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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 stabilized 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. Patent 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, as described in U. S. Patent 2,057,764, can be considerably improved and the range of application greatly extended if small amounts of polythionic acids or their alkali metal salts of the formula

$$MOSO_2—S_n—SO_2OM$$

wherein M is an alkali metal or hydrogen and n is a positive integer, or of the thioanhydrides of sulfonic acids of the formula

$$RSO_2—S_n—SO_2R$$

wherein R is an organic radical and n is a positive integer, are present in the emulsions containing the sulfinates or seleninates. It has been observed that extremely small quantities of polythionates, preferably those containing a total of three or more sulfur atoms and thioanhydrides of sulfonic acids containing a total of three or more sulfur atoms will improve the stabilization characteristic of photographic emulsions containing a sulfinate or seleninate to an extent unobtainable with the sulfinate or seleninate treatment. The remarkably improved result is manifested in a reduction of the fog density to approximately 50% of that obtained when using sulfinate or seleninate alone. Thus, films having a fog density of 25 to 30 density units after having added sulfinate are reduced to a fog density of 12 to 15 density units by adding small amounts of a polythionate or thioanhydride.

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This reduction in fog density produces a better clearness, better keeping quality and an unusual brilliance which is especially desirable in medical and industrial radiographs. Concentrations of 0.025—0.500% by mol of the polythionate or thioanhydride compounds to the sulfinates or seleninates are sufficient to produce this reduction in fog density. Suitable polythionates and thioanhydrides which will produce this desirable effect when used in combination with a sulfinate or seleninate include such compounds as sodium trithionate, sodium tetrathionate, potassium pentathionate, potassium, hexathionate, dibenzene sulfonyl mono-, di-, tri-, and tetrasulfide.

Polythionates have been used in silver halide emulsions without sulfinates or seleninates for the production of photographic effects wherein the polythionate is employed as a ripening substance, that is, a substance capable of enhancing the photographic speed. Such a process is described in U. S. Patent 1,673,522. It is interesting to note that this use of polythionates for enchancing the sensitivity of the emulsion is usually accompanied by a definite loss of clearness. It is, therefore, surprising that polythionates exert a fog-preventing or anti-ripening or stabilizing action when used in combination with sulfinates or seleninates.

The polythionates or thioanhydrides, which produce this increased stabilization, can be formed in the solution of the sulfinate or seleninate by reaction between some of the sulfinate or seleninate and colloidal sulfur added to the sulfinate or seleninate solution, or nascent sulfur or selenium produced by catalytic decomposition of a suitable labile sulfur compound such as sodium thiosulfate which has been added to the sulfinate or seleninate solution. This invention, therefore, contemplates and includes such formation of the polythionates or thioanhydrides in the sulfinate

or seleninate solution. In carrying out this phase of the invention, the colloidal sulfur or selenium, or labile sulfur compound and its decomposition catalyst such as sodium arsenite, is added to the sulfinate or seleninate solution and allowed to stand for several days at room temperature or heated for a short time at a raised temperature of approximately 40° C. The polythionates and thionanhydrides are then formed in the sulfinate or seleninate solution in accordance with the following mechanism:

I. $RSO_2Na + S \longrightarrow RSO_2S.Na$

II. $4RSO_2SNa + nS \longrightarrow RSO_2.Sn.SO_2R + RSSR + Na_2SO_4 + Na_2S$

III. $4RSSR + 2Na_2S + 6NaOH \longrightarrow 8RSNa + Na_2S_2O_3 + 3H_2O$

IV. $Na_2S_2O_3 \xrightarrow[cat]{O} Na_2S_nO_6$ or $NaOSO_2—S_n—SO_2ONa$

wherein R is an organic radical, *n* is a positive integer, and the sulfur may be replaced by selenium.

