Patented Apr. 2, 1940

2,195,405

UNITED STATES PATENT OFFICE

2,195,405

PHOTOGRAPHIC FIXATIVE COMPOSITION

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No Drawing. Application October 11, 1938, Serial No. 234,481

17 Claims. (Cl. 95—88)

This invention relates to photography; more particularly it relates to photographic fixing compositions; and still more particularly it relates to dry photographic fixing powder compositions and to concentrated fixing solutions. In a more limited sense, the invention relates to the preparation of fixing baths and to processes of using such baths.

This invention has for an object the provision of a dry fixing composition. A further object is the provision of a dry photographic fixative composition which does not deteriorate upon standing. A still further object is the provision of an acid hardening fixing composition which may be used for the preparation of photographic fixing baths. A still further object is the preparation of an acid hardening fixing bath which has a long life. A still further object is the preparation of an acid hardening fixing bath which will maintain satisfactory hardening over a wide range of pH values. A still further object is the preparation of an acid hardening fixing bath which is free from sludging tendencies and has a low rate of sulfurization. Other objects include new processes of fixing photographic film and a general advancement of the art. Still other objects will be apparent from the hereafter described invention.

The above and other objects are accomplished by the incorporation of the sulfamic acids or their easily hydrolyzable salts in a fixative composition. In a more limited sense, they are accomplished by the incorporation of the sulfamic acids or their easily hydrolyzable salts as an acid constituent in dry photographic fixing compositions, concentrated photographic fixing solutions and in photographic fixing baths. In a preferred embodiment of the invention they are accomplished by the use of sulfamic acid in dry photographic fixing compositions, concentrated fixing solutions and in photographic fixing baths.

Photographic fixing baths contain at least three basic ingredients, viz: (1) a silver salt solvent or fixative salt such as sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate and their hydration products, e. g. "hypo"; (2) an acid to neutralize the alkali of the developer carried over into the fixing bath by the photographic element; and (3) a soluble sulfite to inhibit the decomposition of the fixative salt. Such baths are known as acid fixing baths. Photographic fixing baths usually contain a fourth basic ingredient, namely, a hardening agent for the emulsion binder which is usually composed of gelatin, e. g. potassium alum, chrome alum, etc. The last mentioned baths are known as acid hardening fixing baths.

The useful life of an acid hardening fixing bath is usually terminated by any one of three events: (1) exhaustion of the fixing agent with consequent excessive clearing time for the emulsion layers, (2) sulfurization, rendering the bath unfit for use, and (3) sludging from excess alkalinity, usually caused by the carrying over of developer from the developer bath by the films, plates or papers processed.

It has been found that the sulfamic acids and substances which readily yield sulfamic acid by hydrolysis in aqueous photographic baths may be used as the acid ingredient of acid fixing and acid hardening fixing compositions, baths and concentrated solutions. These acids are admirably suited for the purpose and maintain the pH of the resulting bath under optimum conditions in that they inhibit sulfurization and sludging and furthermore render the hardening agent effective over a wide pH range.

It has also been found that the water-soluble salts of the sulfamic acids also have a beneficial effect in the above-described baths and compositions. Aqueous photographic baths contain in addition to the initially added ingredients the reaction products of the ingredients. In the case of the sulfamic acids, the water-soluble salts are formed in the bath during use. For instance, if sodium sulfite is used in the bath containing sulfamic acid, sodium sulfamate is formed. Because of the beneficial effect of the salts, it is preferable that they be added initially. Among the beneficial effects are the facts that the salts have a buffering action and certain salts have a hardening effect upon the proteins.

The invention will be further illustrated but is not intended to be limited by the following examples:

EXAMPLE 1

Sodium thiosulfate, $7H_2O$	grams	240
Sodium sulfite, anhydrous	do	15
Sulfamic acid	do	15
Boric acid	do	7.5
Potassium alum	do	15
Water to	liters	1

A fixing bath having the above composition which was a clear faintly yellowish solution was prepared. An exposed film was developed with a standard metol hydroquinone developer and then fixed in the aforespecified bath. The film was fixed rapidly and completely and led to a clean negative. The bath was resistant to sulfurization and sludging.

