United States Patent

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[72] Inventors **David Gerald Alcock;**
Enzo Piccotti, both of Ilford, England

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[73] Assignee **Ilford Limited**
Ilford, England

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[33] **Great Britain**
[31] **35,340/68;**
Apr. 14, 1969, Great Britain, No. 18,934/69

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[54] **BLEACH-FIX PROCESSING**
9 Claims, No Drawings

[52] **U.S. Cl.** **96/50,** 96/52, 96/60, 96/22
[51] **Int. Cl.** **G03c 5/32,** G03c 7/00, G03c 5/26
[50] **Field of Search** ..... 96/60, 60 BF, 61, 50, 52, 22

[56] **References Cited**

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Primary Examiner—Norman G. Torchin
Assistant Examiner—Mary F. Kelley
Attorney—Cushman, Darby & Cushman

ABSTRACT: This application describes a bleach-fix process which comprises bleach-fixing photographic silver halide color material, after development of the silver image, in the presence of a water-soluble selenocyanate salt, selenourea, substituted selenourea or substituted selenouracil.

BLEACH-FIX PROCESSING

This invention relates to color photography and more particularly to the processing of photographic material comprising silver halide emulsion layers and adapted for processing to yield color images, (hereinafter referred to simply as "color photographic material").

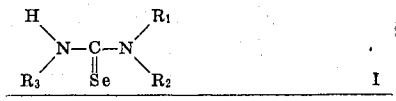
In the conventional processing of such color photographic material a developable silver salt image is developed with an aromatic primary amino developing agent of the paraphenylene diamine type (a so-called "color developer") in the presence of a compound (a so-called "color coupler") which will combine with the oxidation products of the color developer to form an azomethine or quinone-imine dye. The dye is thus formed in situ with the developed silver image. SUbsequently the product must be treated with a bleach bath and a fixing bath or a combined bleach-fix bath thereby to remove silver and any residual silver halide or other silver salt, leaving in the product only the dye image.

The use of a combined bleach-fix bath is preferable because it results in a reduction of the processing time and of the processing equipment required. Normally a bleach-fix bath comprises a mild oxidizing agent for example a ferric-chelate complex, a cupric complex salt or a cobalt (III) complex together with a silver halide solvent or fixing agent for example a water-soluble thiosulfate or a water-soluble thiocyanate.

Stable bleach-fix solutions comprising ferric chelate complexes and sodium thiosulfate may be obtained but because of the weak oxidizing power of the ferric chelate complex such bleach-fix baths can only be used commercially for the processing of photographic materials with a fairly low silver content.

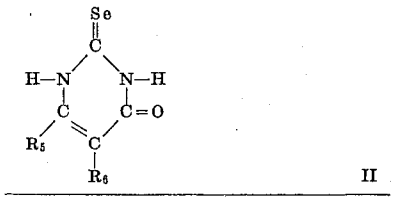
It is the object of the present invention to provide a bleach-fix step which can be used in the processing of color photographic material which have a relatively high-silver content, for example color negative material and color reversal material.

According to the present invention in a color development process for the production of the colored image in exposed color silver halide photographic material there is provided after the development step, the step of treating the photographic material with an aqueous solution of a bleach fix catalyst which is a water-soluble selenocyanate salt, a selenourea of the general formula I:



I

wherein R_1, R_2 and R_3 are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom or a selenouracil of the general formula II:



II

wherein one of R_5 and R_6 is a lower alkyl group and the other a hydrogen atom or both represent hydrogen atoms, and simultaneously or subsequently treating the photographic material in a bleach-fix bath which comprises an aqueous solution comprising an oxidizing agent which is either a ferric chelate or a diaquo-tetrammine-cobalt (III) complex, and a silver halide solvent which is either a water-soluble thiosulfate or a water-soluble thiocyanate.

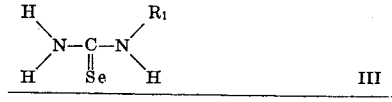
By lower alkyl group is meant an alkyl group which comprises from one to six carbon atoms.

By ferric chelate complex is meant a coordination compound of the ferric ion and a compound which comprises nitrogen and/or oxygen-containing coordinating groups. The most important coordinating groups are amino, nitrogen heterocyclo, carboxyl and carbonyl groups.

