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STABILIZED PHOTOGRAPHIC FIXING POWDER

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This invention relates to photographic fixers.

Photographic fixers depend primarily on a solution of undeveloped silver halides by sodium thiosulfate, although other thiosulfates such as ammonium and potassium thiosulfates may be used. In addition to the thiosulfate which performs the primary dissolving action, photographic fixing baths usually contain sodium sulfite, a suitable acid and a material for hardening gelatin in order to render the gelatin emulsions of films, plates or photographic paper hard and tough. Usually the acid employed to impart a suitable pH is acetic acid, and sometimes buffers such as citric acid and the like may be used. One of the serious disadvantages of the ordinary fixing baths is that they have relatively poor keeping qualities, particularly when exposed to light or heat. There is a serious tendency towards decomposition of the thiosulfate with formation of colloidal or finely precipitated sulfur and as soon as this has taken place, the fixing solution has to be discarded although the thiosulfate may not be totally exhausted. Because of the fact that many amateur photographers do not process large quantities of photographic material at a time, the lack of keeping qualities is a serious factor, particularly in parts of the world where high temperatures are encountered. For this reason, many careful photographers, especially in summer time or in the tropics, keep the components of their fixing baths in solid form and make up fresh fixing solutions each time any photographic material is processed.

According to the present invention, preservatives are introduced to produce a bath or solution which keeps practically indefinitely without decomposition even at elevated temperatures and can therefore be used even in the tropics and, if necessary, can be shipped in solution form. The present invention is applicable both to the ordinary type using potassium alum as a gelatin hardening or tanning agent, and to those which use potassium chrome alum. In the latter case, the stability is even more remarkable as it had been considered up to the present time that chrome alum fixing baths could not be kept in solution form for more than a few hours, or at most a day or two, without decomposition. In fact, the use of chrome alum at the present time is normally in the form of a separate short-stop bath because of its lack of stability.

The present invention depends primarily on the employment of citric or tartaric acids advantageously in conjunction with small amounts of sodium phosphate and preferably in the presence of sodium or other alkaline metal acetates as a buffer. While good results can be obtained with these preservatives alone, even better stability is obtained by the addition of a small amount of a protective colloid such as coagulable albumen with a small amount of benzoic acid as a preservative. The presence of a colloid still further inhibits any tendency to precipitation of sulfur.

It is an advantage of the present invention that it may be used with the usual sodium thiosulfate or other alkali metal thiosulfates, or it may be employed with guanidine thiosulfate fixers where the extraordinary fixing speed of the guanidine thiosulfate justifies its higher price as in certain cases of tropical processing and newspaper work, very short fixing times are necessary. The stability producing effect of the present invention is equally applicable to both types of fixing procedures.

While it is a particular advantage of the present invention that the fixing bath may be kept in solution form, it is advantageous to market prepared fixing powders in solid form, and the ingredients entering into the fixer of the present invention lend themselves readily to this method of distribution as they dissolve readily in water. When packaged in solid form, the ingredients are preferably divided into two powders.

The invention will be described in detail in conjunction with the following specific examples which will describe packaged fixers of the present invention and also the preparation of fixing solutions therefrom. It should be understood that the examples are merely illustrations of the invention which is not limited to the exact proportions set forth as these are not critical which is a further advantage of the invention, permitting the amateur to compound his own fixer without requiring scales of extreme sensitiveness.

EXAMPLE 1

Two powders are prepared as follows:

Powder A

	Grams
Sodium thiosulfate	222.7
Sodium sulfite, des	15.36
Sodium acetate	17.90

Powder B

	Grams
Potassium aluminum sulfate	23.8
Sodium sulfite, des	0.18
Citric acid	10.66
Sodium acid phosphate	0.81

