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[54] **METHOD FOR PREPARING BLEACH-FIX REGENERATOR CONCENTRATE**

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[51] **Int. Cl.** **G03c 5/26,** G03c 5/32, G03c 5/38

[58] **Field of Search** ..... 96/60 BF, 60, 61, 96/50; 423/51

[56] **References Cited**

UNITED STATES PATENTS

2,063,297	12/1936	Crabtree et al.	96/61 R
3,700,450	10/1972	Cooley	96/60 BF

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[57] **ABSTRACT**

A method is described for preparing bleach-fix regenerator concentrates which remain free of crystalized precipitate after prolonged storage and which are useful in the regeneration of photographic bleach-fix solutions which employ a ferric salt of an aminopolycarboxylic acid as a bleaching agent and a thiosulfate as a fixing agent.

The method comprises the steps of:

a. dissolving an aminopolycarboxylic acid and thiosulfate ion in an aqueous alkaline medium; and

b. adding sufficient gaseous sulfur dioxide to the solution of (*a*) to lower the pH thereof to between about 5.4 and 6.0.

10 Claims, No Drawings

METHOD FOR PREPARING BLEACH-FIX REGENERATOR CONCENTRATE

FIELD OF THE INVENTION

This invention relates in general to photographic processing, and in particular to the use of bleach-fix solutions. More specifically, this invention describes a method for preparing a concentrated bleach-fix regenerator useful in the regeneration of spent bleach-fix solutions.

BACKGROUND OF THE INVENTION

United States Pat. Nos. 3,634,088 issued Jan. 11, 1972, and 3,700,450 issued Oct. 24, 1972, describe in detail a technique for regenerating spent photographic bleach-fix compositions which employ a ferric salt of an aminopolycarboxylic acid as a bleaching agent and a thiosulfate as a fixing agent. As described in these references, the regeneration of these bleach-fix compositions is accomplished by reducing the concentration of silver ion in the solution to a low level, (generally below about 1 gram of silver per liter of solution) by metallic replacement, electrolytic recovery or precipitation techniques, mixing the solution with oxygen in an amount sufficient to convert substantially all ferrous ion in the solution to ferric ion and adding to this regenerated solution a sufficient amount of a bleach-fix regenerator concentrate comprising small amounts of necessary chemicals to establish original working solution concentrations and pH. Generally such regenerator concentrates comprise a solution of an aminopolycarboxylic acid, a thiosulfate and sulfite ions and have a pH of between about 5.4 and 6.0.

Although these regenerator concentrates could be supplied in the form of dry powders which are mixed by the film or paper processor, in view of the problems of "on-site" mixing which are well known to those skilled in the photographic processing art, it has been found desirable to supply these regenerators as premixed liquid concentrates which are simply added to the "desilvered" and oxygen regenerated solution.

It is in the preparation and storage of these latter premixed liquid regenerator concentrates that stability problems have occurred in the form of crystal precipitation when conventional sulfite ion addition techniques have been used. Thus, when the source of sulfite ion in the formulation of these bleach-fix regenerator concentrates was, for example, a soluble sulfite or bisulfite salt (i.e. sodium or potassium sulfite or bisulfite) an undesirable crystal formation occurred after storage of the solution at ambient temperature for a period of about two weeks. Although the source of this crystalline precipitate is not perfectly clear, it has now been unexpectedly discovered that crystal formation in this type of system can be eliminated by incorporating the sulfite ion as gaseous SO_2 rather than as sulfite or bisulfite ion from a salt.

SUMMARY OF THE INVENTION

Thus, according to the present invention there is provided a novel technique for preparing a bleach-fix regenerator concentrate comprising an aqueous solution of an aminopolycarboxylic acid, thiosulfate ion and sulfite ion having a pH of between about 5.4 and 6.0 comprising the steps of dissolving the aminopolycarboxylic acid and the thiosulfate ion in water to provide an aqueous alkaline solution thereof, and then adding sufficient gaseous sulfur dioxide to the solution to lower the pH thereof to between about 5.4 and about 6.0.

