

UNITED STATES PATENT OFFICE

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STABILIZING PHOTOGRAPHIC EMULSIONS WITH CHLOROPALLADITES AND CHLORO- PLATINITES

Adrian P. H. Trivelli and William F. Smith, Roch-
ester, N. Y., assignors to Eastman Kodak Com-
pany, Rochester, N. Y., a corporation of New
Jersey

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4 Claims. (Cl. 95—7)

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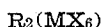
This invention relates to fog-inhibiting agents and stabilizers for photographic emulsions and to photographic emulsions containing them.

This application is a continuation-in-part of our application Serial No. 687,239, filed July 30, 1946, now abandoned. It is known that photographic emulsions, particularly ultra-sensitive emulsions or those containing coloring 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 little leak in the camera. General fog or as it is sometimes known chemical 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. Highly sensitive emulsions are more likely to fog than those of lower sensitivity. We are primarily concerned with general or chemical fog.

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.

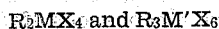
In our prior application, Serial No. 765,818, filed August 2, 1947, we described the use as fog-inhibitors of compounds of the general formula:



of which ammonium chloropalladate is an example. We have now found that the sensitivity and fog of photographic emulsions may be maintained at or close to initial optimum values under

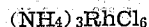
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adverse conditions of temperature and humidity by the use of compounds of the formulas:



5 in which R is hydrogen or an alkali metal including ammonium, M is platinum or palladium, M' is iridium or rhodium and X is a halogen atom.

10 Compounds suitable for use according to our invention are those of the above general formulas in which R is hydrogen or an alkali metal such as potassium or sodium, or ammonium; M is platinum or palladium; M' is iridium or rhodium; and X is a halogen atom such as chlorine or bromine. Suitable compounds are ammonium chloropalladite, $(NH_4)_2(PdCl_4)$; ammonium chloroplatinite $(NH_4)_2PtCl_4$; ammonium chloroiridite $(NH_4)_3IrCl_6$; and ammonium chlororhodite



20 By the use of the compounds of our invention, it is possible to maintain the sensitivity and fog of silver halide emulsions at or close to initial optimum values under conditions of high temperature and humidity. The fog inhibitors which we propose to use are added to the emulsion during the process of manufacture to avoid loss of sensitivity and to inhibit the growth of chemical fog with passage of time under non-ideal conditions of storage. These conditions frequently exist where photographic emulsions are used in tropical countries or on naval vessels or in manufacturing plants where adverse keeping conditions prevail. The advantages of our discovery reside in the extent of stabilizing action secured over a wide range of climatic conditions.

35 A solution of ammonium chloropalladite or other fog inhibitor used according to our invention, when added in suitable concentration to unsensitized or optically sensitized photographic emulsions before coating, does not effect 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, these compounds do stabilize photographic speed and maintain fog at a low level.

40 The preparation of silver halide emulsions involves three separate operations (1) the emulsifi-

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cation and digestion or ripening of the silver halide, (2) the freeing of the emulsion from excess soluble salts, usually by washing, and (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 compounds after the final digestion or after-ripening, although they may be added prior to the final digestion step. Useful concentrations are from 0.25 to 3.9 gram of fog inhibitor per kilogram of silver nitrate converted to silver halide in making the emulsion.

The fog inhibiting and stabilizing action of our compounds was determined by incubation of the emulsions with simulated tropical conditions and also by incubation in dry heat at 120° F. for various lengths of time from 12 days to 2 months. The results of these tests are tabulated below and are compared with the initial speed, gamma and fog of the emulsions with and without the stabilizing compound. The tests from which the following tabulation was made used a high-speed negative silver halide emulsion exposed on an Eastman type IIB sensitometer and developed for five minutes 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 are as follows:

(NH ₄) ₂ PdCl ₄ grams per kg. AgNO ₃	Routine			12 da. at 120° F.			8 wks. Tropical		
	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog
None-----	710	1.48	.08	360	1.51	.18	193	1.34	.47
.464-----	995	1.36	.11	465	1.46	.19	290	1.38	.26
.928-----	775	1.46	.10	473	1.43	.22	325	1.30	.20
1.391-----	1,320	1.13	.07	740	1.15	.20	430	1.38	.13
None-----	870	1.39	.09	343	1.49	.19	153	1.37	.52

(NH ₄) ₂ PtCl ₄ gram per kg. AgNO ₃	Routine			12 da. at 120° F.			8 wks. Tropical		
	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog
None-----	710	1.48	.08	360	1.51	.18	193	1.34	.47
.464-----	880	1.33	.12	510	1.28	.32	330	1.35	.20
.928-----	1,020	1.17	.10	380	1.05	.28	248	1.43	.12
1.391-----	1,230	1.19	.07	400	0.84	.49	455	1.25	.12
None-----	870	1.39	.09	343	1.49	.19	153	1.37	.52

(NH ₄) ₂ IrCl ₆ gram per kg. AgNO ₃	Routine			12 da. at 120° F.			8 wks. Tropical		
	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog	10/i Speed	Gamma	Fog
None-----	710	1.48	.08	360	1.51	.18	193	1.34	.47
.464-----	890	1.35	.10	575	1.29	.20	198	1.40	.30
.928-----	1,380	1.17	.11	490	1.33	.22	218	1.39	.31
1.391-----	935	1.35	.10	535	1.30	.20	210	1.36	.30
None-----	870	1.39	.09	343	1.49	.19	153	1.37	.52

The fog inhibiting agents of our invention are useful principally with emulsions which are developed with organic developing agents not containing metals. Such developing agents are hydroquinone, para-aminophenol and its derivatives, pyrogallol, paraphenylenediamine and its derivatives, phenylhydroxylamine, etc.

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 ortho-chromatic, 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 and mixtures of these. The dispersing agents may be gelatin or other colloid, such as collodion, alubumen, cellulose organic 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 stabilized silver halide emulsion containing silver halide as the sole sensitive ingredient and containing from 0.25 gram to 3.9 grams per kilogram of silver nitrate converted to silver halide in making the emulsion, of a compound having the structure



where R is selected from the group consisting of hydrogen, alkali metals and ammonium, M is selected from the group consisting of platinum and palladium and X is a halogen atom.

2. A stabilized gelatino-silver halide emulsion containing silver halide as the sole sensitive ingredient and containing from 0.25 gram to 3.9 grams per kilogram of silver nitrate converted to

silver halide in making the emulsion, of ammonium chloropalladite.

3. A stabilized gelatino-silver halide emulsion containing silver halide as the sole sensitive ingredient and containing from 0.25 gram to 3.9 grams per kilogram of silver nitrate converted to

5

silver halide in making the emulsion, of ammonium chloroplatinite.

4. The method of stabilizing the speed and reducing the amount of fog produced upon development of a silver halide emulsion containing silver halide as the sole sensitive ingredient, which comprises incorporating in said emulsion from 0.25 gram to 3.9 grams per kilogram of silver nitrate converted to silver halide in making the emulsion, of a compound having the structure



where X is a halogen atom, R is selected from the group consisting of hydrogen, alkali metals and ammonium, and M is selected from the group

6

consisting of platinum and palladium, and developing said emulsion after exposure with an organic developing agent free of a metallic element.

ADRIAN P. H. TRIVELLI.
WILLIAM F. SMITH.

REFERENCES CITED

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

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