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REGENERATION OF BLEACH-FIX SOLUTIONS USED IN PHOTOGRAPHIC PROCESSING

Austin C. Cooley, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Continuation-in-part of application Ser. No. 8,026, Feb. 2, 1970, now Patent No. 3,634,088. This application Jan. 7, 1971, Ser. No. 104,766

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ABSTRACT OF THE DISCLOSURE

Photographic bleach-fix solutions employing a ferric salt of an aminopolycarboxylic acid as bleaching agent and a thiosulfate as fixing agent are regenerated by reducing the concentration of silver ion in the solution to a low level and mixing the solution with oxygen in an amount sufficient to convert substantially all ferrous ion in the solution to ferric ion. Removal of silver from the solution can be effected by addition of a chemical precipitant, by metallic replacement, or by electrolytic recovery and the necessary contact with oxygen after silver removal can be accomplished by aerating the solution. Treatment of spent bleach-fix solutions in this manner will essentially restore their original bleaching and fixing capabilities and thereby permit their reuse in photographic processing.

This application is a continuation-in-part of U.S. patent application Ser. No. 8,026, now U.S. Pat. 3,634,088, filed Feb. 2, 1970.

This invention relates in general to photographic processing and in particular to the use of bleach-fix solutions. More specifically, this invention relates to treatment of spent bleach-fix solutions to substantially restore their original bleaching and fixing capabilities so as to permit their reuse.

Combined bleach and fixing solutions have been known for many years. They are used in processing silver halide photographic materials to simultaneously accomplish the steps of bleaching and fixing and thereby eliminate one step in the conventional processing procedure. The essential components of the solutions are the bleaching agent, i.e. an agent which oxidizes the metallic silver in the silver image to a soluble form, and the fixing agent, i.e. an agent which dissolves the undeveloped silver halide and the silver salts formed by the action of the bleaching agent. While a large number of different bleach-fix formulations are known to the art, of particular importance because of their stability and the excellent results obtained therewith are bleach-fix solutions in which the bleaching agent is a ferric salt of an aminopolycarboxylic acid and the fixing agent is a thiosulfate.

The bleach-fix solutions comprising a thiosulfate and a ferric salt of an aminopolycarboxylic acid are relatively costly and their commercial use has been hampered by this fact, especially in view of the further fact that heretofore they could be used only once and then had to be discarded. Thus, while it is known to regenerate bleach solutions and fixing solutions so as to permit their reuse, the methods employed are not useful for treatment of the aforesaid bleach-fix solutions. For example, ferricyanide bleach solutions can be regenerated by treatment with bromine, as is described in U.S. Pat. 2,515,930, or by treatment with reagents capable of releasing bromine in aqueous solution, as are described in U.S. Pats. 2,611,699 and 2,611,700, or by treatment with a water-soluble persulfate, as is described in U.S. Pat. 2,944,895. Reuse of spent fixing solutions is also rendered feasible by removing all or most of the silver from the fix and making the necessary chemical additions to reconstitute the original formulation. Methods of accomplishing this have been known for many years as evidenced, for example, by U.S. Pats. 1,446,405, 1,527,942 and 3,082,079. However, treatment of a bleach-fix formulation of the type described herein with bromine or a persulfate is not feasible as these agents will not only bring about the desired oxidation of ferrous ion in the solution but at the same time will destroy the ability of the solution to act as a fix by oxidizing thiosulfate ion to sulfate ion or other oxidation products. Accordingly, in the past, whenever these bleach-fix solutions have been employed they have been discarded after a single use, with resulting substantial economic losses as well as the creation of serious pollution problems. This has limited the use of these bleach-fix solutions to special situations, where the advantage of eliminating one processing step has outweighed these disadvantages, and essentially precluded their use in large scale continuous photographic processing.

In accordance with this invention, bleach-fix solutions in which a thiosulfate serves as the fixing agent and a ferric salt of an aminopolycarboxylic acid as the bleaching agent, are regenerated by a method which essentially restores their original bleaching and fixing capabilities and thereby permits their reuse. The method comprises reduction of the concentration of silver in the solution to a low level, as hereinafter described, and mixing of oxygen with the solution in a sufficient amount, as hereinafter described, to convert substantially all ferrous ion in the solution to ferric ion. Appropriate additions of minor amounts of chemicals to restore the solution to its exact original composition are also made, as needed. By this means, the desired oxidation of ferrous ion to ferric ion is effected without significant destruction of thiosulfate so that the solution can be reused, with resulting elimination of the pollution problem and substantial savings in processing costs.

