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STABILIZED SILVER HALIDE EMULSIONS

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This invention relates to the improvement of photographic emulsions and more particularly to the incorporation of antifogging or stabilizing agents into silver halide emulsions.

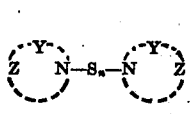
A large number of substances have been described as being effective in preventing an increase in fog and thus stabilizing or controlling the keeping quality of photographic emulsions. Many of these stabilizers have definite limitations in their ability to produce desirable effects without producing unfavorable side reactions. Thus, some stabilizers desensitize or produce fog, when added during the mixing or ripening, but exert favorable effects when added to the melted emulsion before coating. It is one object of this invention, therefore, to produce a stabilizing emulsion of improved photographic quality while incorporating the stabilizing agents over a wider range of application during the manufacture of photographic emulsions.

In U. S. P. 2,057,764 there is described a process of stabilizing photographic silver halide emulsions by incorporating sulfinic or seleninic acids or their salts into the emulsion in the form of a solution in a suitable solvent during the preparation of the emulsion or by incorporating the stabilizer into the finished emulsion by bathing the emulsion layer with a weak solution of the stabilizer. It is stated that the fogging influence of supports, preparation layers, backing layers, intermediate layers, sublayers, protective layers, or baryta layers could be prevented by incorporating these stabilizers into such layers. As compared with films which were not provided with the sulfinic acid or seleninic acid stabilizers, it is stated that the films containing the stabilizer showed a fog density unit of approximately one-half. It has now been discovered that the stabilizing effect of the sulfinic or seleninic acids or their salts, disclosed in U. S. P. 2,057,764, can be considerably improved and the range of application greatly extended if small amounts of certain diamino or N-heterocyclic, mono- or polysulfides are present in the emulsions containing the sulfinates or seleninates. The particular mono and polysulfide compounds which produce this improvement are those which are in the class consisting of aryl-substituted diamino and N-heterocyclic mono and polysulfides having the following structural formulae:

I. $R_1RN—S_n—NRR_1$

and

II.



wherein R stands for an aryl radical, R_1 a member of the group consisting of hydrogen, alkyl and aryl, n is a whole number equal to at least 1, Y is a member of the group consisting of N, O, S, and $—CH_2—$ and Z the remaining component groups or hetero atoms necessary to complete a 5 or 6-membered heterocyclic ring.

It has been observed that extremely small quantities of these mono or polysulfides will improve the stabilizing characteristic of photographic emulsions containing a sulfinate or seleninate to an extent unobtainable with a sulfinate or a seleninate alone. Thus, for example, the photographic effect of sodium sulfinate or seleninate is improved by the addition of 0.00025–0.0050 mol of the following sulfides per mol of sulfinate or seleninate:

Morpholine sulfide
Morpholine disulfide
Morpholine trisulfide
Piperidine tetrasulfide
Proline disulfide
Morpholine tetrasulfide
N-N'-di-thioaniline

The remarkably improved result, expressing fog in terms of density units, is manifested in a reduction of the fog density to a value of ½ the fog density obtained when using a sulfinate or seleninate in accordance with the process of U. S. P. 2,057,764. Thus, freshly coated films having a fog density of 25 to 30 density units are reduced to a fog density of from 12 to 15 density units and films, incubated for 6 days at at 50° C. having a fog density of 25 to 35, are reduced to a fog density of 15 to 19 by adding morpholine disulfide in the above proportion. This reduction in fog density produces better clearness, better heating quality and an unusual brilliance which is especially desirable in medical and industrial radiographs.

The same reduction in fog density is obtained whether the mono or polysulfide compound is added with the sulfinate or seleninate during the ripening stage in the process of making the silver halide emulsion or during mixing of the molten emulsion prior to coating or whether a solution of the sulfinate or seleninate to which has been added a small amount of the sulfide is applied to the cast film as an after-coating. In the latter case, solvents for the stabilizer mixture are employed which do not affect emulsions such as water or organic solvents which are miscible with water, for instance, alcohol. The stabilizing mixture of the sulfinic acid salt or seleninic acid salt and the mono- or polysulfide compound may also be employed in preparation layers, backing layers, intermediate layers, sublayers, protective

layers and baryta layers in order to prevent the fogging influence of such layers.

It has been furthermore discovered that the amount of sodium benzene sulfinate or seleninate necessary to produce the stabilizing effect can be reduced by 60–90% if these salts are used in combination with the mono- or polysulfides. Depending somewhat on the type of gelatin employed, the amount of the stabilizing sodium benzene sulfinate or seleninate can be reduced in many cases to $\frac{1}{10}$ the amount necessary when used without the addition of the mono- or polysulfide. It has been found that in such cases, the reduced amount of the sodium benzene sulfinate in combination with the mono- or polysulfide gives superior results in clearness, gradation and keeping quality, whereas the thus reduced amount of sulfinate, if used without the mono- or polysulfide, would be entirely inadequate for producing a stabilizing effect on the photographic emulsions.

