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QUINONE STABILIZERS AND ANTIFOGGANTS FOR SILVER HALIDE EMULSIONS

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The present invention relates to the use of anti-fogging and stabilizing agents for photographic silver halide emulsions and, more particularly, to the employment of certain benzoquinone derivatives for such purposes.

It is well known in the photographic art that light-sensitive emulsions, such as gelatino-silver halide emulsions exhibit a marked tendency to fog. The fog may be attributable to a number of influences such as excessive ripening of the emulsion by prolonged storage of the film and especially under elevated conditions of temperature and/or humidity and by prolonged development of the exposed emulsion.

To overcome or otherwise mitigate this undesirable property, it has been the practice in the photographic art to add certain chemical compounds to the emulsions to thereby increase their stability and to reduce their tendency to fog. However, many of the stabilizing and antifogging compounds heretofore employed in the art are characterized by the disadvantage that upon addition to the emulsion they cause a loss of speed and/or contrast of the emulsion. This loss of speed is particularly pronounced in those regions of the spectrum to which the emulsions are optically or dye sensitized.

Thus, a primary object of the present invention resides in the provision of improved anti-fogging compounds in which the above disadvantages are eliminated or at least mitigated to a substantial degree.

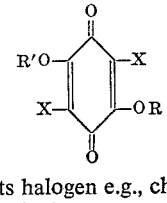
A further object of the present invention resides in the provision of light-sensitive emulsions containing a compound which stabilizes the emulsion against fogging while exhibiting little tendency to reduce the speed and/or contrast of the emulsion.

A still further object of the present invention resides in the provision of light-sensitive emulsions containing a compound which stabilizes the emulsion against fogging while exhibiting little tendency to reduce the sensitivity of the emulsion to light of longer wave length affected by the presence of one or more sensitizing dyes.

Another object of the present invention resides in the provision of improved silver halide developing compositions containing an antifogging compound whereby there is obtained reduced fog, improved contrast, speed, and stability of photographic emulsions developed therewith.

Other objects and advantages of the present invention will become apparent hereinafter from the detailed description thereof.

The attainment of the foregoing and related objects is made possible in accordance with the present invention by the addition to either light-sensitive photographic silver halide emulsions and/or developing compositions and/or other processing solutions associated therewith of at least one compound of the following general formula:



wherein X represents halogen e.g., chlorine, bromine, etc.; R and R' represent hydrogen, or a salt-forming cation such as sodium, potassium, barium, lanthanum, silver,

gold, ammonium; substituted ammonium in which one or more of the hydrogens is replaced by lower alkyl, e.g., methyl, ethyl, propyl, etc.; hydroxy lower alkyl e.g., hydroxy ethyl, and wherein such substituents may be the same or different.

The compounds encompassed by the above formula may be prepared for example by treating 2,5-dihydroxy-3,6-dimethoxy acetophenone with halogen e.g., bromine or chlorine, in acetic acid solution to form the corresponding 3,5-dihalo-2,5 - dihydroxybenzoquinone derivative.

The compound produced by the above method may be readily converted to its salt by reaction with a compound containing the desired cation such as sodium carbonate, potassium carbonate, silver nitrate, ammonium carbonate or the like.

Improved fog reduction and other beneficial effects are obtained when the aforementioned compounds are incorporated in 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. Such additions may be made before, during or after the decomposition of the soluble silver salt such as silver nitrate by means of a soluble halide such as potassium, bromide, sodium chloride or the like in the presence of a colloidal carrier such as gelatin, PVA, solubilized casein, albumen or the like.

"Coating finals" are added to the emulsion just prior to coating on a suitable support such as glass, paper or film at a time when the emulsion has nearly attained its maximum sensitivity.

When used as ripening finals, the antifoggings are best employed in a concentration of 5 to 40 mg. per .6 mole of silver halide and when used as coating finals in a concentration of 100 to 500 mg. per .6 mole of silver halide. The concentration used depends on the type of emulsion employed and it is advisable to determine the optimum concentration from case to case. In some instances, it is advantageous to apply the antifoggant and stabilizers in layers adjacent to the emulsion, that is, in a separate undercoating layer or in the anti-abrasion gelatin surface. In other instances, the desired result may be procured by addition of the antifoggant and stabilizer to one or several processing baths such as developer, fixer or the like. When incorporated into the photographic developer or other processing bath, the antifoggants of the present invention may be employed in concentrations ranging from 0.5 gram to 1 gram per liter, e.g. per liter of developer composition with a range of 0.2 gram to 0.5 gram being particularly preferred.