Thus as a specific example, sodium benzene sulfinate plus sulfur yields sodium benzene thiosulfonate (Equation #I). This sodium benzene thiosulfonate further reacts with sulfur to form the thioanhydrides, dibenzene sulfonyl polysulfides (Equation #II). The by-products are diphenyl disulfides and sodium sulfide. The diphenyl disulfide further reacts to form thiophenol and sodium thiosulfate (Equation III) which latter can be easily oxidized to sodium polythionate (Equation IV). The sodium thiosulfate may, of course, be added as such to the sulfinate or seleninate solution and be directly oxidized to sodium polythionate. In either case, any suitable oxidizing catalyst may be employed, such as salts of arsenic, tin and antimony. I have observed that such catalysts may also accelerate the oxidation to polythionates of thiosulfuric acid ester salts in alkaline solutions. Such thio sulfuric acid ester salts as, for instance, phenyl thiosulfuric acid ester sodium salt or small amounts of thiosulfates or compounds of similar structures may often be present in technical grades of sulfinates regardless of how the sulfinate has been prepared. In order to improve such technical grades of sulfinates or seleninates for the purpose of fog prevention in photographic emulsions and at the same time to eliminate the time consuming and expensive procedure of chemical purification and recrystallization one of the above mentioned catalysts, such as sodium arsenite or a mixture of arsenic and tin salts, may be added to the sulfinates during the manufacture of the sulfinates or seleninates or of the sulfinate or seleninate solutions before using the latter with photographic emulsions. Some technical grades of sulfinates which may contain impurities or by-products which can be easily oxidized to polythionates can be improved by adding a small amount of a mild oxidizing agent such as potassium ferricyanide.

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 the polythionates and thioanhydrides, it is believed that this stabilization improving effect is either a catalytic one or is due to a chemical interaction between the polythionates or thioanhydrides and the sulfinates or seleninates 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 one kilogram of melted gelatino-silver-halide emulsion containing from 6 to 7% of silver halide and approximately 8% gelatin, there were added during ripening:

15 cc. of a 20% solution of the sodium salt of benzene sulfinic acid in water and
5 cc. of potassium pentathionate of a concentration of one gram per liter in water.

After ripening, the emulsion was cast on a film base and cut into test film lengths. Similar test films were made with the same silver halide emulsion but without the addition of either the sodium salt of benzene sulfinic acid or the potassium pentathionate. 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 sulfinic acid as above, but omitting the potassium pentathionate.

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 six days at 50° C. It was observed that the fog density of the films treated with benzene sodium sulfinate solution to which had been added potassium pentathionate 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 sodium benzene sulfinate.

Example II

To one kilogram of melted gelatino-silver-halide emulsion containing from 6 to 7% silver halide and approximately 8% gelatin, there were added during ripening:

5 cc. of a 20% solution of a sodium salt of benzene seleninic acid in water and
5 cc. of sodium tetrathionate of a concentration of one gram per liter in water.

After ripening the emulsion was cast on a film base and cut into test film lengths. Similar test films were made of the silver halide emulsion but without the addition of either of the sodium salt of benzene seleninic acid or the sodium tetrathionate. Additional similar test films were also made with the same silver halide emulsion to which was added the same quantity of the sodium salt of benzene seleninic acid as above, but omitting the sodium tetrathionate.

The fog density of all three types of these test films was determined for the freshly prepared film and the remaining test lengths of each type of test film were then incubated for a period of six days at a temperature of 50° C. It was observed that the fog density of the films treated with sodium benzene seleninate solution to which had been added sodium tetrathionate 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 sodium benzene seleninate.

Example III

Sodium benzene sulfinate was prepared according to the process outlined by Gattermann in Berichte 32, 1140 (1899).

200 grams of the crude sodium salt of the benzene sulfinic acid thus obtained were dissolved in one liter of water.

0.25 to 1 gram of sodium arsenite were added. This solution was allowed to stand at room temperature for 24 hours.

A similar solution of the crude sodium salt of the benzene sulfinic acid and water but omitting the addition of sodium arsenite was made up and also allowed to stand at room temperature for 24 hours.

