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PHOTOGRAPHIC SHORTSTOP CONCENTRATES

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This invention relates to new and improved photographic shortstop concentrates which, on dilution with water, form strong acid photographic shortstop working baths. In one specific aspect thereof, this inveniton relates to new and improved photographic shortstop concentrates which, on dilution with water, form rapid acting photographic shortstop baths.

As is well known, only a small portion of the silver halides present in photographic emulsions is actually utilized in the exposure and development of negatives and prints. After development is complete it is necessary to remove the excess silver halide in order to produce a permanent negative or print. The process of removing this excess silver halide is termed fixing and usually involves treatment of the developed negative or print with a soluiton containing a material capable of forming a water soluble complex with silver halides. Sodium thiosulfate pentahydrate (hypo) and ammonium thiosulfate (Thiamate) are the most commonly used fixing agents, the aqueous fixing bath usually containing, in addition to one or both of the fixing agents named, an emulsion hardening ingredient such as alum. Fixing baths conventionally exhibit an acidic reaction.

An aqueous solution of a suitable organic reducing agent or mixture thereof is usually employed in the development of negatives and prints, the development bath conventionally exhibiting an alkaline reaction.

It is obvious that the direct transfer of developed negatives or prints from the developer solution to the fixing bath results in contamination of the latter due to the carry-over of developer held on the surfaces and absorbed by the emulsion of the developed negatives and prints. This contamination results in the rapid exhaustion of the fixing baths due to the neutralization thereof by the alkaline developer. Developer contamination of the fixing bath also brings about precipitation or sludging out of a portion of the alum hardener in the fixing bath which results in reduction or destruction of the emulsion hardening properties of the bath and frequently in defective finished negatives and prints due to the inclusion of particles of the precipitated sludge by the emulsion.

To avoid the difficulties set forth above it has been common practice to subject developed negatives and prints to a water wash prior to their transfer to the fixing bath. This procedure is entirely satisfactory if a relatively inactive developer has been employed and the time of development is not particularly critical. However, it is obvious that the removal of developer absorbed by the emulsion through use of a water wash is a comparatively slow process, requiring the diffusion of the water into the emulsion and the displacement of the absorbed developer thereby. During all this time the developer present in the emulsion continues to act upon the silver halides and acordingly this water wash process can only be employed if the developer is slow acting and the development time is not particularly critical.

Due to continuing pressures for greater speed in the finishing of exposed negatives and prints, developing baths of higher and higher activity are being employed and with these a water wash following development and prior to fixing is entirely unsatisfactory. The removal of such adsorbed active developers by a water wash is so slow that control of the extent of development is impossible. To overcome this difficulty, it has been common practice to immerse negatives and prints that have been processed in an active development bath in a "shortstop" bath prior to transfer to the fixing bath. Such shortstop baths conventionally consist of a dilute (1% to 5%) aqueous solution of acetic acid. This solution, on diffusing into the emulsion, neutralizes the alkalinity of the absorbed developer, thereby destroying the reducing (developing) action thereof. Such shortstop solutions are adequate when used in connection with active developers.

Normally, it is desirable to process exposed negatives and prints in the shortest possible time consistent with the production of finished negatives and prints of satisfactory quality. In many fields (for example, certain military and medical applications of photography, photofinishes, certain types of theater screen television presentations, et cetera) extreme speed in processing is essential. To reduce processing times to a minimum, superactive developers are being increasingly employed and shortstop baths consisting of dilute aqueous solutions of acetic acid are unsatisfactory for use in connection with such developers. Acetic acid is weakly ionized, a 3% aqueous solution thereof having a pH of about 2.5. In addition, sodium acetate, resulting from the neutralization of the alkalinity of the developer by acetic acid, acts as a buffer and further reduces the ionization of the excess weakly ionized acetic acid remaining after neutralization so the maximum degree of acidity that can be obtained is that represented by a pH appreciably above 2.5. This acidity is not sufficiently high to destroy the action of such superactive developers with the speed necessary to provide a development process that is under complete control.

Accordingly, when such superactive developers are employed it is conventional to use a dilute aqueous solution of a strong acid, such as sulfuric acid or hydrochloric acid, as a shortshop bath. A 2% solution of sulfuric acid has a pH of about 1.0. Such shortstop solutions comprising a dilute aqueous solution of a strong acid destroy the activity of superactive developers quickly and completely and the highly ionized sodium salt produced by the neutralization of the alkalinity of the developer has no great effect on the ionization of the excess highly ionized acid so that the maximum degree of acidity furnished by such strong acid shortstop solutions is about that represented by a pH of 1.0.

