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STABILIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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No Drawing. Application January 5, 1956, Serial No. 557,448

10 Claims. (Cl. 96—109)

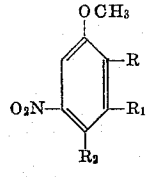
This invention relates to fog-inhibiting agents and stabilizers for photographic emulsions, and to photographic emulsions containing them.

It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given; this is commonly called "fog," and sometimes called "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation; in this invention, we are not concerned with the latter.

Fog depends both on the emulsion and the conditions of development; for a given emulsion it increases with the degree of development. With constant development conditions, it tends to increase with time, temperature and relative humidity of storage conditions; it is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is, of course, desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is non-uniform. Fog may also be caused be exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide vapor, and strongly reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that an antifoggant protects against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

It is, accordingly, an object of our invention to provide a method for stabilizing photographic emulsions. A further 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. A further object is to provide photographic silver halide emulsions containing antifoggants or stabilizers. Other objects will become apparent from a consideration of the following description and examples.

The above objects are accomplished by adding to the photographic emulsion a compound selected from those represented by the following general formula:



wherein R represents a hydrogen atom, a methoxyl group, a nitro group or an amino group, R_1 represents a nitro group or an amino group, and R_2 represents a hydrogen atom, a nitro group or an amino group.

The fog inhibitors which we propose to use are added

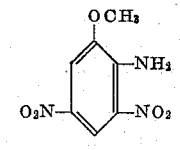
to the emulsion during the process of manufacture, to avoid loss of sensitivity and to inhibit the growth of fog with passage of time under non-ideal conditions of storage.

A solution of the compounds of the invention when added in suitable concentration, before coating, to unsensitized, chemically sensitized, 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 at appreciable intervals of time, at elevated temperatures and dry or somewhat humid conditions, these compounds do 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, 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 agents after the final digestion or after-ripening, although they can advantageously be added prior to digestion.

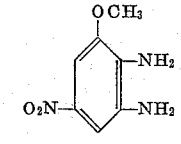
Listed below are a number of compounds coming within the scope of the above general formula, which we have found to be particularly advantageous in practicing our invention. These compounds belong to a group of compounds which we shall designate nitro-anisoles.

1.



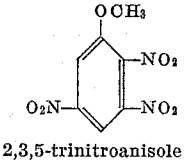
2-amino-3,5-dinitroanisole

2.



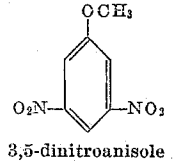
2,3-diamino-5-nitroanisole

3.



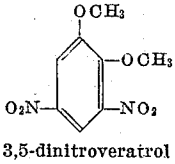
2,3,5-trinitroanisole

4.



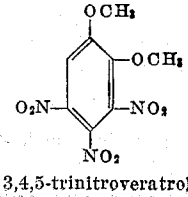
3,5-dinitroanisole

5.



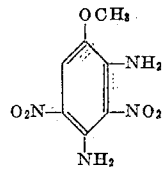
3,5-dinitroveratrol

6.



3,4,5-trinitroveratrol

7.



2,4-diamino-3,5-dinitroanisole

References describing the preparation of the above compounds are:

Compound	Reference
1	"J. A. C. S.," Vol. 76, 3531.
2	"J. A. C. S.," Vol. 76, 3531.
3	"Rec. Trav. Chem.," Vol. 23, 113.
4	"Organ. Syn.," Vol. I, 219.
5	"Beilstein," Vol. 6, 791.
6	"Chem. Abs.," Vol. 37, 5972.
7	"Chem. Abs.," Vol. 22, 230.

The photographic emulsions used in practicing our invention are generally of the developing-out type; also, it is to be understood that photographic emulsions of varying halide content can advantageously be used. The antifoggant compounds used in our invention have been found particularly useful when employed in conjunction with gelatino-silver bromiodide emulsions, although they can also be advantageously employed for stabilizing other silver halide emulsions, such as gelatino-silver chloride, bromide, chlorobromide, chlorobromiodide, etc.

