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STABILIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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11 Claims. (Cl. 96—109)

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

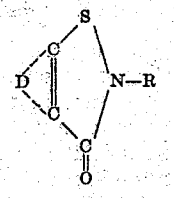
It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given; this is commonly called "fog," 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 by 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 silver halide emulsions. Another object is to maintain the sensitivity and fog of photographic 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.

According to our invention photographic silver halide emulsions are stabilized by incorporating therein a compound selected from those represented by the following general formula:

(I)



wherein R represents a hydrogen atom, an alkyl group

(e. g., methyl, ethyl, n-propyl, n-butyl, isobutyl, n-hexyl, n-octyl, n-dodecyl, n-cetyl, etc., especially a lower alkyl group containing from 1 to 4 carbon atoms) or a heterocyclyl group, such as benzothiazyl, benzoxazyl, pyridyl, etc., and D represents the non-metallic atoms necessary to complete a monocyclic aromatic group of the benzene series, such as benzene or substituted benzenes (i. e., benzene substituted by such radicals as chlorine, bromine, methoxyl, ethoxyl, methyl, ethyl, etc.).

It has also been found in certain instances that a number of the compounds embraced by Formula I above serve to increase the sensitivity of photographic silver halide emulsions, in addition to stabilizing the emulsions or providing an antifoggant effect. However, the fog-inhibiting effect is more general than the sensitizing effect, and for this reason, these compounds are referred to below as antifoggants or fog-inhibitors.

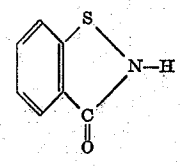
The fog-inhibitors which we propose to use are added to the emulsion during the process of manufacture, to avoid loss of sensitivity and to inhibit the growth of fog with passage of time under non-ideal conditions of storage.

A solution of the compounds of the invention when added in suitable concentration, before coating, to unsensitized, chemically sensitized, or optically sensitized photographic emulsions may 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 of 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.

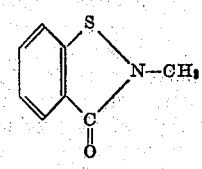
Listed below are a number of compounds coming within the scope of Formula I above which we have found to be particularly advantageous in practicing our invention.

(1)



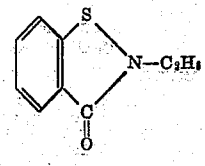
2,3-dihydro-3-oxobenzoisothiazole

(2)



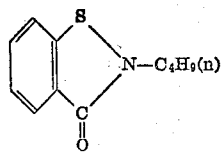
2,3-dihydro-2-methyl-3-oxobenzoisothiazole

(3)



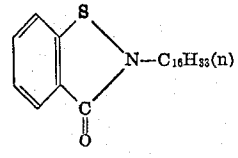
2,3-dihydro-2-ethyl-3-oxobenzoisothiazole

(4)



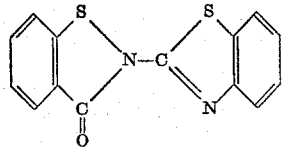
2-n-butyl-2,3-dihydro-3-oxobenzoisothiazole

(5)



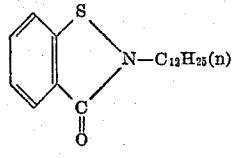
2-cetyl-2,3-dihydro-3-oxobenzoisothiazole

(6)



2-benzothiazyl-2,3-dihydro-3-oxobenzoisothiazole

(7)



2,3-dihydro-2-n-dodecyl-3-oxobenzoisothiazole

The compounds represented by Formula I above wherein R represents a lower alkyl group have been found to be particularly useful in providing the above-mentioned effects in photographic silver halide emulsions. That is, these compounds are particularly outstanding and provide more useful effects than the other compounds embraced by Formula I. This outstanding effect for the alkyl compounds can be readily seen in the data given below.

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 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 emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U. S. Patent 2,728,663, Carroll and Murray U. S. Patent 2,728,664, and Leubner and Murray U. S. Patent 2,728,665.

