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[54] **STABILIZER FOR SILVER HALIDE LIGHT-SENSITIVE MATERIAL**

[75] Inventors: **Kinji Ohkubo; Katsumi Hayashi,** both of Kanagawa, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

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[51] **Int. Cl.** **G03c 5/38,** G03c 1/06

[58] **Field of Search** ..... 96/61, 95, 61 M, 50, 48 QP

[56] **References Cited**

UNITED STATES PATENTS

3,212,895	10/1965	Barbier et al.	96/61
3,238,043	3/1966	Levy	96/61
3,326,684	6/1967	Nishio et al.	96/61
3,352,682	11/1967	Harris et al.	96/95
3,525,567	8/1970	Levine	96/61
3,630,737	12/1971	Kairies	96/61

Primary Examiner—J. Travis Brown

Assistant Examiner—M. Kelley

Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

A stabilizer for photographic silver halide materials, consisting of an acidic aqueous solution containing ammonium thiocyanate, and an aluminum compound, characterized by incorporation therein of (1) a sulfite and (2) an aliphatic aldehyde or aliphatic ketone of one to five carbon atoms.

11 Claims, No Drawings

STABILIZER FOR SILVER HALIDE LIGHT-SENSITIVE MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a stabilizing solution for silver halide photographic materials. Generally a photographic processing of silver halide material consists of four steps, i.e., development, fixing, stopping and water washing. Various treatments have hitherto been proposed to speed up the processing steps.

2. Description of the Prior Art

Among them stabilization processing is more practical. Stabilization processing means a method in which an exposed photographic silver halide material is developed and immersed in an aqueous solution containing a stabilizing agent, illustrated hereinafter, whereby to convert the non-developed silver halide remaining in the emulsion layer into a silver complex salt stable to light. By this stabilizing treatment, the water-washing treatment, after the fixing, which requires a relatively long time, can be omitted and, consequently, rapid treatment of a photographic silver halide material is made possible.

Stabilzing agents used in the stabilizing treatment are mentioned in detail in H. D. Russel and E. C. Yacke: "Stabilizing Treatment of Films and Printing Papers," PSA Journal (Photo. Sci. Tech.), 16B 59 (1950). As stabilizing agents ordinarily alkali metal and ammonium thiocyanates are used.

When an alkali metal thiocyanate or ammonium thiocyanate is used as a stabilizing agent, there is the advantage that the speed of stabilization is high. However, the following disadvantages are unavoidable in this case.

One disadvantage is that a photographic material stabilized by such stabilizing agents is sticky, so that handling thereof after processing is inconvenient. This phenomenon would be due to the fact that alkali metal or ammonium thiocyanates are deliquescent and have the property of softening the gelatin used as a binder of a silver halide emulsion layer.

Another disadvantage is that a photographic material stabilized by such stabilizing agents tends to show a lowering or vanishing of image density when stored for a long period of time. For example, the color of a black image tends to vanish or discolor in yellow during storage for a long period of time. This phenomenon is called "fading." The fading appears often when a stabilized print is stored under high humidity.

In order to get rid of the sticky property of a stabilized print it is proposed in U.S. Pat. No. 2,453,347 to add a hardener, such as, formaldehyde, glyoxal, potassium alum or chrome alum to the stabilizing solution.

In accordance with our investigation, it is found that aluminum compounds, such as, potassium alum (aluminum potassium sulfate) are the most effective to reduce the sticky property of a stabilized print, because the aldehyde type hardener does not show a sufficient hardening effect, within an acidic pH region, to stop development by the stabilizer, and chrome alum has the disadvantage of contaminating a print.

In order to prevent the image fading of a stabilized print, it is well known to add an alkali metal or ammonium sulfite, bisulfite or metabisulfite to a stabilizing solution. (Japanese Patent 540,299)

Preparation of a stabilizer having both a hardening action and an image fading inhibiting action, in addition to a stabilizing action on the silver halide, by using the above-mentioned techniques in combination, encounters the following difficulties.

The first is that the aluminum ion is stable at a pH of 6, or less, but forms a precipitate of aluminum hydroxide at a pH of more than 6. The second is that the ability of aluminum to harden a gelatin is maximum at a pH of about 3. The third is that sulfite is stable at a pH of more than 4, but decomposes at a pH of 4 or less, and the decomposed product contaminates the print. That is to say, the pH region is very narrow wherein both are stably coexistent. The fourth is that a stability enhancing agent, such as, boric acid cannot be used. Since a conventional acidic fixing solution of thiosulfate, wherein an aluminum compound and sulfite are coexistent, is unstable and liable to precipitate, a stability enhancing agent, such as, boric acid is often added to the fixing solution. However, addition of this agent to a stabilizer containing an aluminum compound and a sulfite improves the stability thereof, but lowers markedly the hardening action. The fifth is that an aqueous solution of thiocyanate, which pH is low, tends to corrode stainless steel used for processing machines.

It is one object of the invention to provide a stabilizer such that a print stabilized thereby does not show a sticky property.