Without in any way wishing to be bound by or limited to any particular theory as to the mechanism of the additional stabilizing effect produced by mono- or polysulfides of the above class, it is believed that this additional stabilizing effect is either a catalytic one or is due to a chemical interaction between the sulfide compound and the sulfinate or seleninate with the possible production of a reaction product which exerts the enhanced stabilizing influence on the silver halide emulsion. The following examples will serve to further illustrate the invention, it being understood that the invention is not limited thereto:

Example I

To 1 kilogram of a gelatino-silver-halide emulsion containing from 6 to 7% of silver halide and approximately 8% gelatin there were added as a coating final:

	Cc.
A 20% solution of sodium salt of p-toluene sulfinic acid	15
An alcoholic solution of morpholine disulfide of the concentration of one gram per one liter of methanol	2.5

The melted emulsion was then mixed and cast on a film base and cut into test film lengths. Similar test films were made with the same silver halide emulsion but omitting the addition of either the sodium salt of p-toluene sulfinic acid or of morpholine disulfide. Additional similar test films were made with the same silver halide emulsion to which had been added as a coating final the same quantity of the sodium salt of p-toluene sulfinic acid as above but omitting the morpholine disulphide.

The fog density of each of these types of test film was determined for the freshly prepared film and test pieces of each type were then incubated for a period of six days at 50° C. It was observed that the fog density of the films treated with p-toluene sulfinic acid to which had been added morpholine disulfide was decreased by 50%, in the case of the freshly prepared film, and about 45%, in the case of the incubated film, of the fog density of the films which had been treated only with p-toluene sulfinic acid.

Example II

To 1 kilogram of a gelatino-silver-halide emulsion containing from 6 to 7% of silver halide and approximately 8% gelatin there were added during the ripening stage:

	Cc.
A 20% solution of the sodium salt of benzene seleninic acid	25
An alcoholic solution of morpholine disulfide of the concentration of one gram per liter of methanol	5

The melted emulsion was then mixed and cast on a film base and cut into test film lengths. Similar test films were made with the same silver halide emulsion but omitting the addition of either the sodium salt of benzene seleninic acid or of morpholine disulfide. Additional similar test films were made with the same silver halide emulsion to which had been added during ripening the same quantity of the sodium salt of benzene seleninic acid as above but omitting the morpholine disulfide.

The fog density of each of these types of test film was determined for the freshly prepared film and test pieces of each type were then incubated for a period of six days at 50° C. It was observed that the fog density of the films treated with benzene seleninic acid to which had been added morpholine disulfide was decreased by 50%, in the case of the freshly prepared film, and about 45%, in the case of the incubated film, the fog density of the films which had been treated with benzene seleninic acid alone.

Example III

To 1 kilogram of a gelatinous silver halide emulsion containing 6–7% silver halide and 8% gelatin there was added during the ripening stage:

	Cc.
A 20% solution of the sodium salt of p-chlorobenzene sulfinic acid	15
Morpholine mono-sulfide in a concentration of 1 gram per liter of methanol	5

The clearness of the emulsion and the keeping quality was determined in a similar mannner as described in Example I. Again, it was observed that both clearness and keeping quality were considerably improved over an addition of the chlorobenzene sulfinic acid without the morpholine monosulfide. It may be mentioned that the morpholine monosulfide may be substituted by an equivalent amount of morpholine tetrasulfide. The same reduction in fog density was obtained as in the case of Examples I and II.

Example IV

To a gelatinous silver halide emulsion containing silver halide corresponding to 100 grams silver nitrate, 90 cc. of 20% solution of sodium benzene sulfinate and 20 cc. of a solution of morpholine disulfide in a concentration of 1 gram per liter of methanol were added immediately after the precipitation of the silver halide prior to the first digestion. The emulsion was subsequently washed and after-ripened in a manner familiar to those skilled in the art. The clearness and keeping quality of the emulsion was found to be in all cases improved as compared to one obtained with the addition of the sodium benzene sulfinate without the addition of the polysulfide to the same extent in the case of Examples I and II.