The two solutions were then added to gelatino-silver-halide emulsions in amounts from 5–20 cc. per one kilogram of emulsion during the ripening stage. Similar amounts of the two benzene sulfinate solutions may be also added to silver halide emulsion before coating as a coating final.

Test strips of the films thus produced were examined for fog density when freshly prepared and other test strips of the same films were incubated for a period of six days at a temperature of 50° C. and then examined for fog density.

It was observed that the fog density of the films treated with the sodium benzene sulfinate solution to which had been added sodium arsenite was improved to about the same extent as noted in Examples I and II, as compared with the fog density of the films which had been treated with the blank sodium benzene sulfinate solution.

Example IV

Sodium benzene sulfinate was prepared in accordance with the process outlined by Knoevenaegel et al. in Berichte 41, 3318 (1908).

0.1 gram of potassium ferricyanide was added to one liter of a 20% solution of the crude sodium benzene sulfinate thus prepared. This solution was allowed to stand for 72 hours, then filtered.

1 liter of a 20% solution of this crude sodium benzene sulfinate omitting the addition of potassium ferricyanide was also allowed to stand for 72 hours and filtered.

Samples of each of these solutions were then added to melted gelatino-silver-halide emulsions in amounts of 5 to 20 cc. of the sulfinate solution per 1 kilogram of emulsion during the ripening stage. Similar amounts of the same sulfinate solutions may be also added to a silver halide emulsion before coating as a coating final.

Test strips of the films when freshly prepared were examined for fog density. Additional test strips of these films were then incubated for a period of six days at a temperature of 50° and again tested for fog density.

It was observed that the fog density of the films treated with the sodium benzene sulfinate to which had been added potassium ferricyanide was improved to about the same extent as in the case of the preceding example as compared with the fog density of the films which had been treated with the blank sulfinate solution.

Example V

Sodium benzene sulfinate was prepared according to the process outlined by Smiles et al. in Organic Syntheses Coll. vol. I, page 7 (1932). The sodium benzene sulfinate thus prepared was recrystallized and made up into a 20% solution with water.

0.1 gram colloidal sulfur was added to one liter of the 20% solution of recrystallized sodium benzene sulfinate.

The colloidal sulfur addition was kept in suspension by stirring for 48 hours at room temperature. The temperature was then raised to 40° C. for one hour and the solution filtered.

Samples of this solution of the sodium benzene sulfinate treated with colloidal sulfur and samples of a 20% solution of the same recrystallized sodium benzene sulfinate which had not been treated with the colloidal sulfur were added to a melted gelatino-silver-halide emulsion in amounts of 5 to 20 cc. of the sulfinate solution per 1 kilogram of emulsion during the ripening stage. Similar amounts of these same solutions may be also added to gelatino-silver-halide emulsion before coating as a coating final.

Test strips of the films when freshly prepared were examined for fog density. Additional test strips of these films were then incubated for a period of six days at a temperature of 50° and again tested for fog density.

It was observed that the fog density of the films treated with the sodium benzene sulfinate to which had been added colloidal sulfur was improved to about the same extent as in the case of the preceding example as compared with the fog density of the films which had been treated with the blank sulfinate solution.

Example VI

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

10 cc. of a 20% solution of sodium benzene sulfinate in water and

5 cc. of an alcoholic solution of dibenzene sulfonyl monosulfide of the following formula: $C_6H_5.SO_2.S.SO_2.C_6H_5$ (thioanhydride of benzene thiosulfonic acid)

in a concentration of 1 gram per 1 liter methyl alcohol. The clearness of the film was determined in an identical manner as described in Example I. It was observed that the clearness of the emulsion layer treated with dibenzene sulfonyl monosulfide was improved to about the same extent as in the case of Example I, as compared with the same emulsion to which only sodium benzene sulfinate had been added. It may be mentioned that the dibenzene sulfonyl monosulfide may be substituted by equimolar concentrations of dibenzene sulfonyl di-, tri- and tetrasulfide with similar results.