It is another object of the invention to provide a stabilizer such that when a print stabilized thereby is allowed to stand under high temperatures and high humidities, fading of the image hardly takes place.

It is another object of the invention to provide a stable stabilizer such that no precipitation and no decomposition occur even after storage for a long time. Other objects and advantages of the invention will be apparent from the following description.

We the inventors have found that the above-mentioned objects can be accomplished by adding an aliphatic aldehyde or aliphatic ketone and a sulfite to a stabilizer containing ammonium thiocyanate and aluminum compound.

Compounds having carbon atoms of up to five are preferably used, such as, aliphatic aldehyde or aliphatic ketone, for example, formaldehyde, acetaldehyde, glyoxal, glutaraldehyde, acetone and methyl ethyl ketone.

It is known that an aldehyde or ketone is added to bisulfite ion in aqueous solution to thus form a bisulfite adduct. The aliphatic aldehyde or aliphatic ketone may directly be added to a stabilizer containing a sulfite to form an adduct in the solution or may be added to a stabilizer in the form of a bisulfite adduct. The addition amount of aliphatic aldehyde or ketone used according to the invention must be sufficient to form an adduct with sulfite added to a stabilizer and at least equimolar with the sulfite. Moreover, aldehydes and ketones may be used in admixture.

As the aluminum compound of the invention there may be used any water-soluble compound containing aluminum, for example, potassium alum, aluminum sulfate or aluminum chloride.

Illustrative of the sulfite of the invention are sodium sulfite, sodium bisulfite, potassium sulfite, potassium

metabisulfite and ammonium sulfite. In the invention, sulfite bisulfite and methbisulfite.

The ability of aluminum to harden a gelatin film is the greatest in a range of pH 3–4. A stabilizer containing ammonium thiocyanate and an aluminum compound and having a pH of 3–4 has a marked hardening effect, but a print image stabilized thereby tends to discolor and corrosion occurs remarkably on stainless steel parts of a processing machine, to which this stabilizer adheres.

In a range of pH 3–4, sulfite is unstable and decomposes directly, but, as is evident from the above illustration, an adduct with an aliphatic aldehyde or ketone is stable in this pH region, the combination of the adduct with an aluminum compound give a stabilizer that is stable and not corrosive and has strong hardening ability.

Aluminum ion reacts with various ions in aqueous solution often to form a precipitate. For example, when a stabilizer containing ammonium thiocyanate and aluminum sulfate is allowed to stand at 0°C for one week, crystals of aluminum ammonium sulfate are deposited. Addition of a tartrate, such as, potassium tartrate or sodium tartrate or Rochelle salts to a stabilizer containing ammonium thiocyanate and aluminum compound in a proportion of 0.1–2 g/l prevents deposition of crystals.

Furthermore, in order to prevent image fading when a stabilized print is exposed to conditions of high temperature and high humidity, at least 0.01 percent by weight, based on a stabilizing agent compound having a mercapto group on a heterocyclic ring, as disclosed in Japanese Patent 531,585, may be added to a stabilizer. Typical of this compound are 2-mercaptoimidazole, 2-mercaptobenzimidazole, 2-mercaptobenzotriazole, 2-amino-5-mercapto-1,3,4-thiadiazole and 1-phenyl-5-mercaptotetrazole.

The following examples are to illustrate the invention in detail.

EXAMPLE 1

One kg of a gelatino-silver chlorobromide emulsion consisting of 105 percent by weight of gelatin and 4.9% by weight of a silver chlorobromide containing 5 mol percent of silver bromide and a trace of silver iodide was melted and kept at 35°–50°C, to which an orthosensitizing dye and stabilizer were then added. The pH was adjusted to 5.1 and 20 g of hydroquinone was added in the form of a solid adequate agitation. The emulsion was coated onto a baryta paper with the addition of a hardener followed by drying.

The thus obtained printing paper was exposed and developed in an activator having the following composition for 3 seconds:

Activator	
sodium hydroxide	58 g
sodium sulfite (anhydrous)	23 g
potassium bromide	0.4 g
water	to 1000 ml

Then, it was stabilized in the following stabilizing solution for 10 seconds:

Stabilizer	A	B	C	D
ammonium thiocyanate	200 g	200 g	200 g	200 g
sodium acetate (trihydrate)	52 g	52 g	52 g	52 g
glacial acetic acid	88 g	88 g	88 g	88 g
aluminum chloride (hexahydrate)	—	25 g	25 g	25 g
sodium bisulfite	52 g	—	52 g	52 g
formalin (37% aqueous soln.)	50 g	—	—	50 g
water to 1000 ml				

The properties of a stabilized print are shown in Table 1.

TABLE 1

Stabilizing solution	A	B	C	D
Stickiness of print	high	low	low	low
Image density on print directly after processing	2.01	1.98	2.05	2.05
After 5 hrs. at 30°C and 80% RH	1.78	0.39	1.00	1.80
Whiteness	good	good	bad (yellow)	good

The properties of the stabilizer are shown in Table 2.

