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ACID HARDENING FIXING BATH

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This invention relates to photographic acid hardening fixing baths and particularly to novel compositions for the purpose containing compounds of boron.

I have discovered a group of compounds of boron which are of great advantage in acid hardening fixing baths and have also made certain useful observations concerning the composition of acid hardening fixing baths containing these substances.

The compounds of boron which I use are the soluble salts of the oxygen acids of boron and the esters of these acids, especially the esters of boric acid, or the acids themselves. The esters include particularly such substances as boron triacetate, glycol borate, phenyl borate and the glyceryl esters of boric acid. One of the glyceryl esters is manufactured and sold commercially under the name glyceryl bori-borate. These substances are compounds resulting from the interaction of glycerin and boric acid or borax and while their composition is not exactly known they are understood to be glyceryl esters of boric acid, probably in varying mixtures and proportions.

A number of oxygen acids of boron are known, the soluble salts of any of which would be useful in my invention. The alkali (sodium and potassium particularly) salts are nearly all soluble, cheap and efficient. Among the oxygen acids of boron the compounds of which I may use are:

H_3BO_3 Ortho boric acid
$H_2B_2O_4$ Meta boric acid
$H_4B_2O_5$ Tetrahydrodi boric acid
$H_6B_4O_9$ Hexahydrotetra boric acid
$H_2B_4O_7$ Dihydrotetra boric acid
$H_6B_6O_{12}$ Hexahydrohexa boric acid
$H_2B_6O_{10}$ Dihydrohexa boric acid
$H_6B_8O_{15}$ Hexahydro-octo boric acid
$H_2B_8O_{13}$ Dihydro octo boric acid
$H_2B_{10}O_{16}$ Dihydro deca boric acid
$H_2B_{12}O_{19}$ Dihydro duo deca boric acid

It is understood that any of these acids of themselves may also be employed.

The addition of one of the salts or esters of these boron acids to an acid hardening fixing bath, such, for example, as one containing potassium alum and acetic acid, extends the pH range over which hardening takes place and raises the pH value at which sludging occurs. It is, of course, well known that as an acid hardening fixing bath is subjected to more and more use, the acid in it gradually becomes neutralized by the alkaline developer carried over by the photographic plates, films, or paper. The pH of the solution accordingly rises. Satisfactory hardening with the usual hardening agents, such as ordinary alum, occurs only during a certain range of pH values. As the pH of the solution increases beyond this useful range, the bath ceases to exert much hardening.

At the same time, as the bath becomes more alkaline and the pH value rises, a precipitate begins to be thrown down and this phenomenon is commonly known as sludging, since the precipitate slowly accumulates in the bottom of the tray or tank as a very finely divided sludge. The bath may also become more or less cloudy. This precipitate or sludge probably consists of basic aluminum sulfite, aluminum hydroxide or aluminum oxide, either singly or in mixture, depending on conditions. The boron compounds which I employ raise the pH value at which sludging occurs. These compounds therefore have a very useful effect in prolonging the life of the fixing bath and result in convenience and economy since it is not necessary to replace the fixing bath so soon.

The following formulas are illustrative embodiments of my invention:

1. Sodium thiosulphate	300	grams
Sodium sulfite (desiccated)	15	grams
Propionic acid	20	grams
Potassium alum	15	grams
Boric acid	5	grams
Water to	1	liter
2. Sodium thiosluphate	300	grams
Sodium sulfite (desiccated)	15	grams
Acetic acid	15	c. c.
Potassium alum	15	grams
Glycol borate	10	grams
Water to	1	liter
3. Sodium thiosulphate	300	grams
Sodium sulfite (desiccated)	15	grams
Boron triacetate	15	grams
Potassium alum	15	grams
Water to	1	liter
4. Sodium thiosulphate	300	grams
Sodium sulfite	15	grams
Acetic acid	15	c. c.
Citric acid	1	gram
Potassium alum	15	grams
Boric acid	5	grams
Water to	1	liter
5. Sodium thiosulphate	300	grams
Sodium sulfite	5	grams
Acetic acid	20	c. c.
Sodium acetate	20	grams
Potassium alum	20	grams
Borax	20	grams
Water to	1	liter

The above formulas are all complete acid hardening fixing baths which are useful for either positive or negative material.

It is usually desirable to have present in such a fixing bath an organic acid, such as acetic acid. I have found that propionic acid and butyric acid may be substituted for the acetic acid or their soluble salts may be used if other acids are present. Boron triacetate may be substituted for both the acetic acid and the boron compounds.

Certain fixing baths may be compounded in which a mineral acid is used with the borate ion and the acetate ion. Such an example is the following.

Formula 6

Sodium thiosulphate	300 grams
Sodium sulphite anhydrous	15 grams
Sodium acetate anhydrous	20 grams
Boric acid	5 grams
Sulphuric acid conc.	5 c.c.
Alum	15 grams
Water to	1 liter

I have also found that the sludging tendency of a given bath may be decreased by increasing the concentration of the acid ion such, for example, as the acetate ion, or by increasing the concentration of the boron compound or the borate ion. The addition of small quantities of other acids, such as citric, tartaric, fumaric, malic, maleic, lactic, glycolic, and glycero-phosphoric acids is also effective in decreasing the sludging tendency. These other acids are normally employed in rather small quantities in fixing baths containing potassium alum, as relatively large quantities of these acids decrease the hardening properties of such a bath.

The boron compounds which I have mentioned, in common with most boron compounds that are soluble in water, decompose to give boric acid in solution. Solutions containing these compounds may therefore be said to contain boric acid or the borate ion.

The term "salt of an oxygen acid of boron" is intended to include the inorganic true salts and also the organic compounds or esters.

It will be evident that a large number of acid hardening fixing baths of different proportions and constitutions may be compounded in accordance with the disclosure I have made. All of these modifications I consider as included within my invention as expressed by the appended claims.

What I claim is:

1. An acid hardening fixing bath comprising sodium thiosulfate, alum, an organic acid, a hardening agent, and an ester of boric acid selected from the group consisting of boron triacetate, glycol borate, phenyl borate, and the glyceryl esters of boric acid.

2. An acid hardening fixing bath comprising sodium thiosulphate, alum, an ester of boric acid selected from the group consisting of boron triacetate, glycol borate, phenyl borate and the glyceryl esters of boric acid and an acid selected from the group consisting of citric acid, tartaric acid, fumaric acid, malic acid, maleic acid, lactic acid, glycolic acid and glycero-phosphoric acid.

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