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3,332,776

FOG REDUCTION IN PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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The present invention relates to the employment of compounds which serve as antifoggant and stabilizing agents for photographic silver halide emulsions and, more particularly, to the use of halogen sulfonyl benzoic acid, its salts and esters.

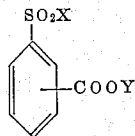
It is known that light-sensitive photographic emulsions, such as gelatino-silver halide emulsions, have a tendency to fog. Fogging is caused in a number of ways as, for example, by excessive ripening of the emulsions during storage of the film or paper, particularly at elevated temperature and humidity or by prolonged development.

Efforts have been made to decrease or inhibit the tendency of silver halide emulsions to fog by the addition thereto of antifogging or stabilizing agents for the purpose of stabilizing or controlling the keeping qualities of the emulsions.

Many compounds have been recommended for this purpose, among which may be mentioned mercapto tetrazoles or their disulfides. Although these compounds have the ability to reduce the fog tendencies and to improve the stability of the emulsions, they have definite shortcomings, particularly in that they lower the sensitivity of the emulsion and in some cases, reduce the optical or dye sensitivity thereof.

We have now discovered a class of stabilizing or fog inhibiting agents which not only prevent the formation of chemical fog in silver halide emulsions but, most important, effect this result without lowering the sensitivity of the emulsions or reducing its sensitivity to light of longer wave lengths induced by sensitizing dyes. The compounds which we use for this purpose may be generally described as halogen sulfonyl benzoic acids, their esters and alkali metal and ammonium salts. The addition of the above compounds as antifogging agents to the emulsions or to a layer adjacent to the emulsion or in a processing bath such as the developer, constitute the purpose and object of our invention.

The antifogging agents, the use of which is contemplated herein, may be typified by the following structural formula:



wherein X is halogen, such as chlorine, bromine, fluorine and iodine, and Y is hydrogen; alkyl such as methyl, ethyl, propyl, butyl or the like; aryl, such as phenyl, tolyl, naphthyl or the like; aralkyl, such as benzyl, phenethyl or the like.

Examples of compounds within the above formula which we have found to be suitable for our purposes are:

- m-Chlorosulfonyl benzoic acid
- o-Chlorosulfonyl benzoic acid
- p-Chlorosulfonyl benzoic acid
- m-Bromosulfonyl benzoic acid
- o-Bromosulfonyl benzoic acid
- p-Bromosulfonyl benzoic acid
- m-Fluorosulfonyl benzoic acid
- o-Chlorosulfonyl methyl benzoate
- m-Chlorosulfonyl ethyl benzoate

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- p-Chlorosulfonyl ethyl benzoate
- m-Chlorosulfonyl benzyl benzoate
- p-Chlorosulfonyl benzyl benzoate

The antifogging agents which have been found to impart such beneficial effects to light-sensitive silver halide emulsions for the prevention of fogging and stabilization of said emulsions can be conveniently prepared in accordance with known procedures, such as described in an article of Smiles and Stewart, J.C.S. 119, 1795 (1921). For example, m-chlorosulfonyl benzoic acid is prepared by reacting a mixture of benzoic acid and 5 mole equivalents of chlorosulfonic acid at a temperature of 125° C. for a period of one hour in an oil bath, until the evolution of hydrogen chloride ceases. After cooling, the mixture is poured over crushed ice and the solid mass ground under ice cold water, collected, washed with ice water and subsequently vacuum dried. The crude product, m-chlorosulfonyl benzoic acid has a melting point of about 122° C. and after recrystallization from benzene the pure material is obtained in the form of colorless prisms having a melting point of 131° C. and an elemental analysis as follows:

Element	Calc., Percent	Found, Percent
Cl.....	16.1	16.0
S.....	14.4	14.3

The above compound may also be obtained by long standing of the m-sulfo benzoic acid dichloride with water according to the method of Limpricht and V. Usear, Ann. 106, 30.

