

[54] REGENERATION OF PHOTOGRAPHIC BLEACH/FIX BATHS

[75] Inventors: Norman Newman; Richard S. Fisch, both of St. Paul, Minn.

[73] Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.

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[56] References Cited

UNITED STATES PATENTS

3,619,188 11/1971 Alcock et al. 96/60

3,634,088 1/1972 Cooley 96/60

3,617,283 11/1971 Ohi et al. 96/60 BF

Primary Examiner—Norman G. Torchin

Assistant Examiner—M. F. Kelley

Attorney—Kinney, Alexander, Sell, Steldt & Delahunt

[57] ABSTRACT

Depleted photographic bleach/fix baths which include bleaching agents (such as the iron III complex of ethylenediaminetetraacetic acid) and a silver halide solvent are regenerated by addition to a recycled stream thereof of an iron, cobalt and copper-free regenerating solution which includes a polycarboxylic acid, a silver halide solvent, and an organic bleach-enhancing compound which includes at least one atom which is different from carbon, hydrogen and nitrogen.

12 Claims, No Drawings

REGENERATION OF PHOTOGRAPHIC BLEACH/FIX BATHS

The present invention relates to silver halide photographic processing and more particularly relates to the regeneration of bleach/fix photographic processing baths.

Bleach baths and bleach/fix baths have long been employed in the photographic processing of silver halide photographic materials, particularly color materials, to oxidize free silver images to silver halide and to remove silver halide from the materials. Early bleach baths employed an alkali metal ferricyanide bleaching agent which was reduced to a ferrocyanide during the bleaching (silver oxidation) reaction. Although such bleach baths met with great success, they were found to contribute greatly to pollution. Ferricyanide-free bleach/fix baths which employ bleaching agents such as the iron III complex of ethylene-diaminetetraacetic acid reduce pollution problems, and have gained wide popularity. In this type of bleach/fix bath, a bleaching agent, which may be exemplified as the iron III - ethylenediaminetetraacetic acid complex, is reduced to the iron II complex during the silver-bleaching reaction. Such bleach/fix baths also include a silver solvent (fixing agent) such as sodium thiosulfate ("hypo"), a source of sulfite ion (as an antioxidant), and various other photographic additives such as wetting agents, etc.

Referring to iron III - ethylenediaminetetraacetic bleach/fix bath as exemplary of ferricyanide-free bleach/fix baths, it will be understood that during the bleaching and fixing reactions, the concentrations of the various bath ingredients change greatly. For example, during the bleaching reaction, iron III is reduced to iron II, the concentration of iron III being reduced. The concentration of silver halide solvent which is available for dissolving or complexing with silver halide is likewise reduced, and the concentration of silver (e.g., as the silver-thiosulfate complex), and of halides increases. Such changes in the bleach/fix bath composition reduce both bleaching and fixing rates, producing "depleted" baths. To avoid this problem, one may replenish such a bath by adding thereto an aqueous replenisher composition which contains the necessary chemicals to maintain the working bleach/fix bath at a working strength. Overflow which results from the addition of the replenisher composition may be discarded or may be re-used by the addition thereto of chemicals necessary to form the replenisher composition. Normally, the overflow is desilvered (e.g., by passage thereof through steel wool), and the iron II complex thereof is oxidized to the iron III complex by, for example, bubbling air therethrough. The chemicals added to the thus-treated overflow will normally contain ethylenediaminetetraacetic acid to replace the ethylenediaminetetraacetic acid which is required to complex with the iron released into the solution during the desilvering operation. Particularly when photographic materials having unusually large quantities of silver therein are processed through such bleach/fix baths, replenishment of the baths must take place at an increasingly rapid rate in order to maintain the concentration of iron III complex, silver halide solvent, and the like, so that rapid bleaching and fixing may be maintained. In some instances, replenishment cannot practically be carried out at a sufficiently rapid rate to maintain the correct balance of chemicals in the bleach/fix

baths. A method for the regeneration of bleach/fix baths which would permit such baths to operate with a reduced replenishment rate and at lower concentration levels of silver halide solvent (e.g., hypo) and bleaching agent (e.g., iron III complexes), and at higher silver levels, is greatly to be desired.

It is thus an object of the present invention to provide a process for the regeneration of photographic bleach/fix baths which permits a reduced replenishment rate.

It is another object of the invention to provide a regenerating composition which may be added to depleted photographic bleach/fix baths for regeneration thereof.

