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# FOG REDUCTION IN PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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The present invention relates to photographic elements containing a light-sensitive silver halide emulsion and to the use in intimate contact with such emulsions of compounds which serve as anti-fogging and stabilizing agents therefor.

It is known that light-sensitive silver halide emulsions have a tendency to fog. Fog is caused in a number of ways, e.g., by prolonged ripening of the emulsions during storage of the film or paper, particularly at elevated temperature and humidity, or by the use of chemical sensitizers, particularly alkylene oxide derivatives, as described in United States Patents 2,704,716, 2,716,062 and 2,728,666. Prolonged developing time may also cause fogging.

A great number of anti-foggants and stabilizers have been described in the literature as being effective in preventing an increase in fog thereby stabilizing or controlling the keeping-quality of the light-sensitive silver halide emulsions.

Mees in "The Theory of the Photographic Process," published by the MacMillan Company, New York, 1946, discusses the use of anti-foggants on pages 459 et seq. Although many of these compounds have the ability to reduce fog tendencies, they have shortcomings in most cases in that they lower the sensitiviey of the emulsions and in many instances reduce the optical or dye sensitization.

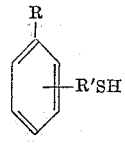
An object of our invention is to provide stabilizers or fog inhibiting agents which tend to prevent the formation of chemical fog in light-sensitive silver halides.

A further object is to provide stabilizers or anti-fogging agents for light-sensitive silver halide emulsions which do not appreciably lower the sensitivity of the emulsions.

A still further object is to provide stabilizers or anti-fogging agents for light-sensitive silver halide emulsions which do not reduce the sensitivity to light of longer wave lengths effected by the presence of sensitizing dyes.

Other objects and advantages will appear from the specification.

It has been discovered that a very effective class of stabilizers or anti-fogging agents for light-sensitive silver halide emulsions are those having the following general formula:

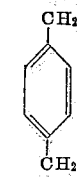



wherein R is methyl, ethyl, methyl mercapto or ethyl mercapto and R' is methylene or ethylene, the alkylene value for R' always being the same as the alkylene value for R and the R'SH group being in a position o-, m- or p- to the R group.

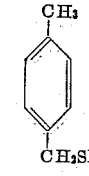


Examples of compounds contemplated by the above general formula are:

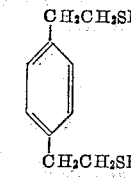
(1) α,α'-Dimercapto-p-xylene of the formula



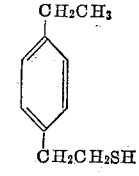

(2) α,α'-Dimercapto-m-xylene.
(3) α,α'-Dimercapto-o-xylene.
(4) α-Mercapto-p-xylene of the formula




(5) α-Mercapto-m-xylene.
(6) α-Mercapto-o-xylene.
(7) β,β'-Dimercapto-p-diethyl benzene of the formula




(8) β,β'-Dimercapto-m-diethyl benzene.
(9) β,β'-Dimercapto-o-diethyl benzene.
(10) β-Mercapto-p-diethyl benzene of the formula




(11) β-Mercapto-m-diethyl benzene.
(12) β-Mercapto-o-diethyl benzene.

Most of the compounds listed are known in the literature and their methods of preparation are described therein. For example, α,α'-dimercapto-p-xylene may be prepared according to Ber. 42, 4349 (1909). In this synthesis a freshly prepared alcoholic solution of potassium hydroxide is saturated under cooling with hydrogen sulfide. To the solution thus prepared (containing slightly more than two equivalents of KSH) is added quickly, with good stirring, a hot solution of p-xylene bromide in 95% ethanol. The reaction proceeds with separation of potassium bromide and is completed by refluxing for a minute. The alcohol is evaporated, the residue diluted with water and extracted with ether. The ether is evaporated to leave an oil which is treated with diluted sodium hydroxide. The alkaline solution is filtered to remove unwanted products, the filtrate acidified with dilute sulfuric acid and the mercaptan extracted with ether. The ether is evaporated and the oily products distilled under vacuum.

α,α'-dimercapto-o-xylene is prepared in the same manner excepting that o-xylene bromide is substituted for the p-xylene bromide.

α,α'-dimercapto-m-xylene is also prepared in the same way but while using m-xylene bromide in lieu of p-xylene bromide.

The α-mercapto xylenes are also prepared in a similar fashion but by using one equivalent of KSH rather than two, as in the preparations previously described.

The diethyl benzene derivatives are prepared in a like manner excepting that the xylene bromide is replaced by diethyl benzene. If dimercapto derivatives of the diethyl benzene are desired two equivalents of KSH are used per one equivalent of diethyl benzene bromide. If the monomercapto derivative is desired, then equal molar quantities of KSH and diethyl benzene bromide are employed.