Similarly, the p-chlorosulfonyl benzoic acid can be obtained by the oxidation of p-toluene sulfonyl chloride with CrO₃ in acetic acid and acetic anhydride at a temperature of 40-45° C. as indicated in C.A. 1923 III 302. Alternatively the p-chlorosulfonyl benzoic acid can be prepared in accordance with the procedures of Smiles and Harrison, J.C.S., 121, 2024 by heating 50 milliliters of chlorosulfonic acid and 35 grams of anhydrous sodium salt of p-sulfo benzoic acid at a temperature of 100° C. for a period of about one hour. The resultant liquid is cooled and poured slowly over crushed ice, the colorless product cooled, washed with ice water and air dried to provide a yield of crude product of from 30-35 grams of p-chlorosulfonyl benzoic acid. The product is moderately soluble in hot acetone and can be recrystallized therefrom in the form of colorless needles having a melting point with decomposition of about 235° C.

Upon analysis, the product has the following properties:

Analysis	Cl	NaOH Equiv., gm.
Found.....	15.87	7.43
Calc.....	16.09	7.35

Meta-compounds containing in the sulfonyl group a halogen atom other than chlorine can be obtained by the process of Smiles and Stewart by the employment of a halogen sulfonic acid other than chlorosulfonic acid. Typically, if m-bromo sulfonyl benzoic acid is desired, bromosulfonic acid is used in place of chlorosulfonic acid in the Smiles and Stewart synthesis. If the ester is the desired end product, it is obvious that the ester may be

formed by refluxing the benzoic acid with the desired alcohol or phenol in the presence of hydrochloric acid.

The method of Smiles and Harrison, on the other hand, is suitable for preparing p-halogen sulfonyl benzoic acid compounds other than the chloro compound by replacing the chlorosulfonic acid by bromosulfonic, iodosulfonic acid, or the like.

The o-chlorosulfonyl benzoic acid can be prepared by the same method as the para derivative in accordance with the procedure of Smiles and Harrison, J.C.S. 121, 2024. The product is isolated in acetone instead of water since it is very unstable in water even at 0° C.

Beneficial effects in fog reduction are obtained when solutions of the antifoggant are incorporated into the silver halide emulsions as "ripening finals" or as "coating finals." "Ripening finals" are added during the ripening or the sensitivity increasing stage of the emulsion-making process whereas "coating finals" are added to the silver halide emulsion just prior to the coating of the emulsion on a suitable support such as, for example, paper, glass or film, when the emulsion has nearly obtained its maximum sensitivity.

The addition of the antifoggants can be made before, during or after the addition of the soluble silver salt to the soluble halide in the presence of a suitable carrier or colloid such as gelatin, polyvinyl alcohol, polyvinyl-pyrrolidone, solubilized casein, albumin and the like.

The amount of antifogging agent employed as additives to the light-sensitive emulsions varies from about 0.02 to about 20.0 milligrams of antifogant per 0.6 mole of silver halide. When the antifogging agents are employed as "ripening finals" it has been found advantageous to employ them in amounts in the range of from about 0.02 to about 5.0 milligrams per 0.6 mole of silver halide whereas, when the antifogging agents are employed in "coating finals," it has been found advantageous to employ amounts in the range of from about 1.0 to about 20 milligrams of antifogant per 0.6 mole of silver halide. Obviously, the development of optimum characteristics within the ranges set forth above will depend in part upon the type of emulsion employed and can be readily determined in each case. The antifoggants can be employed also in various kinds of photographic emulsions such as non-sensitized emulsions, orthochromatic emulsions, panchromatic emulsions, X-ray emulsions, paper emulsions, color emulsions and the like.

In some cases, it has been found advantageous to apply the antifogging agents of the invention in adjacent layers, for example, in a separate undercoating layer or in the antiabrasion gelatin surface. Alternatively, it has been found advantageous, in some cases, to apply the antifogging agents of the invention in one or all processing baths or in pre- and post-baths.

It has also been found that the antifogging agents of the invention can be compatibly employed in combination with other known antifoggants and stabilizers; with sulfur-, reduction and metal-, and noble metal sensitizers as well as in combination with polyoxyalkylene polyols, their derivatives; polyvinyl-pyrrolidones and other accelerators.

The following examples will serve to illustrate the practice of the invention.

