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CONCENTRATED PHOTOGRAPHIC FIXING AND HARDENING SIRUP

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This invention relates to concentrated photographic acid hardener and fixer sirups.

Photographic hardeners and fixers for silver halide photographic material contain usually a thiosulfate, sodium sulfite and hardener ingredients such as alum or chrome alum, with sufficient acetic acid, citric or tartaric acid to provide the right degree of acidity. This means that fixing baths must be prepared either by dissolving dry chemicals, or if the fixer is made up ahead of time either as a single solution or as two stock solutions, the volume of water in both cases is quite large. There is a demand for a concentrated fixer which requires only dilution with water. This demand is of particular importance in connection with users such as dentists or physicians who have to develop X-ray or other photographs and who do not have a regularly operating photographic laboratory.

In the past fixers for such purposes have required the stocking of large volumes of ready-made fixer, or stock solutions in order to make it unnecessary for the user to dissolve up the dry chemicals immediately before use. Attempts have been made to prepare more concentrated fixers, but when the concentration is materially increased, difficulties result from crystallization or precipitation of the solid materials contained therein.

In the prior patent to Barnes U. S. No. 2,174,494 there has been described photographic fixers in which guanidine compounds are present so that part at least of the thiosulfate is present as guanidine thiosulfate. These solutions show higher speed and slower exhaustion of the fixing solution, both desirable characteristics for X-ray work by dentists and physicians, and the higher solubility of guanidine thiosulfate permits making somewhat more concentrated solutions. However, even with the presence of guanidine, it has not been possible heretofore to prepare sufficiently concentrated fixers to eliminate the drawback of large volume of fixing solutions which has to be kept in stock.

According to the present invention higher concentrated fixing solutions are prepared by the use of certain hydrotropic substances which increase the solubility and hence prevent precipitation of the various ingredients. In general, any hydrotropic substance which is capable of increasing the solubility of the components can be used, but different substances exert this property in varying degrees. While the present invention is not limited broadly to any particular single hydrotropic substance, we prefer to use urea. Somewhat less hydrotropic action is obtained with soluble crude carbohydrates such as for example, molasses and salts of dialkyl sulfosuccinic acid such as sodium dioctyl sulfosuccinate. With these hydrotropes alone it is not possible to produce sirups of the maximum concentration even when using guanidine thiosulfate fixers.

The present invention is applicable to concentrated fixing solutions which contain either sodium thiosulfate or guanidine thiosulfate or mixtures thereof. The concentration obtainable with guanidine thiosulfate is of course higher than can be obtained with sodium thiosulfate by reason of the great solubility of the guanidine compound. In both cases, however, the presence of the hydrotropic material permits obtaining concentrations very much higher than would be possible without the presence of the hydrotrope.

In general, in order to obtain a sufficiently concentrated solution, at least 1000 grams of the thiosulfate per liter of water should be present, and the present invention permits obtaining such concentrated sirups with either sodium or guanidine thiosulfate, or mixtures. In the case of guanidine thiosulfate, mixtures of even higher concentrations may be obtained up to 2000 grams per liter when a highly effective hydrotrope such as urea is used.

While the present invention may also be employed to make high concentration sirups of ammonium thiosulfate, these sirups are in general not very satisfactory as they show insufficient keeping powers, tending to precipitate sulfur. Therefore, we prefer to make up fixers which contain sodium or guanidine thiosulfate or mixtures thereof, the amount of the thiosulfate being in excess of that which could be retained as a stable solution in the absence of the hydrotrope. The concentrated sirups of the present invention show excellent stability and keeping qualities and can be used simply by dilution with the requisite amount of water.

While the hydrotrope is important in producing solutions of high concentrations which will keep, it is frequently necessary to employ particular technique in first preparing the solutions. Thus, when guanidine thiosulfate is used, it is desirable to prepare two solutions, one containing the thiosulfate and some of the sulfite, and the other, the remaining ingredients, and then mix the two solutions together. This procedure is not claimed in the present case, forming the subject matter of our copending application Serial No. 367,955 filed November 30, 1940.

The invention will be described in greater de-

tail in conjunction with the following specific examples which set out representative modifications of the invention which however is not limited to the details therein set forth. The parts are by weight.

EXAMPLE 1

A concentrated fixer and hardener sirup was prepared by forming the following two solutions:

Solution A

	Parts
Water	350
Sodium thiosulfate ($5H_2O$)	600
Sodium sulfite (anhydrous)	15

Solution B

	Parts
Water	150
Acetic acid (28%)	100
Boric acid	15
Potassium aluminum sulfate	30
Sodium sulfite (anhydrous)	16

The solutions were mixed together, filtered through unactivated charcoal, and bottled. The solution was clear. After standing for 17 hours a heavy precipitate was noticed and the fixing solution could not be diluted with water to a useful fixing bath.