DETAILED DESCRIPTION OF THE INVENTION

Preparation of bleach-fix regenerator compositions of the type described above comprises dissolving the amino-polycarboxylic acid and thiosulfate ion in water in sufficient quantity to return the concentrations of these components of the bleach-fix solution to their original working solution levels, and then introducing sufficient sulfite ion in the form of gaseous sulfur dioxide into the aqueous solution to adjust the pH thereof to between about 5.4 and 6.0.

Bleach-fix regenerator solutions to which the method of this invention is applicable are solutions comprising an aminopolycarboxylic acid which complexes with iron to form the bleaching agent a water-soluble thiosulfate which serves as the fixing agent in the working bleach-fix formulation and sulfite ion which serves as a control for pH. As is well known, thiosulfates which are useful for this purpose include ammonium thiosulfate and alkali metal thiosulfates such as sodium thiosulfate and potassium thiosulfate.

Illustrative examples of the aminopolycarboxylic acids which are useful in the regenerator compositions and consequently the bleach-fix solutions prepared therefrom are the following:

nitrilotriacetic acid,
ethylenediamine tetraacetic acid,
diethylenetriamine pentaacetic acid,
ortho-diamine cyclohexane tetraacetic acid,
ethylene glycol bis(aminoethyl ether) tetraacetic acid,
diaminopropanol tetraacetic acid,
N-(2-hydroxyethyl)ethylenediamine triacetic acid,
ethyliminodipropionic acid,
and the like.

While the above-described fixing agents and aminopolycarboxylic acids are the essential components of bleach-fix regenerator formulations to which the method of this invention is applicable, the bleach-fix regenerator solutions will usually also include other addenda known to the art to be useful for incorporation into bleach-fix formulations. Thus, for example, they may include an additional silver halide solvent such as water-soluble thiocyanate, e.g. ammonium thiocyanate, sodium thiocyanate or potassium thiocyanate, as well as such compounds as ammonium bromide, alkali metal bromides, amines, mercaptotriazoles, etc.

The concentration of the essential ingredients, i.e. the aminopolycarboxylic acid and the thiosulfate in the regenerator solution will of course vary depending upon the efficiency of the regeneration operation up to the point of addition of the regenerator concentrate, the degree of usage of the bleach-fix before regeneration and the concentration levels of the essential components in the working bleach-fix. Thus, although no definite limits can be established for the quantities of thiosulfate or aminopolycarboxylic acid which are used in the concentrate these will be readily determinable by the skilled artisan based on the foregoing variables as they relate to his particular system.

In one system in which the techniques described herein has been found particularly useful dissolution of from about 0.15 moles to about 0.35 moles of aminopolycarboxylic acid and in particular ethylenediamine tetraacetic acid (which is well known as a com-

ponent of the various ammonium and alkali salts of the ferric complexes thereof in bleaching and bleach-fixing formulations) per 100 ml of water and from about 0.5 moles to about 0.85 moles of thiosulfate per 100 ml of water is achieved using conventional mixing techniques. The solution is then rendered slightly basic, i.e. the pH raised to below about 9 by the addition of a suitable base, e.g. ammonia to insure proper dissolution of the aminopolycarboxylic acid and then the solution acidified with sufficient gaseous sulfur dioxide to lower the pH to from about 5.4 to about 6.0.

Since many aminopolycarboxylic acids and in particular ethylenediaminetetraacetic acid (EDTA) are for practical purposes substantially insoluble in water, dissolution of this component is preferably achieved by either forming a slurry of EDTA with water to which is added enough base (preferably ammonia) to partially neutralize and hence solubilize the EDTA prior to addition of the thiosulfate salt, or the EDTA is added to the water in partially neutralized form, e.g. as a diammonium EDTA solution. After addition of the thiosulfate salt, sufficient base must be added to render the solution basic, i.e. pH = 7 to 9 to insure proper neutralization and dissolution of the EDTA. Generally, from about 0.1 to about 0.25 moles of base per 100 ml of water will be sufficient to achieve this dissolution.

At this point the SO_2 gas is introduced to bring the pH down to the prescribed levels.

Addition of gaseous sulfur dioxide may be achieved using any of the well known techniques for such additions. Most commonly the SO_2 gas is simply bubbled through the solution until the desired pH is achieved.

