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STABILIZED SILVER HALIDE EMULSIONS

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5 Claims. (Cl. 95—7)

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

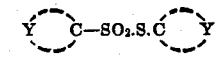
A large number of substances have been described as being effective in preventing an increase in fog and thus stabilizing or controlling the keeping quality of photographic emulsions. Many of these stabilizers have definite limitations in their ability to produce desirable effects without producing unfavorable 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. 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 was found 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 the seleninic acids or their salts, disclosed in U. S. Patent 2,057,764. can be considerably improved and the range of application greatly extended if small amounts of salts or esters of substituted or unsubstituted aliphatic, aromatic or heterocyclic thiosulfonic acids (sulfoxides) are present in the emulsion containing the sulfinates or seleninates. Compounds representing the salts of thiosulfonic acids have the following general formula

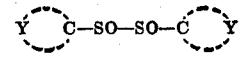
$$Z—SO_2—S—M$$

wherein Z is a substituted or unsubstituted aromatic or heterocyclic ring or a substituted or unsubstituted aliphatic chain and M is a metal, preferably an alkali metal, or ammonium, or guanidinium or another organic cation.

Compounds representing the esters of thiosulfonic acid have the following general formula:



It may be noted that the literature refers to these types of compounds alternatively as disulfoxide representing the following formula:



wherein Y stands for the atoms necessary to complete an aromatic or heterocyclic ring.

It has been observed that extremely small quantities of the aromatic or heterocyclic sulfoxides will improve the stabilizing characteristic of photographic emulsions containing a sulfinate or seleninate to an extent unobtainable with a sulfinate or seleninate alone. Thus, the photographic effect of sodium sulfinate or seleninate is improved by the addition of 0.00025—0.0050 mol per mol of sulfinate or seleninate of salts or esters of triosulfonic acids, such as diphenyl disulfoxide, ditolyl disulfoxide, dinaphthyl disulfoxide, 3-3'-dicarboxy diphenyl disulfoxide, 2.5.2'.5'-tetrachlorodiphenyl disulfoxide, di-chloro - 2.2' - dinitro - diphenyl disulfoxide, dicamphoryl-disulfoxide 1-cystine disulfoxide, diamino diethyl disulfoxide, inorganic and organic salts of benzene thiosulfonic acid such as sodium, potassium and guanidinium. The improved result, expressing fog in terms of density units, is manifested by a reduction of the fog density of approximately one-half the fog density obtained when using a sulfinate or seleninate alone. This reduction in fog density produces better clearness, better keeping quality and an unusual brilliance which is especially desirable in medical and industrial radiographs.

The same reduction in fog density is obtained whether the aromatic or heterocyclic sulfoxide compound is added with the sulfinate or seleninate during mixing or during the ripening stage in the process of making the silver halide emulsion or to molten emulsion prior to 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 sulfoxide 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.

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 aromatic or heterocyclic sulfoxide, it is believed that this additional stabilizing effect is either a catalytic one or is due to a chemical interaction between the sulfoxide 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 during the ripening stage:

15 cc. of a 20% solution of the sodium salt of benzene sulfinic acid in water and
3.5 cc. of an alcoholic solution of diphenyldisulfoxide of the concentration of one gram per liter of methanol.

The melted emulsion was then cast on a film base and cut into test film lengths. 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 diphenyl-disulfoxide.

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 sulfinic acid to which had been added diphenyl-disulfoxide was considerably improved as compared with the fog density of the films which had been treated with benzene sulfinic acid alone. In terms of percentage reduction of the fog density of the film treated only with the benzene sulfinic acid, the addition of the diphenyl disulfoxide in accordance with this example reduced the fog density by 66 to 68% in the case of the freshly prepared film and by 65 to 67% in the case of the incubated film.