Bleach-fix solutions to which the method of this invention is applicable are solutions comprising a water-soluble thiosulfate which serves as the fixing agent. 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.

Use of ferric salts of aminopolycarboxylic acids as bleaching agents in bleach-fix formulations is also well known. Illustrative examples of the aminopolycarboxylic acids 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. The ferric salts of aminopolycarboxylic acids utilized in the practice of this invention may be salts in which all cations are the ferric ion or salts in which one or more of the carboxyl groups have formed a salt with a cation other than iron, e.g. with ammonia or with an alkali metal ion. An example of such a salt is sodium ferric ethylenediamine tetraacetate. The bleach-fix may also contain a non-chelated salt of an aminopolycarboxylic acid, e.g. the tetra sodium salt of ethylenediamine tetraacetic acid, in addition to the ferric salt.

While the above-described fixing agents and bleaching agents are the essential components of bleach-fix formulations to which the method of this invention is applicable, the bleach-fix solutions will usually also include other addenda known to the art to be useful for incorporation in bleach-fix formulations. Thus, for example, they may

include an additional silver halide solvent such as water-soluble thiocyanite, e.g. ammonium thiocyanate, sodium thiocyanate or potassium thiocyanate, as well as such compounds as ammonium bromide, alkali metal bromides, amines, sulfites, mercaptotriazoles, etc. The concentration of thiosulfate in the bleach-fix solution is typically from about 5 to about 200 grams per liter and the concentration of the ferric salt of an aminopolycarboxylic acid is typically from about 5 to about 200 grams per liter.

Any of the methods which are known to the art for recovering silver from a fixing solution can be utilized in accordance with this invention to reduce the concentration of silver ion in the bleach-fix to the desired level. In general, these methods are of three types, namely, precipitation of the silver by addition of a chemical agent which forms an insoluble silver salt, metallic replacement in which the solution is brought into contact with a metal which is more electropositive than silver and thereby serves to replace the dissolved silver, and electrolytic recovery in which the silver is plated out on the cathode of an electrolytic cell. A discussion of the relative advantages and disadvantages of these methods and an extensive listing of the pertinent technical literature is included in an article by M. L. Schreiber entitled "Present Status of Silver Recovery in Motion-Picture Laboratories," Journal of the SMPTE, vol. 74, pp. 505–513, June 1965.

For the purposes of this invention, it is preferred to recover the silver from the bleach-fix solution by metallic replacement, or by the electrolytic method, or by precipitation of silver sulfide through the addition of sulfide ion such as by adding sodium sulfide to the bleach-fix. Metallic replacement is conveniently and inexpensively accomplished by utilizing steel wool as the metal and employing the apparatus described in U.S. Pat. 3,369,801. The silver is effectively recovered from the bleach-fix by this procedure in spite of the fact that it is much more soluble in the bleach-fix solution than in a thio-sulfate fix. When the steel wool cartridge is functioning effectively to remove silver from the bleach-fix solution, the color of the solution changes from deep red to light green, whereas this color change ceases to occur when the cartridge becomes exhausted. Thus, the color of the effluent from the cartridge provides a convenient indicator of its effectiveness and can be used to determine when a new cartridge should be employed. Electrolytic recovery should be carried out using a cell designed to operate with high agitation and high current density. The minimum current density needed to remove silver from the bleach-fix solution is higher than is required with a fixing solution while the tendency to formation of silver sulfide is less with the bleach-fix solution than with most fixing solutions so that use of high current densities is feasible. Good results in electrolytic recovery of silver from the bleach-fix solution will ordinarily be obtained with a current density of greater than about 7 amperes per square foot. Silver recovery cells which are particularly advantageous for use with the bleach-fix solution because they provide high agitation and permit the use of high current density are described in British Pats. 916,348 and 1,123,168.

To accomplish the objectives of this invention, the concentration of silver in the bleach-fix solution should be reduced to a level of less than about one gram of silver per liter of solution and more preferably to a level of less than about 0.5 gram of silver per liter of solution. The spent bleach-fix solution subjected to regeneration may have a silver concentration of up to about 10 grams per liter, or more, but will most usually have a concentration of silver of about two to three grams per liter.