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

The antifoggant and/or 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 about 70° F. and relative humidity about 50–55 percent 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 measurements with those of the same batch of emulsion before incubation. Also, similar measurements were made with a photographic emulsion containing no antifoggant both before and after incubation.

The tests were made using high speed, negative-type silver bromiodide emulsions (coated on cellulose acetate supports), which had been panchromatically sensitized with a cyanine dye and chemically sensitized with sulfur and gold compounds. The test films were exposed on an intensity scale sensitometer and developed for 5 minutes in a developer having the following composition:

	Grams
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite	30.0
Sodium metaborate	10.0
Potassium bromide	0.5
Water to make 1 liter.	

The speed, gamma and fog for each of the emulsion coatings were then measured as indicated above. The results obtained are given in the following table.

Example	Compound (g./mol. AgX)	Fresh Coatings			Incubated Coatings		
		30/E Speed	Gamma	Fog	30/E Speed	Gamma	Fog
1(a)	None	6,900	1.11	.13	6,400	.94	.17
1(b)	1 (0.3)	6,250	1.07	.12	6,150	.93	.12
2(a)	None	8,050	1.03	.11	6,700	.92	.18
2(b)	2 (3.0)	8,250	1.06	.10	7,700	.95	.10
3(a)	None	4,550	1.32	.14	3,800	1.10	.30
3(b)	5 (3.0)	5,350	1.19	.13	4,250	1.01	.24
4(a)	None	4,550	1.32	.14	3,800	1.10	.30
4(b)	6 (.03)	5,350	1.14	.13	4,650	1.09	.19

In a manner similar to that illustrated in the above examples, other compounds selected from those represented by the above general Formula I 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 ortho-

chromatic, 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 given emulsion will vary depending on the presence of emulsion addenda, such as chemical sensitizers, optical sensitizers, etc. In general, we have found that from 0.001 to 5.0 g. of fog-inhibting 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 antifoggants of our invention function advantageously in acid or alkaline photographic silver halide emulsions.

It has also been noted that certain nitrogen-containing compounds other than those of Formula I above can be used in photographic silver halide emulsions, frequently to give antifoggant or stabilizing effects. Such compounds include, for example, ethylfurfurylidenedicarbamate, "The Furans," A. C. S. Monograph No. 119 (1953), page 374, which can also be named furfurylidenebisurethane (ethyl ester). Other related nitrogen-containing compounds, such as ethylidenebisurethane, benzylidenebisurethane, thienylidenebisurethane, etc., can also be used to advantage in certain cases.

Many of the compounds embraced by Formula I above have been previously described in the prior art. These compounds can be prepared according to the method described by McClelland and Gate in "Jour. Chem. Soc." (1926), pages 921–5. This method leads to compounds of Formula I where R is alkyl or heterocyclyl. The method, briefly, comprises reacting a primary organic amine with a dithiodibenzoylchloride. The following examples will describe the preparation of two of these compounds.

Example A.—2-cetyl-2,3-dihydro-3-oxobenzoisothiazole

Two solutions were prepared as follows:

Solution A.—10 grams of n-cetylamine were dissolved in 50 cc. of pyridine and 200 cc. of anhydrous carbon tetrachloride with warming.

Solution B.—7 grams of dithiodibenzoylchloride were added to 100 cc. of carbon tetrachloride and chlorine was passed into the mixture until the dithiodibenzoylchloride had dissolved. Nitrogen was then passed into the container holding the solution to remove excess chlorine. The solution was then filtered.