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:

10 cc. of a 20% solution of sodium salt of benzene seleninic acid and
2 cc. of a solution of sodium benzene thiosulfonate ($C_6H_5.SO_2.SNa.1\frac{1}{2}H_2O$) of the concentration of one gram per liter of water.

The melted emulsion was then mixed and cast on a film base and cut into test film lengths. 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 sodium benzene thiosulfonate.

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 sodium benzene thiosulfonate was considerably improved as compared with the fog density of the films which had been treated with benzene seleninic acid alone. In terms of percentage of the fog density of the film treated only with the benzene seleninic acid the reduction of fog density due to the sodium benzene thiosulfonate was of the same order as in the case of Example I.

Example III

To a gelatino-silver-halide emulsion corresponding to 100 grams of silver, there were added after precipitation of silver halide and prior to the first digestion:

90 cc. of a 20% solution of sodium benzene sulfinate and
20 cc. of a solution of 1-cystine-disulfoxide containing 1 gram in 1 liter of water made slightly alkaline with NH_3

The emulsion thus prepared was then washed and after-ripened in the usual manner. For comparison, a similar emulsion was prepared and treated in the same way but omitting the 1-cystine-disulfoxide addition. It was observed that the clearness and keeping quality of the emulsion prepared in accordance with this example were considerably improved over the comparison emulsion which did not contain the above mentioned cystine derivative.

Tests made for fog density in the same manner as outlined in the preceding examples showed that the addition of the 1-cystine-disulfoxide effected a reduction in the fog density of the film containing only the sodium benzene sulfinate of the same order as observed in cases of the diphenyl-disulfoxide and the sodium benezene thiosulfonate.

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. The following table which expresses average fog values based upon the tests referred to in the examples will serve to further illustrate the improvement which is achieved by using the salts or esters of aromatic or heteocyclic thiosulfonic acids in combination with the sulfinates or seleninates as additions to typical gelatino-silver-halide emulsions:

Type of film	Fog of the freshly coated film	Fog after 6 days incubation at 50°C.
Film with the addition of sodium benzene sulfinate or seleninate as a coating final	*Density units* 0. 25–0. 30	*Density units* 0. 25–0. 35
Film with the addition of sodium benzene sulfinate or selinate and aromatic or heterocyclic sulfoxides	0. 12–0. 15	0. 15–0. 19
Film made from emulsion to which had been added sodium sulfinate or seleninate during ripening	0. 38–0. 45	0. 45–0. 55
Film made from emulsion to which had been added during the ripening sodium sulfinate or seleninate in combination with aromatic or heterocyclic sulfoxide compounds	0. 12–0. 15	0. 15–0. 19

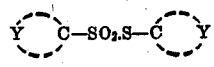
What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A photographic material comprising a silver halide gelatin emulsion in contact with a member of the group consisting of a sulfinic acid, a seleninic acid and their salts, and a sulfoxide compound selected from the group consisting of

aromatic and heterocyclic sulfoxide compounds of the following structural formulae:

I. $Z—SO_2.S—M$

and

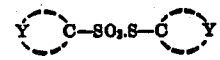
II. 

wherein Z is a member of the group consisting of alkyl, aryl and heterocyclic radicals; Y represents the atoms necessary to complete a member of the group consisting of aromatic and heterocyclic rings; and M is a member of the group consisting of metallic atoms and organic cations.

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 a sulfoxide compound selected from the group consisting of aromatic and heterocyclic sulfoxide compounds having the following structural formulae:

I. $Z—SO_2.S—M$

and

II. 

wherein Z is a member of the group consisting of alkyl, aryl, and heterocyclic radicals; Y represents the atoms necessary to complete a member of the group consisting of aromatic and heterocyclic rings; and M is a member of the group consisting of metallic atoms and organic cations.

3. 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 small amounts of diphenyl disulfoxide.

4. 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 small amounts of 1-cystine-disulfoxide.

5. 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 small amounts of sodium benzene thiosulfonate.

FRITZ W. H. MUELLER.