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PHOTOGRAPHIC ART

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This invention relates to improved photographic acid hardening fixing compositions containing an aluminum compound which acts as a hardening agent.

It is well known that acid alum hardening fixing compositions contain in addition to the alum which acts as a hardening agent, an acid, a soluble sulfite which stabilizes the thiosulfate against sulfurization, and a thiosulfate fixing agent commonly called hypo which may be a sufficiently soluble compound of alkali, alkali earth metals, or ammonium, amine or guanidine radicals which acts as a silver salt solvent. It has been found that an acid is necessary in order to prevent precipitation of basic compounds of the hardening agent and extend the useful life of the fixing solution by neutralizing the alkali carried over from the developer. For aluminum hardening fixing baths mild acetic acid has long been used since it acts to maintain the pH sufficiently low to prevent formation of sludge (basic aluminum sulfite) and does not cause early sulfurization of the fixing bath as do the stronger acids. It has been found by previous investigators that very few other acids will function satisfactorily in such an acid hardening fixing bath. Many acids prematurely decompose the hypo to liberate sulfur or give excessive sulfur dioxide with the sulfite. Others act to decrease the hardening action of the alum. To date acetic acid has been used almost exclusively for this purpose. However, acetic acid is a liquid which is difficult to ship. It is not suitable for any dry package preparations, and due to the war it is not readily available in certain areas.

This invention has for its object to provide acid aluminum hardening fixing compositions which contain a solid acidifying agent for subsequent combination in solution with a soluble sulfite or bisulfite and a soluble salt of a mild aliphatic organic acid, the acidifying agent being a strong acid reacting salt which is readily available and which is satisfactory for compounding dry package fixing preparations. Another object is to provide alum type acid hardening fixing compositions which contain a cheap and readily available acidifying agent which, in the combination does not have the undesirable property of causing decomposition of the hypo or decreasing the hardening action of the hardener. Other objects will appear hereinafter.

These and other objects are accomplished by our invention which includes an acid aluminum hardening fixing composition comprising an aluminum hardening agent and an acid sulfate which upon addition to a salt of an aliphatic acid containing two to four carbon atoms generates the corresponding free aliphatic acid.

We prefer to employ alkali metal acid sulfates such as sodium or potassium as acidifying agents. However, other acid sulfates such as ammonium acid sulfate may be employed for this purpose. It has been found that these materials effectively neutralize the alkali carried over from the developer and effectively maintain the pH of the fixing solution sufficiently low to prevent formation of sludge. Although they are strong acids they do not have the undesirable characteristics of decomposing hypo to liberate sulfur or sulfur dioxide when used in the presence of sufficient alkali metal sulfite or bisulfite and alkali metal salts of mild aliphatic organic acids.

The fixing preparation of our invention includes, in addition to the acid sulfate, a silver salt solvent, a soluble sulfite, a soluble salt of a mild aliphatic organic acid, and alum as discussed above. Examples of silver salt solvents are sodium, potassium, ammonium, and guanidine thiosulfates. Examples of soluble sulfites are ammonium and alkali metal sulfites such as sodium sulfite or bisulfite, potassium sulfite, potassium metabisulfite and ammonium sulfite or bisulfite. Examples of suitable salts of mild aliphatic organic acids are sodium, potassium, and ammonium acetates, propionates, and butyrates. Examples of alum (within the meaning of the specification and claims) are sodium, potassium, and ammonium alums. Other aluminum compounds such as aluminum sulfate, chloride, acetate or propionate may be used instead of the alum.

It is frequently inconvenient to add each of the individual components to water whenever a fixing composition is to be prepared. This difficulty can be overcome by providing a dry packaged fixing agent including the constituents mentioned above. When preparing such dry compositions it is desirable that the alum and acid sulfate be separated in one compartment of the package or in a separate package, and the hypo (preferably anhydrous), sulfite, sodium acetate and boric acid (when desired) be incorporated in the other compartment or a separate package. To prepare the fixing bath the contents of these packages are then dissolved separately, the solutions cooled if at elevated temperature, and the alum-acid sulfate solution added slowly with stirring to the hypo-sulfite-acetate solution. If desired, a three compartment dry package preparation may also be provided with the hypo and sulfite in one compartment, the sodium acid sulfate, alum and boric acid (when desired) in the second and sodium acetate in the third compartment. Other arrangements of the ingredients are possible.