Similar results may be obtained with the following fixing baths:

EXAMPLE 2

Sodium thiosulfate, $7H_2O$	grams	350
Sodium sulfite, anhydrous	do	15
Sulfamic acid	do	10
Boric acid	do	40
Potassium alum	do	32
Water to	liters	1

EXAMPLE 3

Sodium thiosulfate, $7H_2O$	grams	350
Sodium sulfite, anhydrous	do	15
Sodium citrate	do	30
Borax	do	10
Sulfamic acid	do	10
Potassium alum	do	32
Water to	liters	1

EXAMPLE 4

Sodium thiosulfate, $7H_2O$	grams	350
Sodium sulfite, anhydrous	do	18
Sodium acetate	do	18
Sulfamic acid	do	10
Boric acid	do	10
Potassium alum	do	32
Water to	liters	1

EXAMPLE 5

Sodium thiosulfate, crystals	grams	350
Sodium sulfite, anhydrous	do	15
Potassium tartrate	do	30
Sulfamic acid	do	8
Potassium alum	do	30
Water to	liters	1

This bath showed excellent resistance towards sludging and sulfurization.

The sulfamic acids lend themselves remarkably well to the preparation of dry powder mixtures comprising the active ingredients of fixing baths. These photographic fixative compositions when dissolved in water, yield acid fixing baths having exceptional long fixation life and are resistant to sludging and sulfurization. The following examples represent dry powder which, when dissolved in water yields ready-to-use fixing baths. If a hardening fixing bath is desired, alums can be added after the bulk of other ingredients are dissolved.

EXAMPLE 6

	Grams
Sodium thiosulfate, anhydrous	225
Sodium sulfite	15
Sulfamic acid	10
Sodium citrate	30
Boric acid	10

Dissolve in 750 ccs. of hot water, then add 32 grams of potassium alum with constant stirring and add cold water to make the final volume 1 liter.

EXAMPLE 7

A complete, dry powder fixative composition, comprising all the necessary basic ingredients and requiring only to be dissolved in a given amount of water, which can be prepared in advance of use and stored over long periods of time, is as follows:

Mix A

	Grams
Sodium thiosulfate, anhydrous	225
Sodium sulfite, anhydrous	15
Borax	10

Mix B

	Grams
Potassium alum	32
Sulfamic acid	11

To prepare the working bath, Mix A is dissolved in 600 ccs. of hot water. When cooled, Mix B is added with constant stirring and when dissolved, the final volume is brought to 1 liter with cold water.

EXAMPLE 8

Mix A

	Grams
Sodium thiosulfate, anhydrous	350
Sodium sulfite, anhydrous	15
Sodium acetate, crystals	30

Mix B

	Grams
Sulfamic acid	10
Potassium sulfamate	30

For providing a dry powder photographic fixative composition, Mix B is contained in a small carton within the large bulk, Mix A, which can then be stored until required. For use, Mix A is dissolved in 750 ccs. of hot water and then the contents of the inner carton, Mix B, are added with constant stirring. When all ingredients are dissolved, the final volume is brought to 1 liter with cold water.

EXAMPLE 9

Sodium thiosulfate, crystals	grams	300
Sodium sulfite, anhydrous	do	15
Glycol bori-borate	do	10
N-methylol sulfamate	do	30
Sulfamic acid	do	11.5
Water to	liters	1

An exposed and developed film when treated in the above bath fixed rapidly and completely and led to a clean negative. The bath furthermore had good gelatin hardening properties.

EXAMPLE 10

Concentrated bath

Due to its high solubility in water, in comparison with other dry acids suitable for fixing baths, sulfamic acid lends itself particularly well to the preparation of concentrated stock solutions of fixing baths, a suitable formula being:

Hypo	grams	1400
Sodium sulfite, anhydrous	do	60
Sodium citrate	do	95
Sulfamic acid	do	40
Chrome alum	do	120
Hot water to	liters	1

The sodium sulfite is first dissolved in 200 ccs. of boiling hot water. Gentle heat is applied to the solution and the other ingredients are added, one at a time and completely dissolved before adding the next one. The solution is then brought up to one liter. For use, the concentrated stock solution is diluted with 3 volumes of water, yielding a long-life fixing bath having excellent hardening properties.

EXAMPLE 11

Sodium thiosulfate, $7H_2O$	grams	240
Sodium sulfite, anhydrous	do	6
Sulfamic acid	do	6
Aluminum sulfamate	do	8
Water to	liters	1

This bath in addition to its good fixing properties has, by reason of its aluminum sulfamate content, an excellent tanning effect on the protein carrier layers used in photographic emulsions.

EXAMPLE 12

Sodium thiosulfate, $7H_2O$	grams	350
Sodium sulfite, anhydrous	do	15
Sodium citrate	do	18
N-methyl sulfamic acid	do	12
Potassium alum	do	32
Water to	liters	1

In place of the substituted sulfamic acids and sulfamic acid set forth in the preceding examples may be substituted other water soluble sulfamic acids. As examples of suitable derivatives mention is made of the lower N-alkyl sulfamic acids, e. g. N-methylsulfamic, N-ethylsulfamic, N-propylsulfamic, N-diethyl sulfamic, N-dimethyl sulfamic, etc., acids.

