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ACID-FIXING BATH.

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To all whom it may concern:

Be it known that I, SAMUEL E. SHEPPARD, a subject of the King of Great Britain, residing at Rochester, in the county of Monroe and State of New York, have invented certain new and useful Improvements in Acid-Fixing Baths, of which the following is a full, clear, and exact specification.

This invention relates to photographic acid fixing baths. One object is to include in such a bath only materials which will not inhibit the action of any hardener that may be present, nor form objectionable compounds or precipitates with any of the materials present. Another object of this invention is to provide such baths made from constituents which may be prepared in the form of a single dry powder, which will not deteriorate under ordinary conditions or within a reasonable time. Another object is to provide such a powder which will not contain an acid, as such, but which will when dissolved produce an acid through the decomposition of the substances. Another object is to provide in such a bath a "buffer" material, of the nature of those described and claimed in the patent of Felix A. Elliott, No. 1,411,687, granted Apr. 4, 1922, by which the acidity of the bath is maintained within desired limits. As there pointed out, the fixing bath should have an acidity or hydrogen ion concentration not greater than pH=4 and not less than pH=6.5 or, preferably, pH=6.

These and other objects, and the manner in which they are attained, will be more fully set forth in the following specification and claims. In order to make the invention clear, I will first mention a few well known characteristics of such baths and then point out the principles of my invention.

The basis of practically all fixing baths is sodium thiosulfate or "hypo", the best known solvent for photographic silver salts. In operation, there is brought over from the developing bath a considerable amount of alkaline developer, and as a preservative to prevent the harmful oxidation of the developer, a sulfite, usually sodium sulfite, is customarily added to the fixing bath. To increase the preservative action and also to neutralize the alkali, an acid is also usually added. Hypo has a tendency in an acid solution to decompose into sulfurous acid and sulfur, but this is prevented if there is enough sulfite present to maintain the bath in equilibrium. Sometimes an acid bisulfite, such as sodium bisulfite, $NaHSO_3$, or potassium metabisulfite, $K_2S_2O_5$, is used as a preservative in a fixing bath. It is also customary to include in the fixing bath a hardener, such as ammonium alum or potassium alum, but if a bisulfite were present, these alums could not hitherto be used and chrome alum was used. The acidity of the alum, derived from its hydrolysis, is sufficiently suppressed by the sulfite and acid conjointly so that it does not add materially to the acidity of the bath.

Since liquids are inconvenient in packing and shipping, it is desirable that ingredients of an acid fixing bath be in solid form. For this reason it has been customary to use organic acids, which are solid at all ordinary temperatures. It has not been possible to furnish an acetic acid bath in powder form because of the low melting point of this acid. It has been unsatisfactory, moreover, to mix in a single powder all the ingredients including hypo and an acid, because when these in finely divided form are intimately mixed the hypo is decomposed. It has been customary therefore, to furnish two separate powders.

I have discovered that the acid as a separate ingredient may be omitted entirely from such a mixed powder, by the substitution, in place of sulfite and an acid, of a bisulfite and the salt of an organic acid, which when dissolved produce a bath containing bisulfite, sulfite, sulfurous acid, an organic acid and a "buffer" salt of the organic acid. If, for instance, sodium bisulfite and sodium acetate are dissolved, the resulting bath contains sodium bisulfite, sodium sulfite, sulfurous acid, sodium acetate, and acetic acid. For purposes of illustration and without committing myself to an exact statement of reactions that would occur is a fixing bath, the reversible equations connecting these

substances only may be assumed to be as follows:

$$NaHSO_3 + H_2O \rightleftharpoons H_2SO_3 + Na_2SO_3$$
$$H_2SO_3 + Na \cdot C_2H_3O_2 \rightleftharpoons NaHSO_3 + H \cdot C_2H_3O_2$$

There are thus present in equilibrium in the solution two acids, one of them organic, and a salt of an organic acid, the latter being capable of acting as a "buffer" that tends to maintain the hydrogen ion concentration within certain limits as described in the above identified Elliott patent.

This action may, of course, be attained by the use of many other salts such as formates, citrates, tartrates, etc.

The dissociation necessary is attained only when the salts are in true solution as distinguished from suspension or so-called colloidal solution, and obviously only such salts are suitable as enter into a true solution in water.

When the bisulfite and salt are dissolved together with hypo, the reaction is, of course, more complicated, but the nature of the reaction is apparent from the above explanatory remarks.

The reaction is still more complicated when a hardener is also introduced. It has long been known that alum has a hardening effect and that the alum bath should be acid. It has been generally assumed that many acids, particularly organic acids, could be used with equally satisfactory results; but I have discovered that the presence in appreciable quantities of polybasic and hydroxy-organic acids, such as citric, tartaric, lactic, malic, maleic, salicylic, etc., acids or their salts inhibits the hardening action of alum upon the gelatine of photographic emulsions. This is due to the fact that these acids, or rather their anions, form stable complexes with aluminium, chromium and iron (the latter being frequently present as an impurity in commercial alums) whereby the combination of the hydrous oxides with the gelatine is prevented. The monobasic fatty acids and their alkali metal salts and particularly formic and acetic acids and their alkali metal salts, do not form complexes with aluminium of sufficient stability to inhibit hardening, but they do stabilize sufficiently to prevent the precipitation of aluminium hydroxide. For this reason, where, as is usually the case, an alum is present, a formate or acetate is very much preferable to salts of acids of the classes specified above. When I refer to the alkali metals I intend to include ammonium.

