide than when the salt is in the emulsion layer.

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,

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.

What we claim is:

1. A silver halide emulsion containing a compound having the structure RuX₃ where X is a halogen atom.
2. A silver halide emulsion containing a compound having the structure RuX₃ where X is a halogen atom, said compound being present in an amount of from 0.26 to 3.9 grams per kilogram of silver nitrate used in making said emulsion and converted to silver halide.
3. A silver halide emulsion containing ruthenium chloride.
4. A silver halide emulsion containing ruthenium bromide.
5. A silver halide emulsion containing ruthenium iodide.
6. A light-sensitive photographic element comprising a silver halide emulsion layer and a colloid layer contiguous to said silver halide emulsion layer, at least one of said layers containing a compound having the structure RuX₃ where X is a halogen atom.

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REFERENCES CITED

The following references are of record in the file of this patent:

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