Solution A was warmed to 55° C. to keep in solution and Solution B was slowly added to Solution A with stirring. The temperature rose to 60° C. and crystals appearing to be pyridine hydrochloride separated. After cooling to ambient temperature, the reaction mixture was poured onto one liter of ice and made acid (with hydrochloric acid) to Congo red. The carbon tetrachloride layer was separated and washed with cold water. The carbon tetrachloride solution was dried over calcium chloride, decolorized with decolorizing carbon and dried over magnesium sulfate. The solution was filtered and concentrated under reduced pressure on the steam bath. The concentrated solution was dissolved in ethyl alcohol, treated once again with decolorizing carbon, filtered and put in the refrigerator. The desired material crystallized from the solution and was collected on a filter. After drying, 2.3 g. of product remained, melting at 45–47° C.

Example B.—2-benzothiazyl-2,3-dihydro-3-oxobenzoisothiazole

Two solutions were prepared as follows:

Solution A.—7 grams of dithiodibenzoylchloride were added to 100 cc. of carbon tetrachloride and chlorine passed into the mixture until complete solution ensued. Excess chlorine was then removed by passing in nitrogen gas and the solution was filtered.

Solution B.—6 grams of 2-aminobenzothiazole were dissolved in a mixture of 50 cc. of pyridine and 135 cc. of carbon tetrachloride.

Solution A was added to Solution B slowly, the temperature rising to 45° C. during the addition. The desired product separated immediately as crystalline material. The reaction mixture was allowed to stand for an additional 1.5 hours and then filtered. The filter cake was washed with 100 cc. of water to remove any pyridine hydrochloride present.

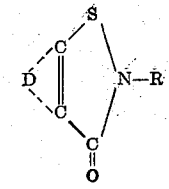
The desired product was recrystallized from dimethylformamide, collected on a filter, leached in diethyl ether, filtered, and dried. It was obtained in 6.1 gram yield as long white needles.

Analysis.—Calcd. for C, 59.2%; H, 2.8%; N, 9.9%. Found: C, 59.4%; H, 2.4%; N, 9.9%.

Compound 1 above has been previously described in "Chemical Abstracts," vol. 17, page 1450.

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:

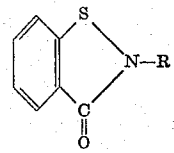


wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a benzothiazyl group, a benzoxazyl group, and a pyridyl group and D represents the non-metallic atoms necessary to complete a benzene ring.

2. A photographic silver halide emulsion as defined in claim 1 wherein the silver halide emulsion is a gelatino-silver halide developing-out emulsion.

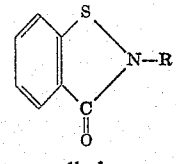
3. A photographic gelatino-silver-halide developing-out emulsion as defined in claim 2 wherein the silver halide is silver bromiodide.

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



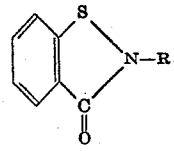
wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a benzothiazyl group, a benzoxazyl group, and a pyridyl group.

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



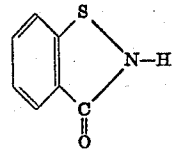
wherein R represents an alkyl group containing from 1 to 4 carbon atoms.

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

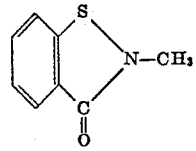


wherein R represents a benzothiazyl group.

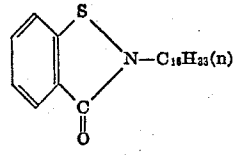
7. A photographic silver-halide emulsion containing the compound represented by the following formula:



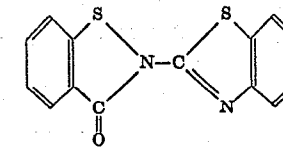
8. A photographic silver-halide emulsion containing the compound represented by the following formula:



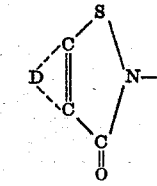
9. A photographic silver-halide emulsion containing the compound represented by the following formula:



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



11. A photographic element comprising a silver-halide emulsion layer and a colloid layer, at least one of said layers having incorporated therein 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, an alkyl group, a benzothiazyl group, a benzoxazyl group, and a pyridyl group, and D represents the non-metallic atoms necessary to complete a benzene ring.

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