I have further discovered that sodium bisulfite or commercial potassium metabisulfite, which hitherto could not be used satisfactorily with an alum containing an aluminium compound because of the formation of insoluble basic aluminium compounds, can be used with such alums if an acetate or formate is also present. A typical formula is the following, the dry powdered salts being mixed in the order given,—

	Grams.
Sodium thiosulfate	240
Sodium acetate	55
Sodium bisulfite	30
Potassium alum	8

For use, the above quantity is made up to 1000 cc. with water. In place of the sodium acetate, 20 grams of sodium formate may be used. Such a powder will not, if stored under ordinary conditions and for reasonable times, release a harmful amount of acid.

While a certain small amount of acid may be released from the hypo and alum in solution, this is negligible, compared to the acid produced by the double decomposition of the bisulfite and the acetate or other salt; so that these constitute substantially the only source of acid.

Where I have referred to the materials as in the form of a powder, I do not mean to limit myself to any particular degree of fineness of the particles and rather coarse crystals or lumps of material may be used. These if desired may be mixed in an inert binding material such as gum arabic and formed into tablets or a paste.

The use of such gums appear to be especially desirable where commercial salts are used, containing impurities. The gum tends to keep any precipitates in a harmless suspended form. At the same time small amounts of alkali citrates or tartrates, or/and salts of the corresponding acids may be included replacing acetate and bisulfite to improve pro rata the clarity of the bath, but the quantity of these must be small if the hardening action of the alum is not to be greatly reduced.

It is apparent that numerous modifications and equivalents are possible, and I contemplate these as within the scope of my invention as defined in the appended claims.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal, and a alkali metal salt of a carboxylic acid, said salt having the property of entering into a true solution in water.

2. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal, and an alkali metal salt of a carboxylic acid, said salt having the properties of entering into a true

solution in water and, when in true aqueous solution in equilibrium with the bisulfite of acidfying the bath and of maintaining the hydrogen ion concentration of the bath at a predetermined strength greater than pH=6.5.

3. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of a carboxylic acid having not over nine carbon atoms.

4. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of a monobasic carboxylic acid having not over nine carbon atoms.

5. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of a monobasic carboxylic acid, said salt having the property of entering into a true solution with water.

6. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of a monobasic carboxylic acid, said salt having the properties of entering into a true solution with water and, when in true aqueous solution in equilibrium with the bisulfite, of acidifying the bath and of maintaining the hydrogen ion concentration of the bath at a predetermined strength greater than pH=6.5.

7. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of a lower fatty acid.

8. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an alkali metal salt of an acid of the aliphatic series having not over two carbon atoms.

9. Material in the form of a single powder adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a bisulfite of an alkali metal and an acetate of an alkali metal.

10. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a hardener and an alkali metal salt of a carboxylic acid, said salt having the property of entering into a true solution in water.

11. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a hardener and an alkali metal salt of a monobasic carboxylic acid, said salt having the property of entering into a true solution with water.

12. Powdered material adapted when dissolved to constitute a photographic fixing bath and comprising sodium thiosulfate, a hardener and an alkali metal salt of a monobasic carboxylic acid, said salt having the properties of entering into a true solution with water and, when in true aqueous solution in equilibrium with the bisulfite, of acidifying the bath and of maintaining the hydrogen ion concentration of the bath at a predetermined strength greater than pH=6.

13. Powdered material in a single mixture adapted to constitute when dissolved a photographic acid fixing bath and comprising sodium thiosulfate, a hardener, a bisulfite of an alkali metal, and an alkali metal salt of a lower fatty acid.

14. Material in the form of a single powder adapted to constitute when dissolved a photographic acid fixing bath and comprising sodium thiosulfate, a hardener, a bisulfite of an alkali metal, and an alkali metal salt of a fatty acid containing not over two carbon atoms.

15. Powdered material in the form of a single mixture adapted to constitute when dissolved a photographic acid fixing bath and comprising sodium thiosulfate, a hardener, a bisulfite of an alkali metal and an acetate of an alkali metal.

16. Powdered material in the form of a single mixture adapted when dissolved to constitute a photographic acid fixing bath, and comprising sodium thiosulfate, an alum, a bisulfite of an alkali metal, and an alkali salt of a lower fatty acid.

17. Material in the form of a single powder adapted when dissolved to constitute a photographic acid fixing bath, and comprising sodium thiosulfate, an alum containing an aluminium compound, a bisulfite of an alkali metal, and an alkali metal salt of a fatty acid containing not over two carbon atoms.

18. Material in the form of a single powder adapted when dissolved to constitute a photographic acid fixing bath, and comprising sodium thiosulfate, an alum, a bisulfite of an alkali metal, and an acetate of an alkali metal, said acetate having the property of entering into a true solution in water.

19. Material in the form of a single powder adapted in aqueous solution to constitute a photographic acid fixing bath and comprising sodium thiosulfate, an alum, a bisulfite of an alkali metal and an acetate of an alkali metal, the powder being substantially free from free acid.

20. Material in the form of a single powder adapted when dissolved to constitute a

photographic acid fixing bath, and comprising sodium thiosulfate, alum, a bisulfite of an alkali metal and an acetate of an alkali metal.

21. Material in the form of a single powder adapted when dissolved to constitute a photographic acid fixing bath and consisting of sodium thiosulfate, a hardener, a bisulfite of an alkali metal, and an acetate of an alkali metal.

Signed at Rochester, New York, this 3rd day of May, 1921.

SAMUEL E. SHEPPARD.