In one embodiment thereof, the present invention relates to an improvement in the process for regeneration of a depleted photographic bleach/fix bath which contains a bleaching agent selected from the group consisting of ferric, cobaltic and cupric complex salts of an acid selected from the group consisting of polycarboxylic acids, hydroxypolycarboxylic acids and aminopolycarboxylic acids, and a silver halide solvent, the process comprising desilvering and oxidizing a withdrawn portion of the bleach/fix bath and then returning the withdrawn portion to the bleach/fix bath. The improvement comprises adding to the withdrawn portion of the bath an iron, cobalt and copper-free regenerating composition which includes a silver halide solvent, said acid of said bleaching agent, and an organic bleach-enhancing compound which includes at least one atom which is different from carbon, hydrogen and oxygen.

Although the regeneration composition referred to above may be supplied in solid form, it has been found desirable to provide this composition as a ready-made aqueous solution which may be added to the withdrawn portion of the bleach/fix bath and the whole diluted with water if desired to provide a replenisher solution which may then be added to the bleach/fix bath. Accordingly, in another embodiment the present invention relates to a regenerating composition for regenerating depleted photographic bleach/fix working baths which contain a bleaching agent selected from the group consisting of ferric, cobaltic and cupric complex salts of an acid selected from the group consisting of polycarboxylic acids, hydroxypolycarboxylic acids and aminopolycarboxylic acids, and a silver halide solvent; which regenerating composition (preferably in solution form) is essentially free of metals which, in complex form, may participate in the silver bleach (redox) process, such as iron, cobalt and copper, and which includes a silver halide solvent, said acid of said bleaching agent, and an organic bleach-enhancing compound which includes at least one atom which is different from carbon, oxygen and hydrogen.

As used herein, "bleach-enhancing compound" refers to an organic compound which includes at least one atom which is different from carbon, hydrogen and oxygen (e.g., sulfur, nitrogen, selenium) and which is capable of enhancing (e.g., accelerating) the rate of bleaching of a silver image in a photographic element treated with a bleach/fix bath to which has been added the compound. Selection of "bleach-enhancing" compounds of the invention is facilitated by the following test:

A gelatino silver halide photographic element which contains 50 milligrams per square decimeter of silver is exposed uniformly to light and is developed in a suitable developer to convert all of the silver halide to me-

tallic silver, and is then washed thoroughly with water. The developed element is then divided into two portions. The first portion is placed in a bleach/fix bath of the following composition for 1½ minutes at 88°F.:

Sodium ferric ethylenediamine-tetraacetic acid	80 g.
Disodium ethylenediaminetetraacetic acid	30 g.
Sodium sulfite (anhydrous)	10 g.
Ammonium thiosulfate (60% aqueous solution)	200 ml.
pH: adjusted to 7.0 by addition of sodium hydroxide or sulfuric acid.	

To a second 1 liter solution of the above-identified bleach/fix bath is added 5 grams of a candidate bleach-enhancing compound, and the second portion of the developer silver halide element is immersed therein at 88°F for 1½ minutes. After withdrawal of the developed silver halide elements from the bleach/fix baths, the elements are thoroughly washed with water and the quantity of silver therein is measured by X-Ray fluorescence by the method reported in "Automatic Direct Reading X-Ray Spectroscopy Applied to the Determination of Silver," *Analytical Chemistry*, Vol. 35, No. 1, January, 1961. A reduction (e.g., of about 15 percent or more) in the amount of residual metallic silver in the developed silver halide element which was treated in the bleach/fix bath containing the candidate compound indicates that this compound is a b"bleach-enhancing" compound as referred to herein.

Preferably, the bleach-enhancing compounds of the invention are organic compounds which include at least one sulfur atom in a thiocarbonyl group (e.g., as in thiosemicarbazide, thiourea, thiocarbohydrazide, etc.); in a thioether group (e.g., as in thio derivatives of polyoxyethylene, etc.); or in a sulfonium group (e.g., as in thionine, 1,6-hexylene dimethylsulfonium dibromide, etc.); or include at least one nitrogen atom in a quaternary ammonium group (e.g., ethylpyridinium chloride, alkyl-, aryl- and cyclo-alkyl pyridinium salts, etc.); or include at least one selenium atom in a selenocarbonyl group (e.g., as in selenourea, selenosemicarbazide, etc.). Most preferably, the bleach-enhancing compounds of the invention include both sulfur and nitrogen atoms in a thioamide group, such as in thiosemicarbazide, thiourea and thiocarbohydrazide, and derivatives thereof such as the alkyl, aryl, cycloalkyl, aralkyl, and heterocyclic derivatives thereof as disclosed in Swiss Pat. No. 336,257 and British Pat. No. 1,150,466. Thiosemicarbazide is most preferred.