Example I

A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was prepared in a conventional manner and brought up to its maximum light sensitivity. It was then readied for coating, finals were added such as sensitizing dyes and hardening agents. A 0.01% solution of m-chlorosulfonyl benzoic acid was added to the emulsion as an antifogant and stabilizer. The emulsion samples contained about 0.6 mole of silver halide. The so-prepared emulsion samples were coated on a suitable cellulose ester base and dried. Samples of these film coatings were then exposed in a Type IB Sensitometer and developed in a developer of the following composition:

	Grams
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
5 Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	0.8
Water to make 1 liter.	

Quantity of Compound Used	Relative Speed	Fog at 12' Dev.	Oven Fog at 6' Dev.
0	100	.25	.24
40 mg.	100	.20	.21
80 mg.	85	.19	.15
120 mg.	87	.20	.14
200 mg.	87	.20	.12

Example II

Exposed samples of a photographic film were developed for twelve minutes at 65° F. in a standard metol-hydroquinone developer. Two tests were made, one with the normal developing solution and one with a developer containing 4 mg. of m-chlorosulfonyl benzoic acid per one liter of developer. Sensitometric strips, developed in the normal developer (control) for twelve minutes showed a fog of .30, whereas those strips which were developed in the developer containing the antifogant had a fog of .18.

Example III

A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was coated on film base in a manner known to the art. After the coating, an aqueous gelatin solution containing 20 grams gelatin in 1 liter H₂O and 80 mg. m-chlorosulfonyl benzoic acid was coated thereon as an antiabrasion layer. After drying, film samples were exposed and processed as described in Example I. The samples exhibited a relative speed of 100 and a fog of .12 compared with type coating of the above emulsion having an antiabrasion layer similar to that described above, but lacking the antifogant and having a speed of 100 and a fog of .18.

Example IV

The procedure is the same as in Example I excepting that the antifogant used was o-bromosulfonyl benzoic acid. The results were substantially the same.

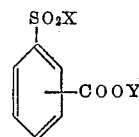
Example V

The procedure was the same as in Example III excepting that the antifogant used was p-chlorosulfonyl ethyl benzoate. Equally good results were thus obtained.

It is to be understood that the above-described embodiments are shown for purposes of illustration only and that other variations can be readily devised by those skilled in the art.

What is claimed is:

1. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor and an antifogant characterized by the general formula:



wherein X represents a halogen atom selected from the group consisting of chlorine, bromine, fluorine and iodine and Y represents a member selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl, toluyl naphthyl, benzyl, phenethyl groups, alkali metal and the ammonium radical, the amount of antifogant being from 0.02 to 200 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

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2. The material as defined in claim 1 wherein the antifoggant is located in the silver halide emulsion, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

3. The material as defined in claim 1 wherein the antifoggant is located in a layer adjacent the silver halide emulsion.

4. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, a chlorosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

5. The article as defined in claim 4, wherein the antifoggant is m-chlorosulfonyl benzoic acid.

6. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, p-chlorosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

7. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, o-chlorosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

8. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, an alkali metal salt of a halosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

9. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, an ammonium salt of halosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

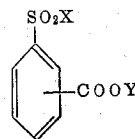
10. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, a halosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

11. A light-sensitive photographic material comprising a light-sensitive silver halide emulsion, a carrier therefor, said emulsion containing, as an antifoggant, a hydrocarbon ester of a halosulfonyl benzoic acid, the amount of antifoggant being from 0.02 to 20 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

12. A process of minimizing and preventing fog in light-sensitive silver halide materials comprising a base

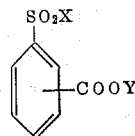
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having a light-sensitive silver halide emulsion thereon, which comprises exposing said emulsion to light and developing the same in the presence of an antifoggant characterized by the general formula:



wherein X represents a halogen atom selected from the group consisting of chlorine, bromine, fluorine and iodine and Y represents a member selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl, toluyl, naphthyl, benzyl, phenethyl groups, alkali metal and the ammonium radical, the amount of antifoggant being from 0.02 to 200 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

13. A photographic developer containing a developing agent and an antifoggant characterized by the general formula:



wherein X represents a halogen atom selected from the group consisting of chlorine, bromine, fluorine and iodine and Y represents a member selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, phenyl, toluyl, naphthyl, benzyl, phenethyl groups, alkali metal and the ammonium radical, the amount of antifoggant being from 0.02 to 200 milligrams per 0.6 mole of silver halide contained in said light-sensitive silver halide emulsion.

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