Dilute aqueous sulfuric acid solutions are conventionally employed as strong acid shortstop baths for use in connection with superactive developers. However, due to the potential hazards involved in the transportation and use of sulfuric acid and the difficulty in measuring the small amounts of sulfuric acid required to give a shortstop bath of the proper acidity, it is common practice to use sodium bisulfate (usually in the form of sodium bisulfate monohydrate) as the source of the sulfuric acid. A solution containing 57 g. sodium bisulfate monohydrate per liter (49.5 g. anhydrous sodium bisulfate per liter) is equivalent to a 2% sulfuric acid solution. Dilute sulfuric acid shortstop solutions exhibit a slightly lower pH value than sodium bisulfate solutions of the same sulfuric acid equivalence. However, the pH value of sodium bisulfate shortstop solutions is sufficiently low to destroy the action of superactive developers with the speed necessary to provide a development process that is under complete control. Accordingly, sodium bisul-

fate is eminently suitable for use in the preparation of such strong acid shortstop solutions.

For certain purposes it is desirable to package and ship bisulfate type shortstop concentrates which are subsequently diluted with an appropriate quantity of water by the user to produce a high acid, rapid acting working shortstop bath. For obvious reasons, such shortstop concentrates should contain a large amount of bisulfate. We have discovered that a mixture of sodium bisulfate and ammonium bisulfate in certain definite proportions can be dissolved in water to produce a shortstop concentrate having a higher sulfuric acid equivalence that can be achieved by using either sodium bisulfate or ammonium bisulfate alone.

One object of this invention is to provide a new and improved shortstop concentrate which forms a strong acid photographic shortstop working solution on dilution with water.

Another object of this invention is to provide a new and improved shortstop concentrate which forms a rapid acting photographic shortstop working solution on dilution with water.

Additional objects of this invention will become apparent as the description thereof proceeds.

We have found that a mixture of from 70 to 85 mole percent ammonium bisulfate and from 30 to 15 mole percent sodium bisulfate (2.33 to 5.67 moles amonium bisulfate per mole sodium bisulfate) can be dissolved in water to produce a solution having a much higher sulfuric acid equivalence than can be achieved through aqueous solutions of either ammonium bisulfate or sodium bisulfate alone. The most concentrated solutions are obtained when using a mixture of approximately 77.5 mole percent ammonium bisulfate and 22.5 mole percent sodium bisulfate (3.44 moles ammonium bisulfate per mole sodium bisulfate).

Ammonium bisulfate is rather uncommon and is a relatively high cost inorganic compound. If desired, this material may be produced in situ by the interaction of ammonium sulfate and the stoichiometrically required amount of sulfuric acid.

For the better understanding of this invention a complete description of a specific embodiment thereof is given but it is to be understood that this specific embodiment is illustrative only and the spirit and scope of the invention is not limited to said illustrative specific embodiment.

Example

The following solution was prepared:

Water	cc.	325
Sulfuric acid (concentrated, 95 to 96%)	cc.	220
Ammonium sulfate	g.	526.9
Sodium bisufate monohydrate	g.	308

Water to make 1000 cc.

The preparation of the above composition involves the use of about four moles ammonium sulfate and a stoichiometric equivalent amount of sulfuric acid, resulting in the formation of eight moles ammonium bisulfate. In addition, 2.23 moles sodium bisulfate are used. Accordingly, the mole percentages of ammonium bisulfate and sodium bisulfate present in the composition are just about those previously given for obtaining solutions of maximum concentration. The composition of this example contains 513.5 g. sulfuric acid equivalent per liter. (An aqueous solution of sulfuric acid (no salts present) containing 513.5 g. sulfuric acid per liter has a sulfuric acid content of 39.5% by weight.) Under the high acidity conditions that here obtain all or practically all of the ammonium sulfate employed in making the composition is present in the composition in the form of ammonium bisulfate.

The composition of this example is a somewhat sirupy liquid at room temperatures. At temperatures approaching the freezing point of water crystals begin to deposit from the solution. In contrast to these properties, solutions having the same sulfuric acid equivalence as the composition of this example, but prepared using ammonium bisulfate and sodium bisulfate in mole percentages falling outside the operative range previously given herein, deposit crystals at ordinary room temperatures (20 to 25° C.).