The second step of the process of this invention is the step of mixing the bleach-fix solution, from which the silver has been removed by one of the methods discussed above, with oxygen in order to oxidize ferrous ion to ferric ion. Whereas the agents which have been used heretofore as oxidants in effecting regeneration of ferricyanide bleaches will cause destruction of thiosulfate, if used with the bleach-fixes described herein, it has unexpectedly been found that oxygen is effective in converting ferrous ion to ferric ion without destruction of thiosulfate. In treating the bleach-fix solution, oxygen should be employed in at least the stoichiometric amount, i.e. at least 0.25 mole of oxygen per mole of ferrous ion in the solution. Preferably, an amount of oxygen of at least about one mole per mole of ferrous ion is used. Any combination of oxygen flow rate and time which will permit adequate contact of the oxygen with the solution can be utilized. Of course, the amount of oxygen necessary will depend upon the composition of the bleach-fix being treated and the optimum amount of oxygen for a particular bleach-fix solution will depend upon the efficiency of the contact procedure employed. Optimum amounts of oxygen in any particular instance may be readily determined by a few routine experiments.

Mixing of oxygen with the bleach-fix solution can be carried out using batch, semi-continuous or continuous techniques, as desired. In carrying out continuous treatment, a portion of the bleach-fix solution can be continuously withdrawn from the processing machine and returned as a recycle stream after regeneration. While pure oxygen can be employed to effect regeneration by the method of this invention, its use is not necessary and it will ordinarily be satisfactory to effect the oxidation by contacting the solution with air. In addition to the use of pure oxygen, or air, oxidation could be carried out using any otherwise inert oxygen-containing gaseous mixture, e.g. a mixture of oxygen and nitrogen or a mixture of oxygen and argon. Aeration will ordinarily be the simplest, most convenient and most inexpensive procedure. The time required for aeration will depend upon such factors as the characteristics of the air distributor, the flow rate, the size and shape of the tank in which the bleach-fix solution is aerated, the method used for removing the silver and so forth. Typical times required for substantially complete oxidation of ferrous ion by aeration are from about 15 to about 90 minutes.

In practicing the method of this invention, the silver should, under ordinary circumstances, be removed from the solution before contact of the solution with oxygen is effected since the common procedures for silver recovery, e.g. metallic replacement or electrolytic recovery, will at the same time as they effect removal of silver bring about reduction of ferric ion to ferrous ion and thus counteract the effect of the oxidation step.

Following removal of the silver and aeration, or other mixing of the bleach-fix solution with oxygen, it is desirable to add small amounts of any necessary chemicals to establish the original concentrations and pH. The additions necessary will depend upon the method of silver recovery which was utilized and the extent to which the solution was contacted with oxygen. To determine the additions that are necessary, the solution can be analyzed using well known analytcial techniques.

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

EXAMPLE 1

The bleach-fix employed in this example had the following composition:

NaFeEDTA [1]	g./l.	67.5
Na_4EDTA [2]	g./l.	7.5
Na_2SO_3	g./l.	15
$(NH_4)2S_2O_3$ (60% soln.)	ml./l.	150
NH_4SCN	g./l.	15

pH=7.0.

[1] Sodium ferric ethylenediaminetetraacetate.
[2] Tetra sodium salt of ethylenediaminetetraacetic acid.

This bleach-fix was used as replenisher in processing Kodak Ektacolor paper in a Kodak Model 4C–3 paper processor. The paper carried superposed silver halide emulsion layers sensitive to red, green and blue light each

containing coupler compounds for formation of substantially colored dye images in the emulsion layers upon reaction with primary aromatic amino color developing agent in a well-known manner. This paper was continuously passed through the tanks of the processor containing color developing solution to obtain dye images and silver images in the exposed areas as well as residual silver halide, and then was passed through the tanks containing the above bleach-fix.