The emulsions can also be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U. S. Patent 1,574,944 and U. S. 1,623,499, and Sheppard and Brigham U. S. Patent 2,410,689.

The emulsions can 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 can also be chemically sensitized with gold salts as described in Waller and Dodd U. S. Patent 2,399,083, or stabilized with gold salts as described in 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 can also be chemically sensitized with reducing agents such as stannous salts (Carroll U. S. Patent 2,487,850), polyamines such 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 emulsions can also be stabilized with the mercury compounds of Allen, Blyers and Murray U. S. application Serial No. 319,611 (now U. S. Patent 2,728,663, issued December 27, 1955), Carroll and Murray U. S. application Serial No. 319,612 (now U. S. Patent 2,728,664, issued December 27, 1955) and Leubner and Murray U. S. application Serial No. 319,613 (now U. S. Patent 2,728,665, issued December 27, 1955), all filed November 8, 1952.

The stabilizing combinations of nitroanisoles 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. We have found, however, that both unsensitized emulsions and emulsions sensitized with cyanine or merocyanine dyes or both can be treated with nitroanisoles according to our invention.

The antifoggant and stabilizing action was determined by incubation of the emulsions for one week at a temperature of 120° F. and constant relative humidity (obtained by placing the emulsions in closed containers, the ambient temperature being 70° F. and relative humidity 55% prior to sealing the containers). The efficiency of the various antifoggants was determined by measuring the speed, gamma and fog of the incubated emulsions containing an antifoggant and comparing these measurement with those of the same batch of emulsion before incubation. Also similar measurements were made on a photographic emulsion containing no antifoggant, both before and after incubation. The tests were made using a high speed silver bromiodide emulsion exposed on an Eastman Type Ib sensitometer and developed for 5 minutes in a developer of the following composition:

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

Example No.	Antifoggant Compound	g./mole AgX	Fresh Test			Incubation Test		
			Speed	Gamma	Fog	Speed	Gamma	Fog
1 (a)	None		7,200	1.06	.13	5,350	.87	.21
1 (b)	1	.15	6,550	1.06	.12	5,000	.88	.16
2 (a)	2	.15	6,700	1.06	.12	5,600	.92	.16
3 (a)	3	.15	4,750	1.10	.09	5,200	.98	.10
4 (a)	4	.15	7,050	1.04	.12	5,450	.93	.16
5 (a)	None		6,900	1.07	.16	2,750	.81	.60
5 (b)	5	.30	6,550	1.15	.14	3,200	.86	.43
5 (c)	5	3.0	5,000	1.20	.13	3,300	.97	.26
6 (a)	6	.03	6,900	1.26	.14	3,200	.99	.33
6 (b)	6	.30	5,200	1.26	.11	3,500	1.17	.22
7 (a)	7	.03	6,250	1.28	.15	2,750	1.00	.48
7 (b)	7	.30	5,850	1.17	.13	3,100	.99	.36

In a manner similar to that illustrated in the above example, other nitroanisoles selected from those represented by the above general formula can be incorporated in photographic emulsions for the purpose of stabilization. The fog-inhibiting agents useful in practicing our invention can be used in various kinds of photographic emulsions. In addition to being useful in ordinary non-sensitized emulsions, they can also be used in orthochromatic, panchromatic and X-ray emulsions. If used with sensitizing dyes, they can be added to the emulsion before or after the dyes are added. Suitable dispersing agents for the silver halide emulsions stabilized according to our invention comprise gelatin, or other colloids, such as collodion, albumen, cellulose organic derivatives, synthetic resins, etc.

