

UNITED STATES PATENT OFFICE

2,057,764

MANUFACTURE OF STABILIZED SILVER
HALIDE EMULSIONSJohannes Brunken, Dessau in Anhalt, Germany,
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ton, N. Y., a corporation of New YorkNo Drawing. Application July 19, 1934, Serial
No. 736,129. In Germany July 22, 1933

16 Claims. (Cl. 95—8)

My present invention relates to stabilizing photographic silver halide emulsions.

One of its objects is a process of stabilizing a photographic silver halide emulsion. Another object is a silver halide emulsion with an improved stability. Further objects will be seen from the detailed specification following hereafter.

I have found that the action of a sulphinic acid or a seleninic acid or a salt of one of these acids on a photographic silver halide emulsion which may be unsensitized or which has been sensitized or hyper-sensitized increases the stability of this emulsion.

As compared with the known stabilizers the sulphinates and the seleninates have the advantage of not affecting the photographic properties of the emulsion, for example the sensitivity and gradation.

For the purpose of the invention there may be used an alkali salt or another soluble salt of an aliphatic or aromatic or hydroaromatic or heterocyclic sulphinic- or seleninic-acid, for instance, such a salt of methane-sulphinic acid, methane disulphinic acid, methane-trisulphinic acid, ethane-sulphinic acid, ethane disulphinic acid, benzene-sulphinic acid, a chlorobenzene-sulphinic acid, toluene-para-sulphinic acid, anisol-para-sulphinic acid, acetanilide-para-sulphinic acid, salicylic-sulphinic acid, benzene-meta-disulphinic acid, naphthalene- β -sulphinic acid, cyclohexyl-sulphinic acid, thiophene-sulphinic acid, benzene-seleninic acid, methane-seleninic acid, ethane-seleninic acid.

Instead of the salts, the free acids likewise may be used. However, if the quantity used is too large, a loss of sensitivity occurs as a consequence of the reduction of the pH-value. Therefore, the stabilizer is preferably added in the form of a salt.

The amount of stabilizer added to 1 kg. of wet emulsion generally varies from 0.5 to 5 grams. However, the invention is not limited to these quantities; the most suitable amount of stabilizer to be used can be easily determined by experiment. The stabilizer may be added to the emulsion in the form of a solution in a suitable solvent during the preparation of the emulsion or it may be incorporated in the finished emulsion by bathing the emulsion layer, for instance, in a 1 per cent solution of the stabilizer. As a solvent there is used a liquid in which the stabilizer is soluble and which does not affect the emulsion. Preferably there is used water or an organic solvent which is miscible with water, for instance, alcohol.

I have furthermore found, that the fogging influence of supports, preparation layers, backing

layers, intermediate layers, sub-layers, protective layers, or baryta-layers can be prevented by incorporating in these layers the salt of a sulphinic or seleninic acid. For instance, an anti-halation layer of glassmaker's soap often causes fogging of the silver halide emulsion layer to which it is attached, so that such photographic materials have a poor stability. Furthermore the paper used for finishing or packing photographic materials causes the emulsion to be fogged and thus shortens the life of the photographic material. The fogging action of the aforesaid materials can be considerably reduced by the incorporation of a salt of a sulphinic acid or a seleninic acid.

The following examples serve to illustrate the invention.

Example 1.—1 kilo of a wet gelatino silver halide emulsion containing 6 to 7 per cent of silver halide and 8.5 per cent of gelatin is molten in the usual way and mixed with a solution of 3 grams of the sodium salt of benzene-sulphinic acid in 25 cc. of water. The emulsion is then cast on a film base and made partly into a roll film and partly into a film pack. These films and films made with the same silver halide emulsion, but without the addition of the sodium salt of benzene-sulphinic acid, showed when freshly prepared the same sensitivity and the same fog of 0.12 density unit. After storing the roll film in a drying stove heated to 50° C. for two weeks the film showed a fog of:

	Density unit
Film without addition.....	0.43
Film with the sodium salt of benzene-sulphinic acid.....	0.25

After storing the film packs in a drying stove heated to 50° C. for three weeks, the films showed a fog:

	Density unit
Film without addition.....	0.55 to 0.60
Film containing the sodium salt of benzene-sulphinic acid.....	0.25 to 0.28

Similar results are obtained when the sodium salt of benzene sulfinic acid is replaced by the sodium salt of ethane sulfinic acid, a chlorobenzene-sulfinic acid, toluene-para-sulfinic acid, or naphthalene-sulfinic acid.

Example 2.—1 kilo of an unsensitized wet emulsion containing 9 per cent of gelatin and 6 to 7 per cent of silver halide is molten and mixed with a solution of 1 gram of the sodium salt of benzene-seleninic acid in 25 cc. of water. The emulsion is then cast on glass plates. In freshly prepared condition the plates made from the

emulsion showed a fog of 0.11 density unit and plates prepared from the same emulsion without the addition of the sodium salt of benzene seleninic acid showed a fog of 0.10 density unit.