The aforesaid antifoggants and stabilizers may be utilized in connection with any type of photographic emulsion, e.g., non-sensitized, orthochromatic, panchromatic, X-ray emulsions, paper emulsions, color emulsions or the like. They may be employed in combination with other known antifoggants and stabilizers, reduction- and metal- and noble metal sensitizers, or in combination with hydroxypolyethanoxy derivatives, i.e., those obtained by reacting ethylene oxide with an alcohol, phenol, amine or the like (see U.S. Patent 1,970,578).

The following examples are given for purposes of illustrating the present invention only and are not to be considered in any way as being limitative thereof.

Example I illustrates the improvements provided by the present invention when the antifoggant is added directly to a silver halide emulsion.

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 2% solution of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone in ethanol was added to the emulsion as an antifoggant 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 I B Sensitometer and developed in a developer of the following composition:

	Grams
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	.8

Water to make 1 liter.

Quantity of Compound Used, mg.	Relative Speed	Fog at 6'	Oven Fog at 6' Development
0	100	.13	.14
200	100	.10	.13
400	100	.09	.10

The antifoggant was prepared as follows: 0.5 g. of 2,5-dihydroxy-3,6-dimethoxyacetophenone in 8 cc. of acetic acid was treated with chlorine (0.6 g.) in acetic acid (2 cc.). The mixture was heated on a steam bath for approximately 1 hr. and allowed to cool. A yellow precipitate formed which was removed and crystallized from acetic acid. The product, 2,5-dichloro-3,6-dihydroxy-p-benzoquinone formed yellow needles and dried to a red powder. (Reference: J. Amer. Chem. Soc., p. 1395, (1953).)

The following example illustrates the improved results obtained by the use of the antifoggant compound as an additive to a conventional black and white developer solution:

Example II

Exposed samples of a photographic film were developed for 12 minutes at 65° F. in a standard metol-hydroquinone developer. Two tests are made, one with the normal developing solution and one with a developer containing 50 milligrams per liter of the antifoggant of Example I.

Sensitometric strips, developed in the normal developer (control) for 12 minutes showed of fog of .30, whereas those strips which were developed in the developer containing the antifoggant, had a fog of .20.

The following example illustrates the improved results obtained when the antifoggant compound is included in an antiabrasion layer.

Example III

A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was coated on filmbase in a manner known to the art. After the coating was applied, an aqueous gelatin solution containing 20 grams of gelatin per 1 liter and 50 mg. of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone, prepared in the manner described above, 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 .20 compared with a type coating of the above, but lacking the antifoggant, and having a speed of 100 and a fog of .30.

Example IV

Silver chlorobromide emulsions for enlarging paper are prepared according to the formulae described on p. 343 of "Photographic Chemistry" by Pierre Glafkides, a a Fountain Press Publication 1958.

Wherever there is acid added to such a formula, e.g., sulfuric acid or citric acid, a portion of this acid is substituted by a solution of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone disilver salt in sulfamic acid, so that 500 mg. of this compound are used per 6 moles of silver halide. The antifoggant is produced by treating the 2,5-dichloro-3,6-dihydroxy-p-benzoquinone prepared in the manner described above with silver nitrate.

Fog reductions have been observed as follows:

Emulsion	Fog	
	Fresh	Oven
Variable Contrast Emulsion		(1)
(a) No stabilizer	.10	.20
(b) 500 mg. per (10 kg. emulsion) 6 moles	.10	.12

[1] 16 hours at 65% RH and 140° F.

Results similar to those described above are obtained when the procedures described in the foregoing examples are repeated but employing in lieu of the antifoggants specified therein one or more of the following compounds:

2,5-dibromo-3,6-dihydroxy-p-benzoquinone
2,5-dibromo-3,6-dihydroxy-p-benzoquinone disilver salt
2,5-dichloro-3,6-dihydroxy-p-benzoquinone diammonium salt
2,5-dichloro-3,6-dihydroxy-p-benzoquinone disodium salt
2,5-dibromo-3,6-dihydroxy-p-benzoquinone diisoamyl amine salt and the like.