Powder A is the fixer proper and Powder B, the

acid hardening component containing the stabilizing and preserving acid. When it is desired to prepare a fixing bath, Powder A is first dissolved in a liter of water at normal room temperature which will result in some lowering of the solution temperature due to the cooling resulting from the negative heat of solution of the thiosulfate. After Powder A has been entirely dissolved, which takes place rapidly if thorough stirring is employed, Powder B is added and thoroughly stirred in. The pH of the resulting solution is approximately 4.4. The solution fixes photographic material, and is in every way equal in its fixing and hardening powers to standard fixing solutions such as for example the Eastman F–5 solution. However, the stability of the solution is very much greater. Thus, for example, when compared with a solution of Eastman Kodak F–5 at 120° F., the solution of Example 1 shows no precipitation of sulfur even after hundreds of hours, whereas the standard solution using acetic acid as the acid shows extensive decomposition with a heavy precipitation of sulfur and is unsuitable for use in film fixation. After hundreds of hours at 120° F., the solution of Example 1 shows no perceptible loss of fixing power and gives excellent results with both film and paper.

When kept at temperatures of 6° C. for extensive periods of time, no sulfurization takes place and the fixing power is unaltered.

EXAMPLE 2

A fixing solution is prepared as in Example 1, but 1 gram of coagulable albumen and 0.5 gram of benzoic acid are added. This solution gives excellent results and shows even greater stability.

EXAMPLE 3

A chrome alum fixer is prepared in the form of two dry powders as follows:

Powder A

	Grams
Sodium thiosulfate	222.7
Sodium sulfite, des	30.7
Sodium acetate	17.9

Powder B

	Grams
Potassium chrome alum	20.0
Sodium sulfite, des	0.36
Citric acid	21.30
Sodium phosphate	2.0

A solution was prepared by dissolving Powder A completely in 500 cc. of water, to which solution Powder B is then added and completely dissolved. The pH of the resulting solution is about 3.65. The solution is an excellent fixer of the chrome alum type and shows extraordinary stability when tested against a standard Eastman F–5 fixer. When compared at 120° F., the F–5 solution showed heavy decomposition and precipitation of sulfur at approximately 90 hours, whereas the solution of Example 3 showed substantially no decomposition even after a period well in excess of 100 hours and maintained its fixing power.

If desired, even greater stability can be obtained by the addition of 1 gram of sodium metasilicate.

EXAMPLE 4

A fixer was prepared as described in Example 1 except that guanidine thiosulfate was substituted for sodium thiosulfate. This fixer has to be used with considerable care as its fixing speed is several times as fast as that of the corresponding sodium thiosulfate and unless care is taken and the photographic material removed from the fixing bath promptly after fixation is complete, reticulation and some loss of developed image will result. The guanidine thiosulfate fixer, which is useful for work at higher temperatures and for other high speed fixing operations such as newspaper work, shows primarily the same stability as with sodium thiosulfate, showing no decomposition after standing for more than 100 hours at 120° F. I do not claim in this application the use of guanidine thiosulfate generally as a fixer, this forming the subject matter of a copending application of Robert Bowling Barnes, Serial No. 264,975 filed March 30, 1939, the use of guanidine thiosulfate being claimed here only in conjunction with the composition of the present invention.

What I claim is:

1. A photographic fixing solution comprising the following:

	Grams
Sodium thiosulfate	about 223
Sodium sulfite	about 16
Sodium acetate	about 18
Citric acid	about 11
An alum	about 20–24

Water sufficient to make about 1 liter of solution.

2. A photographic fixing solution of substantially the following composition:

	Grams
Sodium thiosulfate	about 223
Sodium sulfite	about 16
Sodium acetate	about 18
Citric acid	about 11
An alum	about 20–24
Sodium acid phosphate	about 1

Water sufficient to make about 1 liter of solution.

3. A photographic fixing solution comprising the following:

	Grams
Sodium thiosulfate	about 223
Sodium sulfite	about 16
Sodium acetate	about 18
Citric acid	about 11
Potassium aluminum sulfate	about 24

Water sufficient to make about 1 liter of solution.

4. A photographic fixing solution having substantially the following composition:

	Grams
Sodium thiosulfate	about 223
Sodium sulfite	about 31
Sodium acetate	about 18
Citric acid	about 22
Potassium chrome alum	about 20
Sodium phosphate	about 2

Water sufficient to make about 500 cc. of solution.

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