Acid aluminum hardening fixing baths can be prepared to contain hypo, a soluble sulfite such

as sodium sulfite, an acid sulfate in slightly less than molecular proportion to the sulfite, and alum but such solutions are not particularly practical since they do not have ample exhaustion life with the addition of developer in use and readily produce sludge and scum. They also sulfurize or sludge readily upon standing. Approximately neutral compounds yielding acetate or similar ions and included in the solution prior to the addition of the acid sulfate and alum greatly improve the sulfurization life of the bath. This is the result of the generation of the weaker acetic acid by the action of the strong inorganic acid sulfate on the acetate.

We have mentioned above the materials which are necessary for a satisfactory fixing bath. It has heretofore been found that the presence of the acetate, propionate or butyrate ion is also of value in a fixing bath since it acts to prevent sludge formation during exhaustion. We have found that such ions act in a similar manner in our fixing compositions in addition to the generation of the corresponding acid. It is known that boron compounds in the presence of acetate or similar ions extend the pH range over which hardening action takes place and raise the pH value at which sludging occurs. We, therefore, include within the scope of our invention our new fixing composition as defined and containing boron compounds for these and analogous purposes. While the presence of boron compounds is advantageous in many cases, useful fixing compositions can be prepared without them and our invention is not restricted to the presence of these substances. Also included in our invention we consider dry packaged chemical compositions containing an acid sulfate as the acidifying agent for the preparation of acid hardener solutions adapted to be added to or used in conjunction with thiosulfates in one- or two-step hardening and fixing operations.

The following are examples illustrating our invention:

Example 1

Water	cc.	650
Sodium thiosulfate (anhydrous)	grams	150–240
Sodium sulfite (desiccated)	do	18
Sodium acetate (desiccated)	do	20
Sodium acid sulfate (20% solution [1])		150
Potassum aluminum sulfate (crystals)	grams	15
Water to make	liter	1

[1] Water solution containing sodium acid sulfate (anhydrous) 200 grams per liter of solution. This solution should be cool and should be added slowly with stirring to the cool solution of the preceding chemicals.

Variations in the quantities of the sodium sulfite (or bisulfite), sodium acetate, and sodium acid sulfate are possible provided the pH of the resulting bath is approximately 4.0 or higher, but should not exceed about 5.0 for best sulfurization and exhaustion properties.

Example 2

Sodium thiosulfate (crystals)	grams	240.0
Sodium bisulfite	do	15.0
Sodium acetate (desiccated)	do	20.0
Boric acid	do	7.5
Sodium acid sulfate (20% solution)	cc.	75.0
Alum	grams	15.0
Water to make	liter	1.0

For instructions for mixing, see Example 1.

An example of a packaged composition of dry chemicals contained in two compartments is the following for the preparation of 1 liter of acid hardening fixing solution:

Example 3

	Grams
Compartment A:	
Sodium thiosulfate (anhydrous)	150–240
Sodium bisulfite	15
Sodium acetate (desiccated)	20
Compartment B:	
Sodium acid sulfate (anhydrous)	15
Potassium alum	15

Instructions for mixing.—Dissolve the contents of compartment A in about 650 cc. of water. Dissolve the contents of compartment B in about 200 cc. of water. Add the cool solution of compartment B slowly with stirring to the cool solution of compartment A. Dilute to make 1 liter and the resulting bath is then ready for use.

Example 4

	Grams
Compartment A:	
Sodium thiosulfate (anhydrous)	150–240
Sodium sulfite (desiccated)	18
Sodium acetate (desiccated)	20
Boric acid [1]	5–10
Compartment B:	
Sodium acid sulfate (anhydrous)	30
Ammonium aluminum sulfate (crystals)	15

[1] The boric acid may alternatively be placed in compartment B.

For mixing instructions, see Example 3. This example gives sufficient chemicals to enable the preparation of 1 liter of acid hardening fixing solution.

The following examples are illustrative of alternative methods of packaging which permit the preparation of stock acid hardener solutions which may be added to thiosulfate, thiosulfate-sulfite, or thiosulfate-bisulfite solutions to prepare acid hardening fixing baths.

