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ACID HARDENING FIXING BATH

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This invention relates to photographic fixing baths and particularly to an acid hardening fixing bath in which the hardening life is increased.

Fixing baths containing, in addition to hypo or sodium thio-sulphate, substances like acetic acid, alum, etc., have been known for many years. Fixing baths of this type perform several functions in addition to fixing out the unexposed silver salts. The acid in them neutralizes the developer carried over by films or prints and prevents the fixing bath from becoming alkaline. A hardening agent often included in such formulas also serves to harden the emulsion and protect it from mechanical injury or from slightly elevated temperatures used in drying. As a hardening agent, the most commonly used substance is ordinary alum or potassium aluminum sulphate. Many fixing baths of the acid hardening type contain, in addition to hypo, potassium alum, acetic acid and sodium sulphite.

A fixing bath of this type represents a very complex chemical system and one in which certain factors must be accurately adjusted to give satisfactory results. Qualities of such a fixing bath such as degree of hardening, hardening life, sludging, rate of sulphurization, etc., are all interdependent and are influenced by the amounts of the various ingredients and the ratio of these amounts to each other. It is usually true that if one attempts to adjust the bath for the optimum of one property, one or more of the other properties is sacrificed to some extent. Thus, for example, it is possible that if one attempts to secure the maximum degree of hardening, the rate of sulphurization or of sludging may be adversely affected. Accordingly, nearly every fixing bath of the acid hardening type represents a compromise of some kind.

I have found a successful method of increasing the hardening life of a fixing bath without adversely affecting any of its other qualities. By hardening life, I, of course, mean the amount of fixing which can be done, the fixing bath still maintaining a satisfactory degree of hardening. The hardening life may be measured, for example, by plotting the temperature at which the gelatin film begins to melt against the amount of a given developer which has been added to the fixing bath. This test is closely parallel to the practical conditions under which the bath is used. The type of curve obtained with the usual fixing bath is one that quickly rises to a maximum and then rapidly falls as more developer is added. When a moderate amount of developer has been added, the fixing bath will no longer harden satisfactorily. Fixing baths made in accordance with my invention, on the other hand, will maintain satisfactory hardening over a much wider range, that is, they will still harden satisfactorily when a large amount of developer has been added to them.

Acid fixing baths made according to my invention include a substance capable of furnishing acetate ions (that is, the ion—$OOC.CH_3$) and boric acid. Satisfactory substances which furnish the acetate ion are acetic acid and sodium acetate, though other acetates may be used. The boric acid is added either as such or is supplied by borax and acetic acid in solution. At any rate, a small amount of bric acid is present in the fixing bath simultaneously with the acetate ion.

The following examples will serve to illustrate the invention:

Example I

Water	1 liter
Hypo	320 grams

Add to this the following hardener:

Water	240 c. c.
Sodium sulphite	20 grams
Acetic acid 28%	60 c. c.
Potassium alum	40 grams

When dissolved, add to this hardener 10 grams of borax dissolved in 170 c. c. of hot water. After dissolving the borax in the hardener, the entire hardener is added to the hypo solution.

Example II

Hypo	300 grams
Sodium sulphite	6 grams
Glacial acetic acid	10 grams
Potassium alum	12 grams
Boric acid	5 grams
Water to	1 liter

Example III

Hypo	300 grams
Sodium bi-sulphite	12.5 grams
Potassium alum	15 grams
Sodium acetate crystals	30 grams
Boric acid	5 grams
Water to	1 liter

In these formulas a portion or all of the acetic acid may be replaced by equivalent amounts of citric or tartaric acids. They are not, however, as satisfactory as acetic acid. If all citric or all tartaric acid is used, the fixing baths show a marked improvement over the older acid harden-

ing baths, in that the hardening life is somewhat increased and sludging is less. The improvement is, however, not so great as when acetic acid alone is used.

In the first of these examples, the boric acid will be present in the fixing bath through interaction of the borax with the weak acid, acetic acid. In the second and third examples, boric acid itself is added. All of these fixing baths will give a greatly increased hardening life. They will still harden satisfactorily when from three to four times as much developer is carried over as will render an ordinary bath unfit for further use. In any case the usual range of concentration of the acetate ions is from 10 grams per liter to 40 grams per liter and the concentration of boric acid is at least half that of the acetate ions, but can be more, and the amount of hardeners is not less than 5 grams and is preferably less than 30 grams per liter.

I consider as included in my invention, all equivalents and modifications coming within the scope of the appended claims.

What I claim is:

1. An acid hardening fixing bath comprising an aqueous solution of sodium thio-sulfate, a sulfite, a hardening agent, boric acid and a compound capable of furnishing acetate ions, the concentration of acetate ions being greater than 10 grams per liter and the concentration of boric acid being at least half that of the acetate ions.

2. An acid hardening fixing bath comprising an aqueous solution of sodium thiosulfate, a sulfite, acetic acid, boric acid and a hardener, the acetic acid being present in a concentration greater than 10 grams per liter and the concentration of the boric acid being at least half that of the acetic acid.

3. An acid hardening fixing bath comprising an aqueous solution of sodium thio-sulfate, a sulfite, acetic acid, boric acid and potassium alum, the acetic acid concentration being greater than 10 grams per liter, the boric acid concentration being substantially half that of the acetic acid.

4. An acid hardening fixing bath comprising an aqueous solution of sodium thio-sulfate, a sulfite, acetic acid, boric acid and potassium alum, the acetic acid concentration being greater than 10 grams per liter, the boric acid concentration being substantially half that of the acetic acid and the potassium alum concentration being not over 30 grams per liter.

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