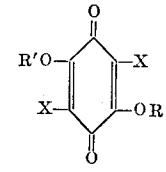
It will be readily appreciated that mixtures of two or more of the antifoggants of the present invention may likewise be employed to advantage in the manner more fully described above. As a further modification, the present invention contemplates the addition of such compounds to one or more of the processing baths conventionally employed in the pre-development and post-development treatment of an exposed silver halide photographic film. For example, they may be added to the fixing solution, rinse bath and/or pre-baths and the like. Particularly beneficial results are obtained, however, according to procedures wherein the antifoggant compound is present during the development operation, e.g., as an additive to the developer solution. The developer composition may be any of those conventionally employed in the development of exposed silver halide emulsions and accordingly may be of the hydroquinone type, i.e., those which contain hydroquinone, potassium metabisulfite and potassium bromide, or they may be of the metol-hydroquinone type, i.e., those which contain p-methylaminophenol, sodium sulfite, sodium bisulfite, hydroquinone, sodium carbonate, and potassium bromide. Alternatively, the developer composition may be of the so-called borax type, i.e., those which contain p-methylaminophenol, sodium sulfite, hydroquinone, borax and potassium bromide.

In any event, it is found that the improvement in the fog characteristic made possible by the antifoggants of the present invention does not entail any adverse effects upon any of the other photographic properties of the silver halide emulsion such as D Max, contrast, speed and the like.

The present invention has been described with respect to certain preferred embodiments and there will become obvious to persons skilled in the art other variations, modifications, and equivalents which are to be understood as coming within the scope of the present invention.

What is claimed is:

1. A light-sensitive silver halide emulsion containing an antifoggant and stabilizer comprising a compound of the following general formula:



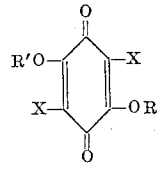
wherein X represents halogen and R and R' are selected from the group consisting of hydrogen and a cation.

2. A light-sensitive silver halide emulsion according to claim 1 wherein said antifoggant comprises 2,5-dichloro-3,6-dihydroxy-p-benzoquinone.

3. A light-sensitive silver halide emulsion according to claim 1 wherein said antifoggant comprises 2,5-dichloro-3,6-dihydroxy-p-benzoquinone disilver salt.

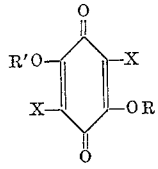
4. A light-sensitive silver halide emulsion according to claim 3 wherein said antifoggant comprises 2,5-dichloro-3,6-dihydroxy-p-benzoquinone disodium salt.

5. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion, said light-sensitive material containing an antifoggant and stabilizer comprising a compound of the following general formula:



wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

6. An aqueous developer solution containing a silver halide photographic developing agent and an antifoggant and stabilizer comprising a compound of the following general formula:

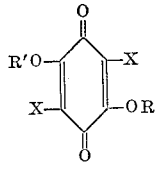


wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

7. A developer composition according to claim 6 wherein said antifoggant comprises 2,5-dichloro-3,6-dihydroxy-p-benzoquinone.

8. An aqueous developer composition according to claim 6 wherein said silver halide developing agent comprises hydroquinone.

9. A process of treating an exposed silver halide emulsion characterized in that at least one of the processing baths employed in the development and treatment of the photographic film contains an antifoggant and stabilizer comprising a compound of the following general formula:

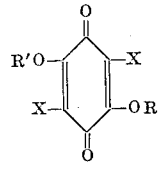


wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

10. A process according to claim 9 wherein said antifoggant is present in the silver halide developer solution.

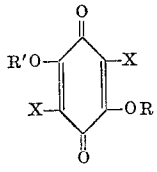
11. A process according to claim 10 wherein said antifoggant comprises 2,5-dichloro-3,6-dihydroxy-p-benzoquinone.

12. A process for the preparation of a photographic emulsion having a reduced tendency to fog which comprises forming the emulsion, ripening the emulsion and, during said ripening, adding thereto an antifoggant and stabilizer comprising a compound of the following general formula:



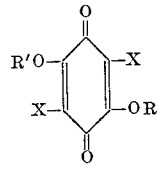
wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

13. A process for the preparation of a photographic emulsion having a reduced tendency to fog which comprises forming the emulsion, ripening the emulsion, coating said emulsion on a base and adding to said emulsion just prior to the coating thereof on the base an antifoggant and stabilizer comprising a compound of the following general formula:



wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

14. Light-sensitive photographic material comprising a base, a light-sensitive silver halide emulsion layer, and an anti-abrasion layer containing an antifoggant and stabilizer comprising a compound of the following general formula:



wherein X represents halogen and R and R′ are selected from the group consisting of hydrogen and a cation.

No references cited.

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