It has surprisingly been found that the present invention permits bleach/fix baths of the type described herein to be operated at significantly lower concentrations of bleaching agent complex and of silver halide solvent available for use (e.g., hypo), and at significantly higher concentrations of silver (e.g., as the thiosulfate-silver complex). Accordingly, the rate at which the working bleach/fix bath need be charged with replenisher solution is significantly reduced.

As used herein, "overflow" refers to portions of spent bleach/fix bath which are removed from the system. After discarding a portion of the overflow, the remainder is combined, either continuously or in separate portions, with the regenerating composition referred to above resulting (after optional dilution with water) in a "replenisher" solution. As will be understood, the rate at which the replenisher solution is supplied to the working bleach/fix bath will be controlled so as to maintain the concentration of ingredients in the

bleach/fix bath at a level which permits essentially complete bleaching to be obtained in a relatively short amount of time (e.g., within about 1 minute at 88°F.). Further, the concentration of ingredients in the regenerating composition, and the ratio of regenerating composition to the retained overflow may also be determined by simple experimentation. It has been found that a concentration of bleach-enhancing compound in the replenisher solution of from about 0.25 to about 10.0 grams per liter will yield acceptable results, although from about 0.5 to about 5.0 grams per liter is preferred.

The bleaching agents employed in the present invention are selected from the group consisting of ferric, cobaltic and cupric complex salts of an acid selected from the group consisting of polycarboxylic acids, hydroxypolycarboxylic acids and aminopolycarboxylic acids (including non-complex salts of such acids, such as the ammonium and alkali metal (e.g., sodium and potassium) salts thereof). Examples of such bleaching agents are the iron III complex salt of ethylenediaminetetraacetic acid, sodium salt, the cobalt III complex salt of nitrilotriacetic acid, the iron III complex salt of ethylenediamine hydroxyethyltriacetic acid; the copper II disodium complex salt of iminodiacetic acid; copper II disodium complex salt of dipicolinic acid, the 3-hydroxy glutaric acid amino cobalt complex (as in British Pat. No. 777,635), and the iron III complex salt of malonic acid.

The regenerating compositions of the present invention include the acid of the bleaching agent; that is, if the iron III salt of ethylenediaminetetraacetic acid is employed in the bleach/fix working bath, then ethylenediaminetetraacetic acid will ordinarily be employed in the regenerating composition.

Silver halide solvents which are useful in the present invention include sources of thiosulfate ion (e.g., sodium thiosulfate), sources of thiocyanate ion (such as sodiumthiocyanate), thioglycollic acid and the like. Such materials are commonly referred to as "fixing agents" and are well known in the photographic art (see U.S. Pat. No. 2,748,000). In addition, the regenerating compositions of the invention may include such standard photographic additives as surfactants, oxidation inhibitors (e.g., sulfite ion precursors such as sodium sulfite), hardeners such as aluminum chloride U.V. absorbers and the like.

As noted above, the regenerating compositions of the present invention are free of iron, cobalt and copper, which metals form complex salts with polycarboxylic acids, hydroxypolycarboxylic acids, and aminopolycarboxylic acids. During the desilvering process, withdrawn portions of overflow may be passed through, for example, iron or copper gauzes, resulting in the deposition of silver thereon and the release therefrom of iron or copper ions. If the bleaching agent of the bleach/fix working bath is an iron III complex, then desilverization may be accomplished by use of an iron material such as steel wool. Similarly, if a cupric complex salt is employed as a bleaching agent, then a copper material such as gauze may be used for desilverization.

