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AZOPYRIDINE COMPOUNDS AS FOG INHIBITORS FOR PHOTOGRAPHIC EMULSIONS

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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 silver sensitized photographic materials contain some silver halide grains which can be reduced to metallic silver in the normal developing process without having been exposed to light. The resulting silver density which extends more or less uniformly over the processed photographic layer is known as fog. More strictly, it is called chemical fog or emulsion fog to differentiate from light fog, which is the developed silver density resulting from unwanted exposure to light, as, for example, by a light leak in the camera bellows.

Emulsion fog varies with the kind of photographic material and with the conditions of storage and processing. The fogging tendency is usually greater with high speed materials and those containing optical sensitizers, and it increases with the age of the emulsion and with the temperature and humidity prevailing during storage. Emulsion fog also varies with the developing formula used and increases with the temperature and duration of development.

It is an object of the invention to provide novel anti-fogging and 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 into a silver halide emulsion small amounts of halogenated 2,2'-azopyridine compounds such as 5,5'-dichloro-2,2'-azopyridine, 5,5'-dibromo-2,2'-azopyridine, 5,5'-diiodo-2,2'-azopyridine, 5-chloro-2,2'-azopyridine, 3,3',5,5'-tetrachloro-2,2'-azopyridine and 5,5'-dichloro-3,3'-dimethyl-2,2'-azopyridine.

Similar azoxy compounds such as 4,4'-dichloro-2,2'-azoxypyridine exhibit fog-inhibiting properties but are not as effective for the prevention of fog as the above compounds and show a tendency to desensitize silver halide emulsions.

The nuclear halogenated 2,2'-azopyridine compounds employed in our invention can be prepared by the methods of Kirpal Ber. 67B, 70–1 (1934) C. A. 28 1701 and Bystritskaya, Kirsanov, J. Gen. Chem. (U. S. S. R.), 10, 1101–1107, #12 (1940); C. A. 35, 40237 (1941).

A wide variety of compounds have been used in photographic emulsions to inhibit fog. For example, mercaptopyrimidine compounds containing a 5-arylazo group are described by Sheppard et al. U. S. Patent 2,304,962 for this purpose.

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Similarly, Davey et al. U. S. Patent 2,273,502 discloses amino hydroxy pyrimidines as anti-foggants. However, we find that compounds more closely related to the compounds of our invention such as 2,2'-azopyrimidine, 2,2'-azopyridine, 3,3'-azoquinoline, 4,4'-dimethyl-2,2'-azothiazole, and 6-azobenzimidazole have little or no anti-foggant effect when used in silver halide emulsions. Borst U. S. Patent 2,192,891 employs salts of halogenated amino pyridines, for example, 5-chloro-2-amino pyridine and 3,5-chloro-2-amino pyridine hydrochloride, in photographic developers to control the tone of silver images. However, our work shows that the halogenated amino pyridines such as 5-iodo-2-amino pyridine and 5-chloro-2-amino pyridine do not inhibit fog formation when employed in emulsions in the manner of our invention. Moreover, the compounds of our invention such as 5,5'-dichloro-2,2'-azopyridine do not function as anti-foggants when employed in photographic developer compositions.

One 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 manufacture to avoid loss of sensitivity and to inhibit the growth of fog with passage of time under non-ideal conditions of storage.

A solution of the compounds of the invention when added in suitable concentration before coating to unsensitized or optically sensitized photographic emulsion does not appreciably affect the sensitometric values for sensitivity and fog when measurements are made soon after coating. When sensitometric measurements are made at appreciable intervals of time under tropical or dry conditions of storage at elevated temperatures, however, these compounds 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 range of concentration of the fog inhibitor compounds of our emulsions is from about 0.0025 to about 0.1 milligram per mol of silver halide in the emulsions as illustrated by the following examples. The quantity will, of course, vary, for example, de-

pending on the silver halide or mixture of silver halides and the particular compound used.

The anti-foggant and stabilizing action was determined by incubation of the emulsions under simulated tropical conditions for various lengths of time. The results of typical tests under these conditions are tabulated below and are compared with the initial speed, gamma and fog of the emulsions not containing the antifoggant and stabilizing compound.

The test from which the following tabulation was made employed, for samples A–H a high-speed bromo-iodide emulsion, and for samples I–N a medium-speed bromoiodide emulsion. The samples were exposed as usual on an Eastman type 1B Sensitometer and developed for five minutes in a developer of the following composition:

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

In the case of the latent image keeping tests supplied below for samples A–H, it will be apparent that exposures were made on these samples in the same manner on the sensitometer but the exposed samples were incubated at 120° F. before processing.