The preferred ferric chelate complex for use in the bleach-fix step of the present invention is a ferric ethylenediaminetetraacetic acid complex. It is to be understood that this compound may be used as such in the preparation of a bleach-fix bath or it may be formed in situ in a bleach-fix bath by ethylenediaminetetraacetic acid reacting with a ferric salt e.g. ferric chloride. In the examples which follow the ferric ethylenediaminetetraacetic acid complex has been formed in situ.

Other ferric chelate complexes which may be used in the present invention are for example pyridine-2:6-dicarboxylatoferrate (III) complex, iminodiacetatoferrate (III) complex and nitrilo-triacetateferrate (III) complex.

The preferred bleach-fix catalysts for use in the process of the present invention is a selenourea of the general formula III:



III

wherein R_1 is a lower alkyl group.

The bleach-fix catalysts of use in the present invention are preferably added to the bleach-fix bath but they may be present during the bleach-fixing treatment adsorbed to or absorbed in the color photographic material. Thus the bleach-fix catalysts of use in the present invention, and in particular the bleach-fix catalysts of formula III may be present in any treatment bath or wash bath which is used in the color development process between the development step and the bleach-fix step. Exemplary of such baths are stop baths and stop-fix baths. However in the case of selenocyanate these compounds cannot be used in an acid bath because they decompose yielding a highly toxic gas.

The bleach-fix catalysts cannot be present, however, in the developing solution as they interfere with the development of the color material. For the same reason the bleach-fix catalysts of use in the present invention can not be present initially in the photographic material.

According to another embodiment of the present invention there is provided a bleach-fix bath which comprises an aqueous solution of an oxidizing agent which is either a ferric chelate complex or a diaquo-tetrammine-cobalt (III) complex, a silver halide solvent which is either a water-soluble thiosulfate or a water-soluble thiocyanate and a bleach-fix catalyst which is a water-soluble selenocyanate salt, a selenourea of the formula I as hereinbefore set forth, or a selenouracil of formula II as hereinbefore set forth.

It is preferred that the concentration of water-soluble selenocyanate salt in the bleach-fix bath is from 0.1 to 200 g. per liter of solution and most preferably approximately 5 g. per liter of solution.

It is preferred that the concentration of selenourea of formula I or of the selenouracil of formula II present in the bleach-fix bath is from 0.5 to 1.5 g. per liter of the solution and most preferably 0.1 g. per liter of solution.

It is preferred that in use the temperature of the bleach-fix bath is approximately 24° C.

It is preferred that the concentration of the selenourea of formula I or of the selenouracil of formula II present in a stop bath or a stop-fix bath or in a wash bath is from 0.5 mg. to 3.0 g. per liter of the solution and most preferably 0.3 g. per liter of solution.

The following Examples with serve to illustrate the invention.

EXAMPLE I

A negative tripack color material comprising a silver halide emulsion containing color couplers, was given a neutral wedge exposure and color processed, the processing sequence being as follows.

Color development	6 minutes	
Sodium metaborate		53.3 g.
Sodium hydroxide		2.0 g.
Sodium sulfite anhydrous		3.9 g.
Potassium bromide		0.70 g.
Hydroxylamine sulfate		2.34 g.
Sodium sulfate anhydrous		7.8 g.
4-Amino-N-ethyl-N-(4-hydroxybutyl)-aniline sulfate		6.0 g.
Water		to 1 liter
pH 10.5		

Stop fix	4 minutes	
Sodium thiosulfate pentahydrate		171.0 g.
Sodium acetate anhydrous		31.4 g.
Sodium sulfite anhydrous		4.3 g.
Acetic acid (glacial)		35 ml.
Potassium alum		17.0 g.
Ammonium chloride		43.0 g.
Water		1 liter
pH 4.3		

Wash	4 minutes

Bleach-fix	25 minutes	
Disodium tetraborate decahydrate		12.5 g.
Boric acid		22.5 g.
Sodium hydroxide		10.0 g.
Ethylenediaminetetraacetic acid		16.2 g.
Disodium salt of ethylenediamine-tetraacetic acid dihydrate		3.5 g.
Ferric chloride (60% W/V soln.)		15 ml.
Sodium thiosulfate pentahydrate		95.0 g.
Sodium sulfite anhydrous		4.0 g.
Water		to 1 liter
pH 7.0		

Wash	4 minutes

COnditioner	4 minutes	
Disodium salt of ethylenediamine-tetraacetic acid dihydrate		0.50 g.
Sodium carbonate anhydrous		4.5 g.
Formaldehyde (40% W/V soln.)		10 ml.
Lissapol (8% soln.)		1.7 ml.
Water		to 1 liter
pH 10.7		

Wash	4 minutes

Dry

The processed material was bleached in the low-exposure areas, but unsatisfactorily bleached in the parts at high-exposure.