The optimum amount of fog-inhibiting agent can be

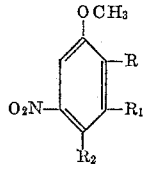
determined by making the customary tests employed in emulsion making. Of course, the optimum amount for a give emulsion will vary depending on the presence of emulsion addenda, such as chemical sensitizers, optical sensitizers, etc. In general, we have found that from 0.05 to 1.0 g. of fog-inhibiting agent per mole of silver halide is sufficient for the purposes of our invention.

Instead of adding the fog-inhibiting agent directly to the photographic emulsion, it is sometimes desirable to incorporate the fog-inhibiting agent in a separate layer which is placed in contact with the silver halide emulsion layer which is to be stabilized. Under such conditions, of course, it is advisable to use a higher concentration of fog-inhibiting agent than indicated above.

The stabilizing compounds of our invention can be added to the photographic emulsions in the form of their solutions, or in certain instances, in the absence of a solvent. Since such small quantities of material are needed to stabilize the emulsions according to our invention, as mentioned above, a small quantity of the solution of stabilizing compound in a solvent, such as methanol, acetone, etc., can be employed. Other well known solvents can likewise be used to advantage.

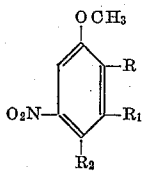
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion containing a compound selected from those represented by the following general formula:



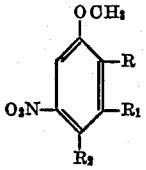
wherein R represents a member selected from the group consisting of a hydrogen atom, a nitro group, an amino group and a methoxyl group, R_1 represents a member selected from the group consisting of a nitro group and an amino group and R_2 represents a member selected from the group consisting of a hydrogen atom, a nitro group and an amino group.

2. A photographic gelatino-silver-halide developing-out emulsion containing a compound selected from those represented by the following general formula:



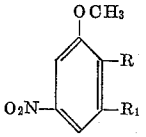
wherein R represents a member selected from the group consisting of a hydrogen atom, a nitro group, an amino group and a methoxyl group, R_1 represents a member selected from the group consisting of a nitro group and an amino group and R_2 represents a member selected from the group consisting of a hydrogen atom, a nitro group and an amino group.

3. A photographic gelatino-silver-bromiodide developing-out emulsion containing a compound selected from those represented by the following general formula:



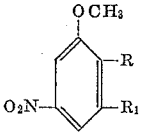
wherein R represents a member selected from the group consisting of a hydrogen atom, a nitro group, an amino group and a methoxyl group, R_1 represents a member selected from the group consisting of a nitro group and an amino group and R_2 represents a member selected from the group consisting of a hydrogen atom, a nitro group and an amino group.

4. A photographic gelatino-silver-halide developing-out emulsion containing a compound selected from those represented by the following general formula:



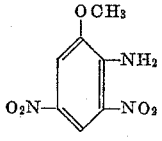
wherein R represents a member selected from the group consisting of a hydrogen atom, a nitro group and an amino group and R_1 represents a member selected from the group consisting of a nitro group and an amino group.

5. A photographic gelatino-silver-bromiodide developing-out emulsion containing a compound selected from those represented by the following general formula:

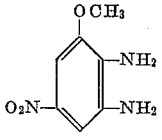


wherein R represents a member selected from the group consisting of a hydrogen atom, a nitro group and an amino group and R_1 represents a member selected from the group consisting of a nitro group and an amino group.

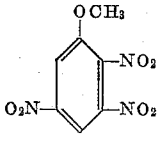
6. A photographic silver halide emulsion containing a compound represented by the following formula:



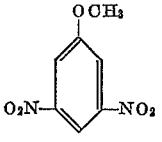
7. A photographic silver halide emulsion containing a compound represented by the following formula:



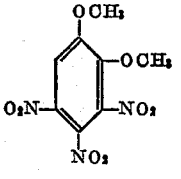
8. A photographic silver halide emulsion containing a compound represented by the following formula:



9. A photographic silver halide emulsion containing a compound represented by the following formula:



10. A photographic silver halide emulsion containing a compound represented by the following formula:



No references cited.