While the above examples describe the use of boric acid, borax, citric acid, sodium citrate, sodium acetate, sodium amino acetate, etc., which yield borate, citrate, acetate, amino acetate, etc., ions, other acidic compounds which yield such ions may be used in place thereof or in admixture therewith. As further examples of suitable compounds, mention is made of sodium metaborate, potassium tetrahydrodiborate, sodium hexahydrotetraborate as well as other water soluble, particularly alkali metal salts of the oxygen acids of boron. The organic esters and salts of ester of the boron acids, e. g. glycol borate, glyceryl borate, glycol and glycerol boriborate, the aryl-boric acids, including phenyl boric, p-carboxylphenylboric, p-tolyl boric acids and their alkali metal and ammonium salts are very effective when used in combination with the sulfamic acids and sulfamates of this invention.

The addition of small quantities of other acids, such as tartaric, fumaric, malic, maleic, lactic, glycolic, glycerophosphoric, propionic and butyric may be resorted to. The lithium, sodium, potassium salts of these acids, as well as any of the above acids may be used as a source of the acid ions. The water-soluble salts of the sulfamic acids herein described such as the sodium, potassium, lithium, ammonium, aluminum, etc. salts are very useful. It has been found that the sodium and potassium salts of the di- and polybasic acids especially the organic acids, are particularly effective in fixing compositions and baths containing sulfamic acids or their substitution derivatives in causing the resulting baths to be highly resistant to sludging and sulfurization. These salts of citric, tartaric, boric, succinic, malic and maleic acids which have 2 or 3 ionizable sodium or potassium groups are more effective than those acids which yield a single sodium or potassium ion such as sodium acetate.

In place of the specific fixing salts set forth in the preceding examples, any water soluble thiosulfate may be substituted. Suitable thiosulfates including ammonium thiosulfate, potassium thiosulfate, lithium thiosulfate, thiosulfate complexes such as potassium and magnesium thiosulfate.

Fixing baths prepared according to the foregoing invention have a number of distinct advantages. They have a long fixation, hardening and stain preventing life. They are remarkably resistant to sulfurization and sludging and in the latter respect will tolerate exceedingly high concentrations of alkali developers before showing tendencies to sludge.

The sulfamic acids and particularly sulfamic acid, are well suited for dry fixing powders and may be packaged and stored for long periods of time.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments hereof except as defined in the appended claims.

I claim:

1. A composition containing a photographic fixing agent and at least one compound taken from the group consisting of sulfamic acids, substances which readily yield sulfamic acids by hydrolysis in aqueous baths and water soluble salts of sulfamic acids.

2. A photographic fixative composition containing a photographic fixing agent and a sulfamic acid.

3. A composition containing a photographic fixing agent and sulfamic acid.

4. A photographic fixative composition comprising a soluble thiosulfate and a sulfamic acid.

5. A photographic fixative composition comprising a soluble thiosulfate and a sulfamic acid salt, and a sulfamic acid.

6. A photographic fixative composition comprising an alkali metal thiosulfate and sulfamic acid.

7. An acid hardening photographic fixing composition comprising an alkali metal thiosulfate, sulfamic acid, a water soluble sulfite, and a protein hardening agent.

8. An acid hardening photographic fixing composition comprising an alkali metal thiosulfate, an alkali metal sulfite, sulfamic acid, a protein hardening agent and a substance capable of yielding different acid ions.

9. A dry photographic fixative composition comprising sodium thiosulfate, sulfamic acid and an additional solid substance capable of yielding acid ions.

10. A composition as set forth in claim 9 wherein the additional solid substance produces borate ions.

11. A composition as set forth in claim 9 wherein the additional solid substance is borax.

12. A composition as set forth in claim 9 wherein the additional solid substance is sodium citrate.

13. A photographic fixing composition comprising a concentrated aqueous solution containing a water-soluble thio sulfate, a water soluble sulfite, a sulfamic acid and a protein hardening agent.

14. An aqueous photographic fixing bath containing a fixing agent and sulfamic acid.

15. A photographic fixing bath comprising an alkali metal thiosulfate, an alkali metal sulfite, sulfamic acid, and a protein hardening agent.

16. The process which comprises fixing a photographic element in the presence of a sulfamic acid.

17. The process which comprises fixing a photographic element in the presence of sulfamic acid.

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