- 5 After storing the plates in a drying stove heated to 50° C. for 9 days the plates showed a fog:

	Density unit
Emulsion without addition.....	0.43
10 Emulsion containing the sodium salt of benzene-seleninic acid.....	0.21

Example 3:—An "Agfa-Isochrome" plate (registered trade-mark) is bathed for 10 minutes in the following solution:

15 Water.....	liter... 1
Crystalline sodium carbonate.....	grams... 5
Concentrated ammonia solution.....	cc... 5
20 Sodium salt of hexahydrobenzene-sulfinic acid.....	grams... 10

- After having been thoroughly rinsed the plate is dried in a current of warm air. The plate is stored in a drying stove heated to 50° C. for three days together with a plate of the same brand of emulsion which has not been bathed. After this treatment the plates showed a fog:

	Density unit
Plate without addition.....	2.1
30 Plate containing the sodium salt of hexahydrobenzene-sulfinic acid.....	1.3

- Example 4:*—To 1 kilo of an emulsion of glassmaker's soap in gelatin containing about 8 per cent of gelatin there is added a solution of 5 grams of the sodium salt of ethane-sulfinic acid in 25 cc. of water, and the emulsion is cast on a support to form an anti-halation layer. On the dry anti-halation layer there is cast a photographic emulsion containing 6 to 7 per cent of silver halide and 8.5 per cent of gelatin and sensitized with 1.1'-diethyl-6'-methyl-benzthiopseudocyanine iodide or 1.1'-diethyl-benzselenopseudocyanine perchlorate. (The emulsion contains about 15 mgr. of sensitizer in 1 kilo of wet emulsion.) The photographic material thus made was stored in a drying stove heated to 50° C. together with photographic material made in the same manner but without the addition of the sodium salt of ethane-sulfinic acid. After 9 days' storing the materials showed a fog:

	Density unit
Material without addition.....	0.94
55 Material with addition of the sodium salt of ethane sulfinic acid.....	0.48

- Example 5:*—Black-red paper such as is used in winding roll films is bathed for 10 minutes in a 10 per cent solution of the sodium salt of thiophene-sulfinic acid in methanol of 50 per cent strength. This paper, as well as paper which has been treated with methanol of 50 per cent strength without addition and paper which has not been treated at all were placed in contact with the emulsion side of a photographic film in a drying stove heated to 50° C. The film showed a fog of 0.08 density unit before beginning the test. After a 9 days' storing the films showed a fog:

	Density unit
70 Film in contact with the untreated paper....	0.50
Film in contact with the paper treated with methanol.....	0.50
75 Film in contact with the paper treated with the solution of thiophene-sulfinic acid.....	0.34

The test in the above examples was performed by developing the photographic emulsion for 5 minutes in a developer of the following composition:

Water.....	liter... 1
Para-methylaminophenol sulfate.....	grams... 1.5
Hydroquinone.....	do... 2.5
Potassium carbonate.....	do... 18.0
Potassium bromide.....	do... 1.0
10 Sodium sulfite sicc.....	do... 18.0

The film was then fixed, and after drying the density was determined in the Martens densitometer.

In the examples gelatin is used as a binding agent for the emulsion, however, the stabilizing effect of the described stabilizers is not limited to emulsions prepared with this binding agent, but there may be used also other binding agents, for instance, collodium, agar-agar, casein, albumen, and polyglucuronic acid.

As above described the stabilizer may be added to the emulsion at any stage of its production, but it may also be added already to the parent material for making the emulsions. When the stabilizing agent is to be added to the support to which the emulsion is attached, it is preferably added before the support is cast. To a preparation layer, an intermediate layer, a backing, a sub-layer or a protective layer the stabilizer is added shortly before casting these layers. In the case of paper it is preferably added to the paper pulp. In the case of paper coated with gelatin and barium sulfate it is added to the casting solution from which the layer is made.

What I claim is:

1. A method of preventing a silver halide emulsion from becoming fogged which comprises bring the emulsion in contact with a soluble compound selected from the group consisting of a sulfinic acid, a seleninic acid and their salts.
2. A method of preventing a silver halide emulsion from becoming fogged which comprises bringing the emulsion in contact with a soluble salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.
3. A method of preventing a silver halide emulsion from becoming fogged which comprises bringing the emulsion in contact with an alkali salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.
4. A method of preventing a silver halide emulsion from becoming fogged which comprises incorporating in a layer which is in contact with the emulsion layer a soluble salt of an acid selected from the group consisting of sulfinic acid and seleninic acid.
5. A method of preventing a silver halide emulsion from becoming fogged which comprises incorporating in the emulsion a soluble salt of an acid selected from the group consisting of sulfinic acid and seleninic acid.
6. A method of preventing a silver halide emulsion from becoming fogged which comprises adding to a wet and molten gelatino silver halide emulsion sodium salt of benzene-sulfinic acid dissolved in 25 cc. of water and casting the photographic material from this emulsion.
7. A method of preventing a silver halide emulsion from becoming fogged which comprises adding to a wet emulsion of gelatin and glassmaker's soap sodium salt of ethane-sulfinic acid dissolved in 25 cc. of water, casting the emulsion on a support to form an anti-halation layer, drying

this layer, and casting on this layer a gelatino silver halide emulsion containing a sensitizer.

8. A method of preventing a silver halide emulsion from becoming fogged which comprises adding to a wet gelatino silver halide emulsion sodium salt of benzene-seleninic acid dissolved in 25 cc. of water and casting the emulsion from this solution.

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

10. A photographic material comprising a silver halide emulsion in contact with a soluble salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.

11. A photographic material comprising a silver halide emulsion in contact with an alkali salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.

12. A photographic material comprising a silver halide emulsion containing as an addition a

soluble salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.

13. A photographic material comprising a gelatino silver halide emulsion in contact with a layer containing a soluble salt of an acid selected from the group consisting of a sulfinic acid and a seleninic acid.

14. A photographic material comprising a silver halide emulsion containing the sodium salt of benzene-sulfinic acid.

15. A photographic material comprising a gelatino silver halide emulsion containing the sodium salt of benzene-seleninic acid.

16. A photographic material comprising a support, attached to said support an anti-halation layer comprising gelatin as a binding agent and having incorporated glassmaker's soap and the sodium salt of ethane-disulfinic acid, and attached to this anti-halation layer a gelatino silver halide emulsion layer containing a sensitizer.

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