Example V

To 1 kilogram gelatinous silver halide emulsion there was added during the ripening stage:

10 cc. of a 20% solution of sodium benzenesulfinate and 5 cc. of alcoholic solution contain-

ing proline disulfide in a concentration obtained as follows: 230 mg. of l-proline were suspended in approximately 70 cc. of carbontetrachloride at a temperature of —2 to —5° C. This suspension was treated with 134 mg. of sulfur monochloride in the presence of 124 mg. of sodium carbonate (monohydrate) with frequent vigorous agitation. The solvent was distilled off under diminished pressure at 40–45° C. The residue was washed from the flask with absolute ethyl alcohol, filtered and the filtrate evaporated to dryness. The residue was extracted with ethyl alcohol; the extract was filtered and adjusted to a final volume of 500 cc. with ethyl alcohol. The disulfide was not isolated.

The stabilizing effect obtained with the combination of sodium benzene sulfinate and this preparation of proline disulfide gave a similarly favorable effect as described in detail in Example II.

Example VI

To 1 kilogram of a gelatinous silver halide emulsion of high speed Portrait type ready for coating, 2.5 cc. of the following solution was added as a stabilizer:

Part 1: 5.0 cc. 20% solution benzene sulfinate (c. p.) 2.0 cc. water.
Part 2: 14 cc. methanol, 29 mg. morpholine disulfide (recrystallized. M. P. 123–4°).
Part 3: 4.0 cc. of 0.1 n-sulfuric acid.

Parts 1 to 3 were mixed (total vol. 25 cc.) in the order listed and used after filtering out a small quantity of a precipitate which had precipitated out after several hours. The stabilizing effect of this solution was equal or slightly superior to that obtained otherwise only with 1500 cc. of a 20% solution of sodium benzene sulfinate.

Similar results may be obtained when the sodium benzene sulfinate or seleninate is replaced by, for instance, naphthalene sulfinic acid, ethane sulfinic acid or other sulfinic or seleninic acids such as described in U. S. P. 2,057,764. The preparation of the various mono- and polysulfides such as morpholine disulfide has been described in the literature and in U. S. P. 2,343,524. The manufacture of these substances does not form any part of this invention.

In a similar way to that described in U. S. P. 2,057,764, paper can be impregnated with the sodium salts of thiophene sulfinic acid to which small quantities of one of the above class of mono- or polysulfides have been added. Film in contact with the paper treated in such a manner shows superior clearness as compared to paper which has received a treatment with the sodium salt of the thiophene sulfinic acid without the mono- or polysulfide.

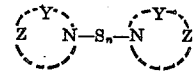
It is within the scope of this invention to add combinations of sulfinates or seleninates and mono- or polysulfides also to antihalation and surface layers, a procedure which yields results which cannot be attained when using only the sulfinates or seleninates.

What I claim as my invention and desire to secure by Letters Patent of the United States is:

1. A photographic material comprising a silver-halide gelatin emulsion in contact with a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and an organic sulfide compound selected from the group consisting of aryl-substituted diamino and N-heterocyclic mono- and polysulfides having the following formulae:

I. $R_1RN—S_n—NRR_1$

and

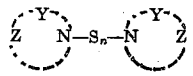
II. 

wherein R stands for an aryl radical, R_1 a member of the group consisting of hydrogen, alkyl, and aryl, n is a positive integer, Y is a member of the group consisting of N, O, S, and —CH_2—, and Z represents the remaining components necessary to complete up to a 6-membered heterocyclic ring.

2. A photographic material comprising a silver-halide gelatin emulsion containing a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and an organic sulfide compound selected from the group consisting of aryl-substituted diamino and N-heterocyclic mono- and polysulfides having the following formulae:

I. $R_1RN—S_n—NRR_1$

and

II. 

wherein R stands for an aryl radical, R_1 a member of the group consisting of hydrogen, alkyl, and aryl, n is a positive integer, Y is a member of the group consisting of N, O, S, and —CH_2—, and Z represents the remaining components necessary to complete up to a 6-membered heterocyclic ring.

3. A photographic material comprising a silver halide gelatin emulsion in contact with a member of the group consisting of seleninic acid, a sulfinic acid and their salts and small amounts of morpholine disulfide.

4. A photographic material comprisiig a silver halide gelatin emulsion in contact with a member of the group consisting of a seleninic acid, a sulfinic acid and their salts and small amounts of morpholine tetrasulfide.

5. A photographic material comprising a silver halide gelatin emulsion in contact with a member of the group consisting of a seleninic acid, a sulfinic acid and their salts and small amounts of proline disulfide.

6. A photographic material comprising a silver halide gelatin emulsion containing a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and small amounts of morpholine disulfide.

7. A photographic material comprising a silver halide gelatin emulsion containing a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and small amounts of morpholine tetrasulfide.

8. A photographic material comprising a silver halide gelatin emulsion containing a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and small amounts of proline disulfide.

9. A photographic material comprising a silver halide gelatin emulsion containing a mixture of sodium benzene sulfinate, morpholine disulfide and sulfuric acid.

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