A sample of the same photographic material was instead satisfactorily processed by using the same processing sequence, but bleach-fixing it for only 6 minutes, when 300 mg. of selenourea were added to the stop-fix bath described above.

EXAMPLE 2.

A color negative tripack as in example 1, was given a neutral wedge exposure and processed, the processing sequence being as in example 1, except for the stop-fix stage which was carried out in this example by treating the material for 4 minutes in the following stop-fix bath.

Sodium thiosulfate pentahydrate	171.0 g.
Sodium acetate anhydrous	31.4 g.
Sodium sulfite anhydrous	4.3 g.
Acetic acid (glacial)	35 ml.
Potassium alum	17.0 g.
Ammonium chloride	43.0 g.
N-methyl-selenourea	300 mg.
Water	to 1 liter

The sample was found to be satisfactorily processed.

EXAMPLE 3.

A color negative tripack material as in example 1, was given a neutral wedge exposure and processed, the processing sequence being as in example 1, except for the stop-fix stage which was carried out by treating the material for 6 minutes in a stop-fix bath of the following composition.

Sodium thiosulfate pentahydrate	171.0 g.
Sodium acetate anhydrous	31.4 g.
Sodium sulfite anhydrous	4.3 g.
Acetic acid (glacial)	35 ml.
Potassium alum	17.0 g.
Ammonium chloride	43.0 g.
N,N-dimethyl-selenourea	200 mg.
Water	to 1 liter

The bleach-fixing time was 9 minutes and the sample was found to be satisfactorily processed.

EXAMPLE 4.

The tests described in the examples 1, 2 and 3 were repeated, but the 4 minutes wash between the stop-fix and the bleach-fix stage was omitted.

The neutral wedge exposed photographic material was again satisfactorily processed.

EXAMPLE 5.

A color negative tripack material as in example 1, was given a neutral wedge exposure and satisfactorily processed using a similar processing sequence to that of example 1 except that the wash bath between the stop-fix and the bleach-fix bath was replaced by another stop-fix bath having the same composition as the first stop-fix bath except that 300 mg. of selenourea was added to it. The bleach-fixing time was 6 minutes.

EXAMPLE 6.

A color negative tripack as in example 1 was given a neutral wedge exposure and satisfactorily processed by using a processing sequence similar to that described in example 1, except that instead of the stop-fix bath a stop bath of the following composition was used.

Sodium acetate	9.0 g.
Acetic acid (glacial)	5.2 ml.
Sodium metalsulfite	5.0 g.
Selenourea	300 mg.
Water	to 1 liter

The bleach-fix bath used in this test has a composition similar to that of the bleach-fix bath described in example 1, except that its sodium thiosulfate pentahydrate content was raised to 180 g.

The bleach-fixing time was 6 minutes.

EXAMPLE 7.

A sample of the same photographic material as used in example 1 was given a neutral wedge exposure and color processed using the same processing sequence and processing solutions as set forth in example 1 except that 100 mg. of selenourea were present in the bleach-fix bath. The bleach-fix time required was only 6 minutes and the material was found to be satisfactorily bleached in the high-exposure areas.

EXAMPLE 8.

A color negative tripack material as in example 1, was given a neutral wedge exposure and satisfactorily processed, the processing sequence being as in example 1 except for the bleach-fix stage, which was carried out by treating the material for 8 minutes in the following bath.

Bleach-Fix

Disodium tetraborate decahydrate	12.5 g.
Boric acid	22.5 g.
Sodium hydroxide	10.0 g.
Ethylenediaminetetraacetic acid	16.2 g.
Disodium salt of ethylenediamine-tetraacetic acid dihydrate	3.5 g.
Ferric chloride (60% W/V soln.)	15 ml.
Sodium thiosulfate pentahydrate	95.0 g.
Sodium sulfite anhydrous	4.0 g.
2-Selenouracil	0.50 g.
Water	to 1 liter
pH 7.0	

EXAMPLE 9.