The invention may be more clearly understood by reference to the following illustrative, non-limiting example:

EXAMPLE

Silver halide color print paper having three silver ha-

5

lide, coupler-containing layers sensitized to different regions of the spectrum, which contained in total 20 milligrams of silver (as silver halide) was uniformly exposed to white light and thereafter was continuously processed in a processing sequence which consisted of development in a paraphenylenediamine type color photographic developer solution, treatment in a bleach/fix working bath (see infra), water wash, treatment in a stabilizing bath at pH 3.8, water rinse and drying. The bleach/fix working bath consisted of 600 ml. of a solution having the following composition:

Sodium ferric ethylenediamine-tetraacetic acid	80 g.
Disodium ethylenediamine-tetraacetic acid	30 g.
Sodium sulfite (anhydrous)	10 g.
Ammonium thiosulfate (60% aqueous solution)	200 ml.
Water to	1000 ml.
pH: adjusted to 7.0 by addition of sodium hydroxide or sulfuric acid.	

In order to maintain a proper balance of chemicals in the path during continuous processing of the color print paper, a replenisher solution was continuously supplied to the bath. The resulting overflow from the bath was collected, desilvered by passage through steel wool, and oxidized by bubbling air therethrough. One-fifth of the volume thereof was described. To the remaining four-fifths of the desilvered and oxidized overflow was added a regenerating composition (in aqueous solution form) of the following composition:

Disodium ethylenediamine-tetraacetic acid	6.5 g.
Sodium sulfite	3.5 g.
Ammonium thiosulfate (60% aqueous solution)	45 ml.
Water to	160 ml.

The regenerating composition was added in a volume ratio of one part thereof to five parts of retained overflow solution, the resulting solution being made up with water to a volume of 1.25 times the volume of the retained overflow. The resulting replenisher solution was then used to continuously replenish the working bleach/fix bath. The rate at which the replenisher solution was continuously added to the working bleach/fix bath was controlled so as to assure complete bleaching of the silver image on the color print paper which was continuously fed through the process. The rate of addition of the replenisher solution of the bleach/fix bath was approximately 45.7 ml. of replenisher solution per square foot of print paper (the dwell time of the print paper in the bath being about 1.4 minutes). The process was continued until over 600 milliliters of the bleach/fix working bath had been replaced by the replenisher solution.

The above experiment was repeated exactly except that the regenerating composition in addition contained 1 gram of thiosemicarbazide. In order to assure

6

complete bleaching of the color print paper, only 28.6 milliliters of the resulting replenisher solution was required to be added per square foot of color print paper.

We claim:

1. In the process for regeneration of a depleted photographic bleach/fix bath which contains a bleaching agent selected from the group consisting of ferric, cobaltic and cupric complex salts of an acid selected from the group consisting of polycarboxylic acids, hydroxypolycarboxylic acids and aminopolycarboxylic acids, and a silver halide solvent, which process comprises desilvering and oxidizing a withdrawn portion of said bath and then returning said withdrawn portion to said bleach/fix bath, the improvement which comprises adding to said withdrawn portion an iron, cobalt, and copper-free regenerating composition which includes a silver halide solvent, said acid of said bleaching agent, and an organic bleach-enhancing compound which includes at least one atom which is different from carbon, hydrogen or oxygen.
2. The process according to claim 1 wherein said bleach-enhancing compound is thiosemicarbazide.
3. The process according to claim 1 wherein said bleach-enhancing compound is thiocarbohydrazide.
4. The process according to claim 1 wherein said bleaching agent is iron (III) complex of ethylenediaminetetraacetic acid.
5. The process according to claim 1 wherein said bleaching agent is the iron (III) salt of nitrilotriacetic acid.
6. The process according to claim 1 wherein said regenerating composition is in aqueous solution form.
7. A regenerating composition for regenerating depleted photographic bleach/fix working baths which contains a bleaching agent selected from the group consisting of ferric, cobaltic and cupric complex salts of an acid selected from the group consisting of polycarboxylic acids, hydroxypolycarboxylic acids and aminopolycarboxylic acids, and a silver halide solvent, said composition being essentially free of iron, cobalt and copper and including a silver halide solvent, said acid of said bleaching agent, and an organic bleach-enhancing compound which includes at least one sulfur or at least one nitrogen atom.
8. The composition of claim 7 wherein said bleach-enhancing compound is thiosemicarbazide.
9. The composition of claim 7 wherein said bleach-enhancing compound is thiocarbohydrazide.
10. The composition of claim 7 wherein said bleaching agent is iron (III) complex of ethylenediaminetetraacetic acid.
11. The composition of claim 7 wherein said bleaching agent is the iron (III) salt of nitrilotriacetic acid.
12. The composition of claim 7 wherein said composition is in aqueous solution form.

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