If it is desired to prpeare shortstop concentrates in accordance with this invention that remain completely liquid at temperatures below the freezing point of water, this is easily accomplished by somewhat reducing the sulfuric acid equivalence of the concentrate while maintaining the mole percentages of ammonium bisulfate and sodium bisulfate within the operative range previously given. However, if the sulfuric acid equivalence of the concentrate is reduced to less than say 100 g. per liter, the dilution required to produce a working shortstop solution is so small as to make such concentrates of questionable utility as a source of working shortstop solutions. Accordingly, the shortstop concentrates of this invention should have a sulfuric acid equivalence of at least 100 g. and preferably 500 g. or more per liter.

Shortstop concentrates prepared in accordance with this invention may be diluted with water to the required extent to produce a working shortstop solution. The degree of dilution to be employed is determined by considering the alkalinity of the developer used in conjunction with the capacity desired of the working shortstop solution. The amount of developer carried over to the working shortstop solution is essentially directly proportional to the area of the developed negatives or prints transferred thereto, other conditions being constant. With a superactive developer, strong acid shortstop solutions become too sluggish for satisfactory control of the high speed developing process when the pH of the shortstop solution has increased to about 2.0 to 2.5 as the result of neutralizing the alkalinity of developer solution transferred to the short stop solution. Such superactive developers are usually strongly alkaline and as a result, unless the srtong acid shortstop baths have a comparatively high acid content they soon become exhausted when used in connection with such developers. A commercially acceptable capacity for strong acid shortstop baths can be set, somewhat arbitrarily, and the acid content of the working shortstop bath that will achieve this standard capacity can be determined on the basis of the alkalinity of the developer to be used in conjunction therewith. As a specific example of the interrelation of these various factors, if it is desired that one liter of the working strong acid shortstop solution stop development of at least thirty developed and transferred eight by ten inch film negatives with sufficient speed to give satisfactory control of the development process when a widely used superactive developer of high alkalinity is employed, then one volume of the shortstop concentrate of the example is diluted with about ten volumes of water. Such a 1:10 dilution produces a working shortstop solution having a sulfuric acid equivalent concentration of almost 4% by weight.

It is evident that the capacity of the strong acid shortstop solutions, prepared from the shortstop concentrates of this invention, may be varied at will over a considerable range. The actual capacity of such working solutions is in large measure determined by the particular preferences of individual users and the dilutions required to satisfy such preferences are easily determined.

Be it remembered, that while this invention has been described in connection with specific details of a specific embodiment thereof, these details and said embodiment are illustrative only and are not to be considered limitations on the spirit or scope of said invention except insofar as these may be incorporated in the appended claims.

We claim:

1. The composition of matter comprising an aqueous

solution of ammonium bisulfate and sodium bisulfate containing 2.33 to 5.67 moles ammonium bisulfate per mole sodium bisulfate, the equivalent sulfuric acid content of said composition being at least 100 g. per liter.

2. The composition of matter comprising an aqueous solution of ammonium bisulfate and sodium bisulfate containing 2.33 to 5.67 moles ammonium bisulfate per mole sodium bisulfate, the equivalent sulfuric acid content of said composition being at least 500 g. per liter.

3. The composition of matter comprising an aqueous solution of ammonium bisulfate and sodium bisulfate containing approximately 3.4 moles ammonium bisulfate per mole sodium bisulfate, the equivalent sulfuric acid content of said composition being at least 100 g. per liter.

4. The composition of matter comprising an aqueous solution of ammonium bisulfate and sodium bisulfate containing approximately 3.4 moles ammonium bisulfate per mole sodium bisulfate, the equivalent sulfuric acid content of said composition being at least 500 g. per liter.

5. The composition of matter comprising

Sodium bisulfate, about	g--	268
Ammonium sulfate, about	g--	526.9
Sulfuric acid, concentrated, about	cc--	220
Water, sufficient to give 1000 cc.		

6. A shortstop concentrate consisting essentially of water having dissolved therein ammonium bisulfate and sodium bisulfate in the ratio between about 2.33 moles and about 5.67 moles of ammonium bisulfate per mole of sodium bisulfate, the sulfuric acid equivalent of said concentrate being at least 100 grams per liter.

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