Beneficial effects in fog reduction may be obtained with solutions of the above compounds incorporated in the silver halide emulsions as "ripening finals" or as "coating finals." Ripening finals are added during the ripening or the sensitivity stage of the emulsion making process. Such additions may be effected before, during or after the addition of a soluble silver salt to the soluble halide in the presence of a soluble photographic colloid, such as gelatin, PVA, PVP, solubilized casein or albumin.

Coating finals are added to the emulsion just prior to coating it on a suitable support, i.e., glass, paper or film when the emulsion has nearly obtained its maximum sensitivity.

When used as ripening finals our anti-foggants or stabilizers are best used in a concentration of .02 to 5 milligrams per .6 mole of silver halide and when used as coating finals in a concentration of 1 to 20 milligrams per .6 mole of silver halide. In many emulsions we prefer to apply our anti-foggants or stabilizers in a gelatin surface coating for maximum effectiveness. The concentration used depends very much on the type of emulsion employed and it is advisable to determine the optimum concentration from case to case.

The anti-foggants and stabilizers may be employed in various types of photographic emulsions, e.g., non-sensitized, orthochromatic, panchromatic, X-ray emulsions, paper emulsions and color emulsions. They may be used in combination with other known anti-foggants or stabilizers or in combination with sulfur-, reduction-metal-and noble metal sensitizers, or in combination with polyoxyalkylenes and their derivatives.

Equally good results are obtained in the event that the anti-foggants or stabilizers are used in one or all processing baths or in pre- and post-baths, particularly in the photographic developer.

The invention is further illustrated by the following examples which are exemplary and not limitative:

*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 and finals were added such as sensitizing dyes and hardening agents. A 0.01% solution of α,α'-dimercapto para-xylene was added to the emulsion as an anti-foggant and stabilizer. The emulsion samples contained about 0.6 mole of silver halide. The so prepared emulsion samples were coated on a 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 |
| Hydroquinone | 3 |
| Sodium carbonate, monohydrate | 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 | .28 | .22 |
| 1 mg | 100 | .25 | .21 |
| 2 mg | 100 | .20 | .15 |
| 5 mg | 90 | .20 | .14 |

*Example II*

The procedure is the same as in Example I excepting that there is added β,β'-dimercapto-p-diethyl benzene in lieu of the p-xylene derivative. The results are substantially the same.

*Example III*

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 a developer containing 4 mg. of α,α'-dimercapto para-xylene 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 antifoggant, had a fog of .18.

*Example IV*

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 of gelatin in 1 liter of $H_2O$ and 8 mg. of α,α'-dimercapto para-xylene 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 .18 compared with type coating of the above emulsion having an antiabrasion layer similar to that described above, but lacking the antifoggant and having a speed of 100 and a fog of .30.

*Example V*

The procedure is the same as in Example I except that the p-xylene derivative thereof is replaced by an equivalent quantity of α-mercapto-p-xylene. Equivalent results are obtained.

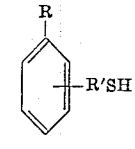
*Example VI*

The procedure is the same as in Example IV excepting that the p-xylene derivative is replaced by an equivalent quantity of β-mercapto-m-diethyl benzene. The results are comparable with those of Example IV.

Modifications of the invention will occur to persons skilled in the art and we therefore do not intend to be limited in the patent granted except as necessitated by the appended claims.

We claim:

**1.** A light-sensitive photographic element containing a base with a silver halide emulsion thereon, said emulsion having in intimate contact therewith a compound of the following formula:




wherein R is selected from the class consisting of methyl, ethyl, methyl mercapto, and ethyl mercapto and R' is selected from the class consisting of methylene and ethylene, the alkylene value for R' always being the same as the alkylene value for R and the R'SH group being in a position selected from the class consisting of the o-, m-, and p-positions to the R group.

**2.** The product as defined in claim **1** wherein the compound is located in the silver halide emulsion.

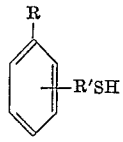
3. The product as defined in claim 1 wherein the compound is located in an antiabrasion overcoating for the silver halide emulsion.

4. The product as defined in claim 1 wherein the compound is $\alpha,\alpha'$-dimercapto-p-xylene.

5. The product as defined in claim 1 wherein the compound is $\alpha$-mercapto-p-xylene.

6. The product as defined in claim 1 wherein the compound is $\beta,\beta'$-dimercapto-p diethyl benzene.

7. A process of reducing the tendency of an exposed photographic silver halide emulsion to fog on development which comprises developing said emulsion with a developer containing a compound of the following formula:






wherein R is selected from the class consisting of methyl, ethyl, methyl mercapto and ethyl mercapto and R' is selected from the class consisting of methylene and ethylene, the alkylene value for R' always being the same as the alkylene value for R and the R'SH group being in a position selected from the class consisting of the o-, m- and p-positions to the R group.

8. A process of reducing the tendency of a photographic silver halide emulsion to fog on development which comprises exposing the emulsion and developing it in a metol-hydroquinone developer containing a small amount of $\alpha,\alpha'$-dimercapto-p-xylene.

**References Cited by the Examiner**

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