Example VII

To a gelatino-silver-halide emulsion containing silver halide corresponding to 100 grams silver nitrate there were added

50 cc. of a 20% solution of sodium benzene seleninate and

25 cc. of a solution of sodium trithionate

in a concentration of 1 gram per liter water immediately after the precipitation of silver halide and prior to the surface digestion. The emulsion was washed and after-ripened in a manner familiar to those skilled in the art. The clearness and the keeping quality of the emulsion while depending on the type of gelatin employed was found to be in all cases improved as compared to one obtained with the addition of sodium benzene seleninate without the addition of sodium trithionate to about the same extent as in the case of Example I.

The sodium salt of benzene sulfinic acid and the sodium salt of benzene seleninic acid used in the above examples can be substituted by

equimolar concentrations of other sulfinic or seleninic acid salts such as the sodium salt of ethane-sulfinic acid, chlorobenzene-sulfinic acid, toluene-p-sulfinic acid, naphthalene-sulfinic acid, hexahydrobenzene-sulfinic acid and thiophene-sulfnic acid. The potassium pentathionate and sodium tetrathionate used in Examples I and II can be substituted by equimolecular concentrations of soluble salts of any thionic acid compounds having three or more sulfur atoms such as, for instance, hexathionic acid and any thioanhydride having one or more central sulfur atoms.

The improvement obtainable when the fog characteristic is expressed in density units will, of course, vary somewhat depending upon the type of gelatin and the formula used in making the gelatino-silver-halide emulsion. However, it has been found that the result, as compared with the same film treated only with the sulfinic or seleninic acid salt is invariably a decrease in fog density of approximately 50% for freshly prepared film and approximately 45% after six days incubation.

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

1. A photographic material comprising a silver halide gelatin emulsion, a member of the group consisting of a sulfinic acid, a seleninic acid and their salts and a member of the group consisting of polythionic acids and their salts of the formula

$$MOSO_2—S_n—SO_2OM$$

wherein M is a member of the group consisting of alkali metals and hydrogen and n is a positive integer, and thioanhydrides of the formula

$$RSO_2—S_n—SO_2R$$

wherein R is an organic radical and n is a positive integer, in concentrations of from 0.025 to 0.500% by mol of the member of the last named group to the member of the first named group.

2. A photographic material comprising a silver halide gelatin emulsion containing a member of the group consisting of sulfinic acid, a seleninic acid and their salts, and a member of the group consisting of polythionic acids and their salts of the formula

$$MOSO_2—S_n—SO_2OM$$

wherein M is a member of the group consisting of alkali metals and hydrogen and n is a positive integer, and thioanhydrides of the formula

$$RSO_2—S_n—SO_2R$$

wherein R is an organic radical and n is a positive integer, in concentrations of from 0.025 to 0.500% by mol of the member of the last named group to the member of the first named group.

3. A photographic material comprising a silver halide gelatin emulsion, a member of the group consisting of a sulfinic acid, a seleninic acid and their salts and a member of the group consisting of dibenzene sulfonyl mono-, di-, tri-, and tetrasulfide in concentrations of from 0.025 to 0.500% by mol of the member of the last named group to the member of the first named group.

4. A photographic material comprising a silver halide gelatin emulsion, sodium benzene sulfinate and potassium pentathionate in concentrations of from 0.025 to 0.500% by mol of the potassium pentathionate to the sodium benzene sulfinate.

5. A photographic material comprising a silver halide gelatin emulsion, sodium benzene seleninate and sodium tetrathionate in concentrations of from 0.025 to 0.500% by mol of the sodium tetrathionate to the sodium benzene seleninate.

6. A photographic material comprising a silver halide gelatin emulsion, sodium benzene sulfinate and dibenzene sulfonyl monosulfide in concentrations of from 0.025 to 0.500% by mol of the dibenzene sulfonyl monosulfide to the sodium benzene sulfinate.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,673,522	Matthies et al.	June 12, 1928
2,057,764	Brunken	Oct. 20, 1936