TABLE 2

Stabilizer	A	B	C	D
Color	colorless	colorless	yellow	colorless
Immersion of stainless steel (SUS27) for one day	not corroded	not corroded	not corroded	not corroded

As is evident from the above results, a stabilizer which has a hardening capacity, but shows little image fading, and does not corrode stainless steel, can be obtained by the combined use of an aluminum compound and sulfite adduct.

EXAMPLE 2

One kg of a gelatino-silver chlorobromide emulsion consisting of 115 percent by weight of gelatin and 5.3 percent by weight of silver chlorobromide containing 15 mol percent of silver bromide was melted and to this melt an orthosensitizing dye was added. The pH was adjusted to 5.0, the temperature was kept at 40°C and 12 g of hydroquinone was added with adequate agitation. It was then coated onto a baryta paper without adding a hardener, followed by drying.

The resulting printing paper was exposed and developed in an activator having the following composition for 3 seconds:

Activator	
sodium hydroxide	58 g
sodium sulfite (anhydrous)	23 g
silver bromide	1 g
water to 1000 ml	

Then, it was stabilized in a stabilizer having the following composition for 10 seconds:

Stabilizer

ammonium thiocyanate	200 g
sodium acetate (trihydrate)	50 g
glacial acetic acid	70 g
aluminum potassium sulfate (12-hydrate)	80 g
potassium metabisulfite	66.5 g
glutaraldehyde	70 g
1-phenyl-5-mercaptotetrazole (0.5% methanol)	50 ml
water to 1,000 ml	

The stabilized print showed no stickiness and, even after storage for a long time, no lowering of image density. When a piece of stainless steel (SUS27) was immersed in the above stabilizer for one day, it was not corroded.

EXAMPLE 3

In Example 2 the stabilizer was substituted by the following solution:

Stabilizer

ammonium thiocyanate	250 g
sodium acetate (trihydrate)	42 g
glacial acetic acid	18 g
aluminum sulfate (18-hydrate)	54 g
Rochelle salts	2 g
adduct salt solution	290 ml
2-amino-5-mercapto-1,3,4-thiadiazole (0.5% methanol)	80 ml
water to 1000 ml	

The adduct salt solution was prepared as follows:

Two hundred and sixty g of sodium bisulfite was dissolved in 550 ml of water, and mixed gradually with 190 ml of acetone, followed by dilution with water to 1000 ml. The results were similar to those of Example 2.

What is claimed is:

1. A stabilizer for photographic silver halide materials, comprising an acidic aqueous solution containing ammonium thiocyanate, and a water-soluble compound containing aluminum selected from the group consisting of potassium alum, aluminum sulfate, and aluminum chloride, characterized by incorporation therein of (1) a sulfite and (2) an aliphatic aldehyde or aliphatic ketone of one to five carbon atoms, the pH of said stabilizer ranging from 3 to 4,

said aliphatic aldehyde or ketone being present in an amount sufficient to form an adduct with the sulfite added to the stabilizer and being present in at least an equimolar amount with the sulfite.

2. The stabilizer as claimed in claim **1** wherein said aliphatic aldehyde is formaldehyde, acetoaldehyde, glyoxal or glutaraldehyde.

3. The stabilizer as claimed in claim **1** wherein said ketone is acetone or methylethyl-ketone.

4. The stabilizer as claimed in claim **1** wherein said sulfite is sodium sulfite, sodium bisulfite, potassium sulfite, potassium metabisulfite or ammonium sulfite.

5. The stabilizer as claimed in claim **1** wherein said stabilizer contains a tartrate.

6. The stabilizer as claimed in claim **5** wherein said tartrate is sodium tartrate, potassium tartrate or potassium sodium tartrate.

7. The stabilizer as claimed in claim **5** wherein the amount of said tartrate is 0.1 – 2 g per one liter.

8. The stabilizer as claimed in claim **1** wherein said stabilizer contains a heterocyclic mercapto compound.

9. The stabilizer as claimed in claim **8** wherein the amount of said mercapto compound is at least 0.01 percent by weight based on ammonium thiocyanate.

10. The stabilizer as claimed in claim **8** wherein said mercapto compound is 2-mercaptoimidazole, 2-mercaptobenzimidazole, 2-mercaptobenzotriazole, 2-amino-5-mercapto-1,3,4-thiadiazole or 1-phenyl-5-mercaptotetrazole.

11. A method for rapidly processing an exposed silver halide photographic emulsion layer containing a developing agent therein which comprises treating the layer with an aqueous alkali solution, and stabilizing it with an acidic aqueous solution containing (1) ammonium thiocyanate, (2) a water-soluble compound containing aluminum selected from the group consisting of potassium alum, aluminum sulfate, and aluminum chloride, (3) a sulfite and (4) an aliphatic aldehyde or aliphatic ketone of one to five carbon atoms, the pH of said acidic aqueous solution ranging from 3–4,

said aliphatic aldehyde or ketone being present in an amount sufficient to form an adduct with the sulfite added to the stabilizer and being present in at least an equimolar amount with the sulfite.

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