EXAMPLE 2

Two solutions were prepared as in Example 1, but before the solutions were mixed, three parts of sodium dioctyl sulfosuccinate were added. The finished solution before bottling was divided into two portions, one of which was maintained at 43° F. and the other at 120° F. At the end of a number of days, both bottles of solution were quite clear and when diluted with three parts of water gave a satisfactory fixing bath.

EXAMPLE 3

Two solutions were prepared as in Example 1 but before mixing, 7½ parts of urea was added. The mixed solution was again divided into two portions and stored respectively at 43° F. and 120° F. After a number of days both solutions were entirely clear.

EXAMPLE 4

Two solutions were prepared as in Example 1 but to solution A was added 5 parts of molasses before the solutions were mixed. The mixed solution after filtering was divided as described in the foregoing examples and after a number of days both portions remained entirely clear.

EXAMPLE 5

Solutions were prepared as in Example 1 but before mixing, 7 parts of diethylene glycol was added to solution A. After filtering through unactivated charcoal the solution was divided into two portions and treated as in Example 3. After standing a number of days both portions were entirely clear and as in the case of Example 2 gave satisfactory fixing solutions on dilution with three parts of water.

EXAMPLE 6

Two solutions were prepared as follows:

Solution A

	Parts
Water	700
Sodium sulfite (anhydrous)	48
Sodium thiosulfate ($5H_2O$)	1750
Guanidine nitrate	330

The materials were mixed in order at 60° C., cooled to 25° C. and allowed to stand for a short period of time and then filtered through unactivated charcoal. The second solution B was prepared as follows:

Solution B

	Parts
Water	300
Acetic acid	200
Boric acid	30
Potassium aluminum sulfate	70
Sodium sulfite (anhydrous)	32

The components were added in the order shown, heated to 60° C., cooled to 25° C. and then slowly poured into solution A. A heavy precipitate was obtained and the product was entirely unsatisfactory.

EXAMPLE 7

Solutions were prepared as in Example 6 but to solution A there was added 30 parts of urea. When the solutions were poured together, they remained clear and a portion kept at 43° F. and another at 120° F. showed only a very slight deposit after 12 hours which did not increase even after eight days under the same temperature conditions and which could be readily removed by filtration but could be permitted to remain as it does not affect the action of the sirup. After eight days, a portion of the solution diluted with water at 24° C. will fix X-ray film in less than 1¼ minutes without reticulation or other faults in the quality of the finished film.

We claim:

1. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite and alum and a hydrotrope, the amount of soluble thiosulfate being in excess of that which will remain in solution without the hydrotrope and the amount of the hydrotrope being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

2. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite and alum and urea, the amount of soluble thiosulfate being in excess of that which will remain in solution without the urea and the amount of urea being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

3. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite and alum and a hydrotrope, the soluble thiosulfate being present in a concentration of about 480 parts of anhydrous thiosulfate per thousand parts of water, and the amount of the hydrotrope being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

4. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite, alum, and urea, the soluble thiosulfate being present in a concentration of about 480 parts of anhydrous thiosulfate per thousand parts of water, and the amount of urea being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

5. A concentrated acid hardening and fixing

sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite and alum and a crude carbohydrate, the amount of soluble thiosulfate being in excess of that which will remain in solution without the crude carbohydrate, and the amount of the carbohydrate being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

6. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite and alum and a crude carbohydrate, the soluble thiosulfate being present in a concentration of about 480 parts of anhydrous thiosulfate per thousand parts of water, and the amount of the crude carbohydrate being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

7. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite, alum and a salt of a dialkyl sulfosuccinic acid, the amount of soluble thiosulfate being in excess of that which will remain in solution without the salt, and the amount of the salt of the dialkyl sufosuccinic acid being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

8. A concentrated acid hardening and fixing sirup for the fixation of silver halide photographic material comprising a soluble thiosulfate, sodium sulfite, alum, and a salt of a dialkyl sulfosuccinic acid, the soluble thiosulfate being present in a concentration of about 480 part of anhydrous thiosulfate per thousand parts of water, and the amount of the salt of dialkyl sulfosuccinic acid being sufficient to maintain the acid hardener and fixer in solution without substantial precipitation.

9. A concentrated acid fixer and hardener for silver halide photographic material containing mixed guanidine and sodium thiosulfate, sulfite, acid hardening constituents, and urea, the amount of thiosulfates being in excess of that which will remain in solution without the urea and the amount of the urea being sufficient to be effective in keeping the constituents of the fixer in solution without substantial precipitation.

10. A concentrated acid fixer and hardener for silver halide photographic material containing mixed guanidine and sodium thiosulfate, sulfite, acid hardening constituents, and urea, the concentration of thiosulfates being at least one mol. of thiosulfate per fourteen mols of water and the amount of the urea being sufficient to be effective in keeping the constituents of the fixer in solution without substantial precipitation.

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