Sample	Compound	Mgs. per Mol AgX in Emulsion	Fresh Tests			1 wk. 120° F.		
			Speed	Gamma	Fog	Speed	Gamma	Fog
A	Control		3,200	0.97	0.06	1,400	0.77	0.50
B	5,5′-dibromo-2,2′-azopyridine	0.021	3,100	0.93	.05	2,200	0.87	.16
C	do	0.042	2,500	1.00	.04	2,100	0.92	.12
D	do	0.084	1,950	1.11	.05	1,650	0.96	.11
E	5,5′-diiodo-2,2′-azopyridine	0.021	2,650	0.99	.05	2,700	0.85	.14
F	do	0.042	2,450	1.02	.05	2,100	0.97	.12
G	do	0.084	2,000	1.06	.05	1,750	0.97	.12
H	5,5′-dichloro-2,2′-azopyridine	0.084	2,400	1.03	.05	1,750	0.97	.20
I	Control		1,620	0.95	.07	1,080	0.90	.22
J	5-chloro-2,2′-azopyridine	0.003	1,600	0.90	.06	1,620	0.94	.16
K	do	0.03	1,550	0.88	.06	1,050	1.15	.14
L	3,3′-dimethyl-5,5′-dichloro-2,2′-azopyridine.	0.06	2,200	1.06	.06	2,500	1.05	.16
M	do	0.6	1,700	1.11	.05	2,450	1.01	.09
N	3,3′,5,5′-tetra-chloro-2,2′-azopyridine.	0.06	2,550	1.19	.08	2,350	0.87	.16

Sample	Latent Image Keeping, 1 wk. 120° F.		
	Speed	Gamma	Fog
A	4,100	0.97	0.44
B	3,600	1.17	.13
C	3,300	1.21	.07
D	2,500	1.23	.09
E	3,700	1.19	.10
F	3,300	1.15	.10
G	2,500	1.24	.03
H	3,100	1.28	.14

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 and mixtures of these. The dispersing agents may be gelatin or other colloid such as collodion, albumen, cellulose organic derivatives or synthetic resins.

We also contemplate as a part of our invention those cases where it is desirable to coat the antifoggant in a colloid layer such as gelatin on either or both sides of or also in a silver halide emulsion layer, so that the antifoggant is contiguous to the silver halide emulsion. In these cases we use the same or a slightly greater ratio of the halogenated 2,2′-azopyridine compounds to silver halide than when the compounds are present in the emulsion.

What we claim is:

1. A light-sensitive photographic emulsion comprising silver halide and a halogenated 2,2′-azopyridine in antifoggant amount.

2. A light-sensitive photographic emulsion comprising silver halide and a member selected from the group consisting of 5,5′-dichloro-2,2′-azopyridine, 5,5′-dibromo-2,2′-azopyridine, 5,5′-diiodo-2,2′-azopyridine, 5-chloro-2,2′-azopyridine, 3,3′,5,5′-tetrachlo-2,2′-azopyridine, and 5,5′-dichloro-3,3′-dimethyl-2,2′-azopyridine in antifoggant amount.

3. A light-sensitive photographic emulsion comprising silver halide and a chlorinated 2,2′-azopyridine in antifoggant amount.

4. A light-sensitive photographic emulsion comprising silver halide and a brominated 2,2′-azopyridine in antifoggant amount.

5. A light-sensitive photographic emulsion comprising silver halide and an iodated 2,2′-azopyridine in antifoggant amount.

6. A light-sensitive photographic emulsion comprising silver halide and 5,5′-dichloro-2,2′-azopyridine in antifoggant amount.

7. A light-sensitive photographic emulsion comprising silver halide and 5,5′-dibromo-2,2′-azopyridine in antifoggant amount.

8. A light-sensitive photographic emulsion comprising silver halide and 5,5′-diiodo-2,2′-azopyridine in antifoggant amount.

9. A light-sensitive photographic emulsion comprising silver halide and 5-chloro-2,2′-azopyridine in antifoggant amount.

10. A light-sensitive photographic emulsion comprising silver halide and 3,3′,5,5′-tetrachloro-2,2′-azopyridine in antifoggant amount.

11. A light-sensitive photographic element comprising a silver halide emulsion layer and an organic colloid layer contiguous to said emulsion layer, at least one of said layers containing a halogenated 2,2′-azopyridine.

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No references cited.