The seasoned bleach-fix overflow from the machine was passed continuously at a rate of ten gallons per hour through steel wool packed cartridges of the type described in U.S. Pat. 3,369,801, with two cartridges being connected together in series. Chemical analysis of the effluent from the second cartridge showed that the steel wool had removed essentially all of the silver from the bleach-fix and reduced most of the iron from ferric to ferrous. A one-liter sample of this effluent was placed in a 1000-ml. graduated cylinder and a sintered glass air sparger was placed in the bottom of the cylinder and air was bubbled through the bleach-fix for one hour. Chemical analysis of the aerated bleach-fix showed that the aeration had oxidized substantially all of the ferrous iron in the desilvered bleach-fix back to the ferric form, thereby restoring the oxidation potential of the bleach-fix. Analysis of the seasoned bleach-fix, i.e. before regeneration, of the desilvered bleach-fix, i.e. after passage through the cartridges, and of the regenerated bleach-fix, i.e. after aeration, gave the following results:

	Seasoned bleach-fix	Desilvered bleach-fix	Regenerated bleach-fix
pH	7.19	7.97	8.02
Specific gravity	1.103	1.099	1.099
Ag, g./l.	2.47	0	0
NH_4CNS, g./l.	19	15	15
$(NH_4)_2S_2O_3$ (60% soln.), ml./l.	131	138	128
Na_2SO_3, g./l.	10.7	5.5	1.9
Total EDTA (as Na_4EDTA), g./l.	63.1	62.8	66.1
Free EDTA (as Na_4EDTA), g./l.	4.24	0.44	0.34
Total iron, g./l.	8.75	9.24	8.98
Fe^{++}, g./l.	0.95	7.31	0.06
Fe^{+++}, g./l.	7.80	1.93	8.92

EXAMPLE 2

The bleach-fix employed in this example had the following composition:

NaFeEDTA	g./l.	67.5
Na_4EDTA	g./l.	60.0
Na_2SO_3	g./l.	15
$(NH_4)_2S_2O_3$ (60% soln.)	ml./l.	150
NH_4SCN	g./l.	15

pH=7.0.

This bleach-fix was used in the same manner as described in Example 1 and the seasoned bleach-fix overflow from the machine was passed through a single steel wool packed cartridge at a rate of 5 gallons per hour. The effluent from the cartridge was aerated for one hour using a 20-micron pore sintered stainless steel air sparger and an air flow rate of 40 cubic feet per hour. The aerated bleach-fix was then diluted by 25% with water to reduce the iron concentration and the following chemical additions were made to the bleach-fix so that it could be reused as replenisher:

Na_2EDTA	g./l.	53
Na_2SO_3	g./l.	10
$(NH_4)_2S_2O_3$ (60% soln.)	ml./l.	60
NH_4SCN	g./l.	6

The pH of the bleach-fix was adjusted to 7.0 and it was used as replenisher in the process. The regenerated bleach-fix was found to be only slightly less active than fresh bleach-fix and no photographic differences were observed as a result of its use.

Analysis of seasoned bleach-fix from the process using fresh replenisher, of the regenerated bleach-fix, i.e. after aeration, and of seasoned bleach-fix from the process using regenerated replenisher gave the following results:

	Seasoned bleach-fix from fresh replenisher	Regenerated bleach-fix	Seasoned bleach-fix from regenerated replenisher
pH	6.92	8.13	7.19
Specific gravity	1.122	1.127	1.132
Ag, g./l.	2.42	0.01	2.20
NH_4CNS, g./l.	13.9	14.8	13.4
$(NH_4)_2S_2O_3$ (60% soln.), ml./l.	117	118	118
Na_2SO_3	7.2	8.6	9.4
Total EDTA (as Na_4EDTA), g./l.	91.5	97.6	93.3
Free EDTA (as Na_4EDTA), g./l.	40.4	9.3	44.5
Total iron, g./l.	7.53	13.2	7.20
Fe^{++}, g./l.	1.09	0.4	0.88
Fe^{+++}, g./l.	6.44	12.8	6.32

EXAMPLE 3

A bleach-fix of the same composition as that described in Example 1 was used in the same manner as described in Example 1 and the seasoned bleach-fix overflow from the machine was metered continuously at 100 ml./min. through a 1 ft.^{2} cathode area electrolytic cell operating with a current of 30 amps DC. The effluent from the electrolytic cell was passed continuously into a 5-gallon aeration tank in which it was continuously aerated using a 20-micron pore sintered stainless steel air sparger and an air flow rate of 15 cubic feet per hour. To enable the aerated bleach-fix to be used as replenisher, the following chemical additions were made:

NaFeEDTA	gl./l.	6.2
Na_4EDTA	g./l.	2
Na_2SO_3	g./l.	15
$(NH_4)_2S_2O_3$ (60% soln.)	ml./l.	28
NH_4SCN	g./l.	1

The pH of the bleach-fix was adjusted to 7.0 and it was used as replenisher in the process. The regenerated bleach-fix was found to be only slightly less active than fresh bleach-fix and no photographic differences were observed as a result of its use. Analysis of the seasoned bleach-fix from the process using fresh replenisher, of the effluents from the electrolytic cell and from the aeration tank, and of seasoned bleach-fix from the process using regenerated replenisher gave the following results:

	Seasoned bleach-fix from fresh replenisher	Bleach-fix effluent from electrolytic cell	Bleach-fix effluent from aeration tank	Seasoned bleach-fix from regenerated replenisher
pH	7.05	7.05	7.87	6.98
Ag, g./l.	1.84	0.34	0.37	2.30
NH_4CNS, g./l.	14.7	17.0	16.5	15.6
$(NH_4)_2S_2O_3$ (60% soln.), ml./l.	126	122	123	128
Na_2SO_3	11.6	11.1	1.05	11.6
Total EDTA (as Na_4EDTA), g./l.	69.1	69	66.7	69
Free EDTA (as Na_4EDTA), g./l.	3.21	3.21	3.21	3.78
Total iron, g./l.	9.77	9.75	9.41	9.62
Fe^{++}, g./l.	1.20	5.05	1.33	0.91
Fe^{+++}, g./l.	8.57	4.70	8.08	8.71

EXAMPLE 4

The following example illustrates a process for continuously regenerating a used bleach-fix composition and adjusting the level of bleaching agent and fixing agent so the composition can be continuously recycled to the bleach-fix tanks of the processor to maintain the bleach-fix solution at a constant level of activity.

The process of Example 1 was carried except that seasoned bleach-fix solution in the first of two tanks of the processing machine contained the ingredients shown in the first column of the table below. The overflow from this tank was treated as in Example 1 to remove silver from the solution and aerated to convert ferrous ion to ferric ion. The resulting regenerated bleach-fix had the composition shown in the second column of the table. To 800 parts by volumes of this regenerated bleach-fix was added 40 parts of water and 160 parts of the bleach-fix regenerator composition shown in the third column of the table. The resultant replenisher solution has the composition shown in column four of the table and was used as a replenisher for recycling to the second tank of seasoned bleach-fix at the desired rate so as to maintain a constant level of the bleaching and fixing activity.

The above regenerator solution of column three of the table is representative of compositions which can be supplied to the trade for continuous replenishment of the bleach-fix solution in use, and consist essentially of a mixture of about 0.194 to 0.292 mole of an aminopolycarboxylic acid, about 0.269 to 0.336 mole of a thiosulfate as well as sulfite ions such as provided by sodium bisulfite. The pH of the composition should be about 5.4 to 6.0. These solutions are not useful per se for bleaching and fixing of the silver in the emulsion layers since they contain little or no ferric salt of the aminopolycarboxylic.

In the following table it will be understood that the formulas all contain a sulfite as a preservative.

	Seasoned bleach-fix	Desilvered bleach-fix	Bleach-fix regenerator	Bleach-fix replenisher
Ammonium thiosulfate (mol/l.)	0.57	0.57	0.336	0.800
EDTA (mol/l.)	0.274	0.274	0.121	0.377
Fe (mol/l.)	0.125	0.215	0	0.179

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 regenerator composition for addition to a used photographic bleach-fix solution which has been treated by (a) removing silver ion therefrom and (b) mixing oxygen therewith in an amount sufficient to convert ferrous ions to ferric ions, said regenerator composition consisting essentially of an aqueous solution of an aminopolycarboxylic acid, a thiosulfate and sulfite ions, the solution having a pH of between about 5.4 and 6.

2. The composition according to claim 1 wherein about 0.269 to 0.336 mol per liter of the thiosulfate and about 0.194 to 0.290 mol per liter of the aminopolycarboxylic acid are present.

3. The composition according to claim 2 wherein the aminopolycarboxylic acid is ethylenediaminetetraacetic acid.

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NORMAN G. TORCHIN, Primary Examiner

M. F. KELLEY, Assistant Examiner

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