Example 5

	Grams
Compartment A:	
Sodium acetate (desiccated)	100.0
Compartment B:	
Sodium acid sulfate (anhydrous)	75–150.0
Potassium alum	75.0
Boric acid, crystals (when desired)	37.5
Compartment C:	
Sodium thiosulfate (anhydrous)	1,000.0
Sodium sulfite (desiccated)	90.0

To utilize this example the stock acid hardening solution is prepared by dissolving the contents of compartment A and B in succession in 600 cc. of water at 125° F. and adding water to make 1 liter. The contents of compartment C are dissolved in about 2,400 cc. of water and water added to make 4 liters. When both solutions are cool the stock hardener solution is added slowly with stirring to the thiosulfate-sulfite solution in the proportion of 1 part of hardener to 4 parts of thiosulfate-sulfite solution.

Example 6

	Grams
Compartment A:	
Sodium acetate (desiccated)	100
Sodium bisulfite	75
Compartment B:	
Sodium acid sulfate (anhydrous)	75
Boric acid, crystal (when desired)	15–50
Potassium alum	75
Compartment C:	
Sodium thiosulfate (crystals)	1,500

The instructions for preparation of a stock hardener and acid hardening fixing solution are the same as for Example 5.

What we claim is:

1. In the process of preparing an acid hardening fixing bath for a photographic element bearing a silver image which bath in its final condition for use contains an aluminum hardening agent, a soluble sulfite and a fixing agent, the step which comprises adding to the bath a salt of an aliphatic acid having at least two but not more than four carbon atoms and an acid sulfate as the generator of free aliphatic acid from the salt thereof.

2. A dry acid hardening fixing composition comprising a fixing agent, a soluble sulfite, a salt of an aliphatic acid containing two to four carbon atoms, an aluminum hardening agent and an acid sulfate as the generator of free aliphatic acid from the salt thereof.

3. A package containing the components of an acid hardening fixing agent in dry condition and including a fixing agent, a soluble sulfite, a salt of an aliphatic acid containing two to four carbon atoms, an aluminum hardening agent and an acid sulfate as the generator of free aliphatic acid from the salt thereof.

4. A package containing the components of an acid hardening fixing agent in dry condition and including a fixing agent, a soluble sulfite and a salt of an aliphatic acid containing at least two but not more than four carbon atoms, an aluminum hardening agent and an acid sulfate as the main acidifying agent, the acid sulfate being segregated from the other components and serving as the generator of free aliphatic acid by reaction with the salt thereof.

5. A package containing the components of an acid hardening fixing agent in dry condition and including a fixing agent, a soluble sulfite, an alkali metal salt of an aliphatic acid containing at least two but not more than four carbon atoms, aluminum alum and an alkali metal acid sulfate as the generator of free aliphatic acid by reaction with the salt thereof, the acid sulfate and the alum being segregated from the other components.

6. A dry, packaged photographic composition adapted to form an acid hardening fixing bath when mixed in aqueous solution with a fixing agent, a soluble sulfite and a salt of an aliphatic acid containing two to four carbon atoms, which composition comprises aluminum alum and an acid sulfate as the generator of free aliphatic acid by reaction with the salt thereof.

7. A dry, packaged photographic composition adapted to form an acid hardening fixing bath when mixed in aqueous solution with a fixing agent, a soluble sulfite and an alkali metal salt of a member of the group consisting of acetic and propionic acids, which composition comprises a potassium aluminum alum and an alkali metal acid sulfate as the generator of acetic or propionic acid by reaction with the salt thereof.

8. A dry packaged photographic composition adapted to form an acid hardening fixing bath when mixed in aqueous solution with a fixing agent, a soluble sulfite and a salt of an aliphatic acid containing two to four carbon atoms which composition comprises an aluminum hardening agent, and potassium acid sulfate as the generator of free aliphatic acid by reaction with the salt thereof.

9. A dry packaged photographic composition adapted for the preparation of an acid hardening fixing bath when mixed in aqueous solution with a fixing agent, a soluble sulfite, and a salt of a monobasic saturated aliphatic acid containing two to four carbon atoms comprising an aluminum alum and an acid sulfate in sufficient amount to react with the salt of the aliphatic acid to give an acid hardening fixing solution equal in properties to one utilizing the corresponding organic acid.

10. A dry packaged photographic composition adapted to form an acid hardening fixing bath when mixed in aqueous solution with a fixing agent, a soluble sulfite, and a salt of a monobasic saturated aliphatic acid containing at least two but no more than four carbon atoms, said dry packaged composition comprising an aluminum hardening agent, and anhydrous sodium acid sulfate as an acidifying agent for generating the organic acid.

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