When the sulfite ion is introduced in this fashion, rather than as a sulfite or bisulfite salt objectionable crystal formation which appears on storage is substantially eliminated. Although the source of these crystals is not perfectly clear, it appears that they comprise primarily precipitated salts of the aminopolycarboxylic acid, since solutions containing these crystals when used to regenerate a bleach-fix solution produce a regenerated solution which demonstrates an unsatisfactory bleaching capability.

The utility of the bleach-fix regenerator solution prepared according to the technique described herein is clearly set forth in the aforementioned U. S. Pat. No. 3,634,088 described hereinabove.

The invention is further illustrated by the following examples of its practice.

EXAMPLE I

220.6 grams (0.76 m) EDTA was slurried with 312.5 ml of water at about 70°–80° F; 125 grams (2.06 m) of 28 percent aqueous NH_3 was added to partially solubilize the EDTA. Next 536.2 grams (2.10 m) of 58 percent ammonium thiosulfate solution were added. Sufficient 28 percent aqueous NH_3 (20.9 grams, 0.34 m) was added to raise pH of the solution to 8.15 ± 0.10 at 80° F. 38.1 grams (0.6 m) of SO_2 (gas) was added to the solution to lower the pH to 5.70 ± 0.05 at 80° F. Storage of this solution at 120°F for 3 months produced no visible crystalline precipitate contamination.

EXAMPLE II

551.6 grams (0.76 m in EDTA) of 45% diammonium EDTA solution was added to 81.3 ml of water at about 70°–80° F. 536.2 grams (2.10 m) of 58 percent ammonium thiosulfate solution was then added. Sufficient 28 percent aqueous NH_3 (55.3 grams, 0.88 m) was added to raise pH of the solution to 8.15 ± 0.10 at 80° F. 38.1 grams (0.6 m) of SO_2 (gas) was added to the solution to lower the pH to 5.70 ± 0.05 at 80° F. Storage of this solution at 120°F for three months produced no noticeable crystalline precipitate.

EXAMPLE III

220.6 grams (0.76 m) EDTA was slurried with 295 ml of water at about 70°–75°F; 125 grams (2.06 m) of 28 percent aqueous NH_3 was added to partially solubilize the EDTA. Next 536.2 grams (2.10 m) of 58 percent ammonium thiosulfate were added. 20.9 grams (0.35 m) of 28 percent aqueous NH_3 was added to raise the pH of the solution to 8.15 at 80°F. 94.8 grams (0.6 m) of $Na_2S_2O_3$ was added to the solution to lower the pH to 5.70 at 80°F. The resulting solution showed crystalline contamination after storage for three weeks at room temperature (70°–80°F).

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method for preparing bleach-fix regenerator concentrates which remain free of crystallized precipitate after periods of prolonged storage and which are useful in the regeneration of photographic bleach-fix solutions which employ a ferric salt of an aminopolycarboxylic acid as a bleaching agent and thiosulfate ion as fixing agent said method comprising the steps of:

a. dissolving an aminopolycarboxylic acid and thiosulfate ion in an aqueous alkaline-medium; and

b. adding sufficient gaseous sulfur dioxide to the solution of (a) to lower the pH thereof to between about 5.4 and 6.0.

2. The method of claim **1** wherein said aqueous medium has a pH of between about 7 and about 9.

3. The method of claim **2** wherein from about 0.15 to about 0.35 moles of aminopolycarboxylic acid and from about 0.5 to about 0.85 moles of thiosulfate ion are dissolved per 100 ml of water.

4. The method of claim **3** wherein said aminopolycarboxylic acid is ethylenediaminetetraacetic acid.

5. The method of claim **3** wherein said aqueous medium comprises an aqueous solution of ammonium hydroxide.

6. The method of claim **5** wherein said aminopolycarboxylic acid is supplied in the form of the partially neutralized acid.

7. The method of claim **6** wherein said partially neutralized aminopolycarboxylic acid is made by forming an aqueous slurry of ethylendeiaminetetraactic acid, and adding sufficient base to partially neutralize and hence solubilize the ethylenediaminetetraacetic acid.

8. The method of claim **7** wherein said base is ammonium hydroxide.

9. The method of claim **5** wherein said aminopolycarboxylic acid and thiosulfate are added to water and the solution rendered basic by the addition of from about 0.1 to about 0.25 moles of base per 100 ml of water.

10. The method of claim **9** wherein said base is ammonium hydroxide.

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