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PHOTOGRAPHIC DEVELOPER

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This invention relates to photographic developers and particularly to alkalies for use in developers.

Borax and boric acid have been used in developers of various kinds for some years. In most of the formulæ thus far proposed, however, the amount of borax or boric acid has been relatively small and in most cases where borax was used no other alkali was present. It is, of course, well known that borax has an alkaline reaction. In most of these prior formulæ, for example, borax was used at a concentration of less than 10 grams per liter.

I have found that excellent developers may be made if much greater concentrations of borax or boric acid are used together with suitable and relatively large amounts of strong alkalies. I have further found that the boron compound and the alkali may be prepared in the form of a dry substance which is a product of the interaction of the alkali and the boron compound. Such a compound in dry form of itself offers many advantages. Compounds of any degree of alkalinity ranging from that of borax itself, which is a relatively weak alkali, to that of caustic soda, for example, may be prepared. These compounds will then provide in a single dry harmless substance all the alkali that is needed for any formula. They offer marked advantages in use over the stronger alkalies such as caustic soda, particularly in handling. Other advantages will also appear from the following specification.

The substances which I use for the preparation of these alkalies in dry form are, first, a substance containing the radical of one of the oxygen acids of boron and, second, a strong alkali. Of the first group borax or boric acid are particularly useful. Of the second group useful substances are caustic soda (sodium hydroxide), caustic potash (potassium hydroxide), ammonium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, and tri-sodium phosphate.

A number of oxygen acids of boron are known, the alkali salts of any of which would be useful for making compounds more alkaline than borax. Among these substances are the following:

Orthoboric acid	H_3BO_3
Metaboric	$H_2B_2O_4$
Tetrahydrodiboric	$H_4B_2O_5$
Hexahydrotetra boric	$H_6B_4O_9$
Dihydrotetra boric	$H_2B_4O_7$
Hexahydrohexa boric	$H_6B_6O_{12}$
Dihydrohexa boric	$H_2B_6O_{10}$
Hexahydro octo boric	$H_6B_8O_{15}$
Dihydro octo boric	$H_2B_8O_{13}$
Dihydro deca boric	$H_2B_{10}O_{16}$
Dihydro duodeca boric	$H_2B_{12}O_{19}$

Various alkali salts of these acids have been described in the literature. With the exception of boric acid (ortho boric, H_3BO_3) and borax (sodium tetraborate, $Na_2B_4O_7.10H_2O$), none of these compounds, have found any application in photographic developers.

It will be understood in what follows that the alkali salts of any of these acids are useful in the manner described. Of the sodium salts, I employ only those which are more alkaline than borax. It is also true that in using these substances in various proportions with the alkalies as indicated a large variety and mixtures of compounds may be formed. It is not essential, of course, for the carrying out of my invention to ascertain the definite identity of the compounds present.

Of the various satisfactory acids of boron any one may be used interchangeably for another, and each can be evaluated in terms of equivalents of another. Equivalents are calculated on the basis of the boron content. Thus, referring to the preceding list, the following are equivalent weights, based on molecular weights:

$$H_3BO_3,\ \frac{H_2B_2O_4}{2},\ \frac{H_4B_2O_5}{2},\ \frac{H_6B_4O_9}{4},\ \text{etc.}$$

Compounds of the acids of boron which are as satisfactory as any for my purpose are those made from borax and caustic soda and I will illustrate my invention by their use, though not being limited in any way by the particular example given.

Compounds or mixtures of compounds varying in alkalinity from the alkalinity of borax to that of caustic soda itself may be prepared by the addition of caustic soda to a solution of borax. For example, 100 grams of borax and 50 grams of caustic soda are dissolved in 75 cc. of hot water. On cooling, a white crystalline solid separates which, dried in air free from carbon dioxide, is not as deliquescent as caustic soda, and is very alkaline when dissolved in water. Instead of allowing to crystallize, the mixture may be evaporated to dryness.

Similar substances may be prepared by the addition of more or less caustic soda. For the formation of the sodium salt of ortho boric acid (H_3BO_3), which contains the greatest number of hydrogen atoms per atom of borax, 1.05 grams of caustic soda are required for one gram of borax. White crystalline solids have been prepared with quantities of caustic varying from 0.1 gram to 1.0 gram per gram of borax. Similar compounds may be prepared by the addition of different quantities of caustic soda to boric acid. Other alkalies such as potassium hydroxide, lithium hydroxide or ammonium hydroxide may be substituted for sodium hydroxide or caustic soda in most cases.

These compounds may be used as alkalies in

photographic developers and as stated, developers with widely varying activities may be prepared with them. The following is an example of a developer containing one of these compounds. A compound as described is formed from 100 grams of borax and 50 grams of caustic soda. This is then used in the following developer formula:

Mono-methyl p-amino phenol sulfate	1 gram
Hydroquinone	5 grams
Sodium sulfite	50 grams
Borax-caustic compound	20 grams
Potassium bromide	1 gram
Water to	1 liter

As already stated a large number of the borax-caustic compounds can be prepared and they may be used in varying proportions to give developers of quite a wide range in characteristics. The particular one just described is given by way of example only.

