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CONCENTRATED PHOTOGRAPHIC FIXING SOLUTIONS

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This invention relates to photographic fixing agents and more particularly to concentrated photographic fixing solutions and methods for their preparation.

Heretofore concentrated fixing solutions have been prepared which employed only those ingredients which would conveniently dissolve, or allowed some excess of crystals to accumulate in the solution. These excess crystals required vigorous application of shaking and stirring to resuspend before dilution and, due to coarseness, are slow to dissolve.

An object of the present invention is therefore to provide novel methods of obtaining highly concentrated fixing solutions. Another object is to provide methods of preparing stable, readily soluble suspensions of the ingredients of photographic fixing baths. Another object is to provide fixing solution concentrates which provide rapid solution and obviate dusting. Other objects will appear hereinafter.

In accordance with one feature of the present invention these objects are by suspending finely ground or finely divided crystalline elements of the fixing solution in a highly soluble colloid. Colloids particularly suitable for this purpose are esters of alginic acid. These are available commercially under the trade names Kelcoloid LV, Kelcoloid LVF, Kelcoloid HV, and Kelcoloid HVF.

In accordance with another feature of this invention, in case of fixing solutions containing sodium thiosulfate, no extraneous colloid need be added, the stability being apparently achieved through the hydrating action of the anhydrous form of sodium thiosulfate.

It is proposed as a mechanism, the correctness of which, of course, in no way limits my invention, that the stable suspension is formed in the first instance through a weak gelation or cross-linking of the polymeric alginic acid ester, and the concentration of the solid ingredients has not been found to be critical. In the second instance, it is presumed that the formation of a stable suspension occurs through the hydrating action of the sodium thiosulfate which takes up most of the excess water, but this hydrating action is not sufficient to remove entirely all fluidity. In this instance the proportion of water included is more critical than when the algin colloid is employed.

It is considered desirable, when preparing these gels, to obtain a stiffly fluid state, rather than a complete rigidity. Suitable particle size for the suspended solid particles lies between 40 mesh and 100 mesh, although there would be no objection to finer particles. The optimum concentration of the colloid protectant will vary with its molecular weight (viscosity) and with the composition of the fixing bath. In the case of the low viscosity form of the propylene glycol ester of polymeric alginic acid (marketed under the trade name of Kelcoloid LV), a concentration of 2 to 4 per cent is appropriate, if little assistance is obtained from the hydrating action of the ingredients. A concentration of chemical ingredients in the order of 1 gram per cc. is common.

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The incorporation of an antifoaming material is advantageous in some instances, particularly where the colloidal algin is employed, and a silicone preparation; Dow-Corning "D. C. Antifoam Emulsion" has been found suitable.

The invention is further illustrated in the following examples:

Example 1.—Sodium thiosulfate fixer

A mixture containing:

	Grams
Sodium thiosulfate, anhydrous	70.0
Potassium aluminum sulfate : 12H ₂ O	12.0
Boric acid	7.4
Sodium bisulfite	6.0
Sodium acetate	7.2

was added to 60 cc. of a 0.1% solution of Kelcoloid LV. The mixture was finely ground and produced a stiffly fluid solution of about 100 cc. volume. It dissolved rapidly and without difficulty to produce a solution of normal fixing properties.

Example 2.—Sodium-ammonium thiosulfate fixer

The following hardener constituents

	Grams
Sodium acetate	30.0
Potassium aluminum sulfate : 12H ₂ O	30.0
Boric acid	15.0
Sodium bisulfite	10.0
Sodium citrate	3.0

were combined with 150 grams of anhydrous sodium thiosulfate, and 130 cc. of a 76% ammonium thiosulfate solution were added slowly. Following partial addition, the mixture was finely ground and then the remainder of the solution added. Grinding was continued until the entire mixture set to a stiff fluid. This stayed in solution over a period of 4 weeks during which the tests were conducted and dissolved readily to produce a clear, rapidly acting fixer when diluted with 7 to 9 parts of water.

Example 3.—Ammonium thiosulfate fixer

To 130 cc. of 76% ammonium thiosulfate solution were added 5.2 grams of Kelcoloid LV, which was allowed to stand for 4 days, until dissolved. Then 4 drops of DC Antifoam Emulsion were added and 60 grams of a hardener, prepared in the proportions of Example 2. This produced a stable fixer of about 150 cc. volume which dissolved readily and without foam difficulty. A higher thiosulfate ion concentration was achieved, however, without essentially increasing volume, by the further addition of 50 grams of anhydrous sodium thiosulfate. This alternative mixture was also readily soluble and stable, and produced an active fixer when diluted 1 part to 7 parts of water.

Example 4.—Sodium-ammonium thiosulfate fixer

To a mixture of the following hardener ingredients

	Grams
Sodium acetate	15.0
Boric acid	7.5
Sodium citrate	1.5
Ammonium aluminum sulfate	5.0
Sodium bisulfite	5.0

60 cc. of a 76% solution of ammonium thiosulfate was added slowly, with grinding and stirring. Then 80 grams of anhydrous sodium thiosulfate were added, and grinding continued. Finally, an additional 5 cc. of the ammonium thiosulfate solution were added. This formed a stiffly fluid mixture, which dissolved readily on dilution with water and proved stable in prolonged incubation tests.

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Example 5

The following ingredients were ground together in a mortar:

Sodium acetate.....	grams..	15.0	5
Boric acid.....	do.....	7.5	
Sodium citrate.....	do.....	1.5	
Ammonium alum.....	do.....	5.0	
Sodium bisulfite.....	do.....	5.0	
Ammonium thiosulfate, 76% solution, weight			10
volume	cc..	65.0	
Sodium thiosulfate, anhydrous.....	grams..	75.0	

This gel was found to be entirely stable in accelerated aging tests including incubation at 110° F. for a period in excess of four months. Added to ten parts of water, it produced a clear solution which actively fixed both negative and positive films.

I have found that the concentrate made in accordance with this invention is quite effective and provides faster solution and obviates dusting.

I claim:

1. A photographic fixing composition in suspension in a colloidal gel, comprising a water soluble colloidal gel of an ester of alginic acid and suspended therein a thio-sulfate selected from an alkali sulfite and an ammonium sulfite, a hardening agent, boric acid and a salt of a solid

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organic acid selected from the group consisting of acetic acid and citric acid.

2. A photographic fixing composition in suspension in a colloidal gel comprising a water soluble colloidal gel of an ester of alginic acid and suspended therein sodium thiosulfate, potassium aluminum sulfate, boric acid, sodium bisulfite and sodium acetate.

3. A photographic fixing composition in suspension in a colloidal gel comprising a water soluble colloidal gel consisting of propylene glycol alginate and suspended therein sodium thiosulfate, potassium aluminum sulfate, boric acid, sodium bisulfite and sodium acetate.

4. A photographic fixing composition in suspension in a colloidal gel comprising propylene glycol alginate gel, sodium acetate, boric acid, sodium citrate, ammonium alum, sodium bisulfite, ammonium thiosulfate, and sodium thiosulfate.

5. A photographic fixing composition in suspension in a colloidal gel comprising propylene glycol alginate gel, sodium acetate, boric acid, sodium citrate, ammonium alum, sodium bisulfite and sodium thiosulfate.

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