Instead of using the dry compounds the substance containing the radical of one of the oxygen acids of boron and the strong alkali may be added separately. The following formula is analogous to the formula above but contains the substances separately instead of the compound:

Mono-methyl p-amino phenol sulfate	1 gram
Hydroquinone	5 grams
Sodium sulfite	50 grams
Borax	20 grams
Sodium hydroxide	5 grams
Potassium bromide	1 gram
Water to	1 liter

This developer and others containing the separate boron compounds and alkalies may be made equivelent in every way to those containing the dry compounds prepared by the addition of the alkalies to the boron compounds described. They are, of course, not so conveniently prepared but function equally well.

When the boron compounds and the alkalies are used separately, the useful alkalies include not only those already mentioned but all the strong organic bases such as certain primary, secondary bases, and the hydroxy alkyl substituted amines such as those described in my copending application Ser. No. 590,517 filed February 2, 1932, and that of M. L. Dundon Ser. No. 590,520 filed February 2, 1932, which has matured into Patent 1,925,557, granted Sept. 5, 1933.

It is to be pointed out that the compounds of the type I have described prepared by the addition of strong alkali to a suitable boron compound exert buffering action on the alkalinity of the developer, that is, they tend to maintain the solution at a fixed degree of alkalinity. This was not true in the prior use of borax or boric acid in developers where the concentration of borax, for example, was relatively low with a concentration of another alkali. This characteristic is in itself a valuable advantage.

A further advantage in the use of developers such as I have described is that they reduce the possibility of blisters forming on photographic prints and films during the usual processing steps. As is well understood, blisters are likely to be formed when a photographic print, for example, is developed in a developer containing a soluble carbonate and is then passed over into an acid fixing bath. A certain amount of the carbonate is carried over with the print and on reaction with the acid of the fixing bath forms carbon dioxide gas (CO_2). A certain amount of this gas may become entrapped in the gelatin emulsion and as it expands on its formation will form a blister. Most of the compounds of the type described do not liberate CO_2 or any other gas and the tendency to blister is thereby eliminated. The only compounds which might liberate CO_2 are those made with sodium or potassium carbonates.

Developers containing the compounds described or larger amounts of the boron compounds and the alkalies separately also have another advantage which has only recently been discovered. In the copending application, Serial No. 588,502, filed January 22, 1932 by R. S. Becker is described a fixing hardening bath containing boric acid and the acetate ion. It was found that such fixing baths show greatly increased hardening life and a greatly decreased tendency to sludge. It has now been found that the small amounts of the boron compounds which are carried over from developers of the kind here under consideration by films and prints into the fixing bath are also sufficient to exert this very beneficial influence on the hardening life and sludging properties. In other words, prints or films developed in developers containing larger amounts of the boron compounds as indicated, briefly rinsed, and then placed in the usual type of acid hardening bath carry over in the emulsion sufficient of the boron compounds to materially increase the hardening life of the bath and to decrease the tendency to sludge. This in itself is an important advantage.

It has already been indicated that wide variation is possible not only in the making of the compounds between the substances containing the radical of the boron acids and the alkalies but also in the formulæ of developers containing them or the boron compounds and alkalies separately.

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

What I claim is:

1. A photographic developer comprising a developing agent, a sulfite, and a metaborate.

2. A photographic developer comprising a silver-halide developing agent, a sulfite and a chemical product selected from the products resulting from the interaction of sodium hydroxide and borax where the proportion of sodium hydroxide to borax lies between one tenth and unity.

3. A photographic developer comprising a silver-halide developing agent and sodium metaborate.

4. A photographic developer comprising a silver-halide developing agent and potassium metaborate.

5. A photographic developer comprising a developing agent and ammonium metaborate.

6. A photographic developer comprising a silver-halide developing agent, an alkaline-reacting salt of an oxygen acid of boron, a caustic alkali, the proportion of the alkaline-reacting salt of an oxygen acid of boron to the caustic alkali being between 1:1 and 10:1.

7. A photographic developer comprising a silver-halide developing agent, an alkaline-reacting salt of an oxygen acid of boron, a caustic alkali, the proportion of the alkaline-reacting salt of an oxygen acid of boron to the caustic alkali being between 1:1 and 10:1, said alkaline-reacting salt of an oxygen acid of boron and said caustic alkali having at least partially reacted to form a metaborate.

8. A photographic developer comprising a silver-halide developing agent and a metaborate.

9. A photographic developer comprising a silver-halide developing agent and an alkali metaborate.

10. A photographic developer comprising a silver-halide developing agent and an alkali metaborate, in aqueous solution.

11. A photographic developer comprising a silver-halide developing agent, an alkaline-reacting salt of an oxygen acid of boron, and a caustic alkali, the proportion of the alkaline-reacting salt of an oxygen acid of boron to the caustic alkali being approximately 2:1.

12. A photographic developer comprising a silver-halide developing agent, borax, and a caustic alkali, the proportion of the borax to the caustic alkali being approximately 2:1.

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