A color negative tripack material as in example 1, was given a neutral wedge exposure and satisfactorily processed, the processing sequence being as in example 1, except for the bleach fix stage which was carried out for 6 minutes in a bath having the following composition.

Bleach-Fix

Disodium tetraborate decahydrate	12.5 g.
Boric acid	22.5 g.
Sodium hydroxide	10.0 g.
Ethylenediaminetetraacetic acid	16.2 g.
Disodium salt of ethylenediamine-tetraacetic acid dihydrate	3.5 g.
Ferric chloride (60% W/V soln.)	15 ml.
Sodium thiosulfatec pentahydrate	95.0 g.
Sodium sulfite anhydrous	4.0 g.
Potassium selenocyanate	5.0 g.
Water	to 1 liter
pH 7.1	

EXAMPLE 10.

A color negative tripack material was given a neutral wedge exposure and satisfactorily processed by a processing sequence similar to that given in example 1, but differing in the bleach-fix stage which was carried out by treating the photographic material for 6 minutes, in the following bath.

Bleach-Fix

Diaquo-tetrammine cobalt (III) sulfate monohydrate	30.0 g.
Sodium thiosulphate pentahydrate	140.0 g.
Selenourea	360 mg.
Water	to 1 liter

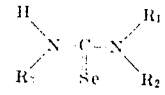
The same negative material was largely unbleached when processed for the same time in a similar bleach fix bath but from which the selenourea had been omitted.

Although the examples given are based on the results obtained for a typical color negative material, similar improvements are obtained when color reversal material is bleach-fixed with the exemplified compositions.

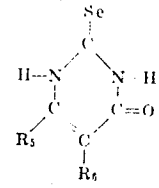
The pHs of the solutions quoted are not a limiting factor for the catalytic activity of the compounds disclosed, although soluble selenocyanates are unstable in acid solutions and tend to decompose with evolution of toxic gases.

We claim as our invention:

1. In a color development process for the production of a colored image in exposed color silver halide photographic material, after the development step, the step of treating the photographic material with an aqueous solution of a bleach-fix catalyst which is a water-soluble selenocyanate salt, a selenourea of the general formula:



wherein R_1, R_2 and R_3 are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom or a selenouracil of the general formula:



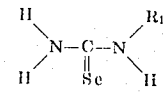
wherein one of R_5 and R_6 is a lower alkyl group and the other a hydrogen atom or both represent hydrogen atoms, and simultaneously or subsequently treating the photographic material in a bleach-fix bath which comprises an aqueous solution comprising an oxidizing agent which is either a ferric chelate or a diaquo-tetrammine-cobalt (III) complex, and a silver halide solvent which is either a water-soluble thiosulfate or a water-soluble thiocyanate.

2. A process according to claim 1 wherein the bleach-fix catalyst is present in the bleach-fix bath.

3. A process according to claim 1 wherein the bleach-fix catalyst is present in a stop bath or stop-fix bath which is used to treat the photographic material after development and prior to the bleach-fix step.

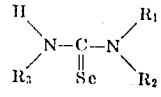
4. A process according to claim 1 wherein the bleach-fix catalyst is present in a wash bath wherein the photographic material is washed after development and prior to the bleach-fix step.

5. A process according to claim 1 wherein the bleach-fix catalyst is a selenourea of the general formula:

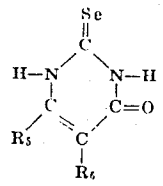


wherein R_1 is a lower alkyl group. either

6. A bleach-fix bath which comprises an aqueous solution of an oxidizing agent which is either a ferric chelate complex or a diaquo-tetrammine-cobalt (III) complex, a silver halide solvent which is either a water soluble thiosulfate or a water-soluble thiocyanate and a bleach-fix catalyst which is a water-soluble selenocyanate salt, a selenourea of the general formula:

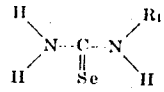


wherein R_1, R_2 and R_3 are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom or a selenouracil of the general formula:



wherein one of R_5 and R_6 is a lower alkyl group and the other a hydrogen atom or both represent hydrogen atoms.

7. A bleach-fix bath according to claim 6 wherein the bleach-fix catalyst is a selenourea of the general formula:



wherein R_1 is a lower alkyl group.

8. A bleach-fix bath according to claim 6 wherein the concentration of water-soluble selenocyanate salt therein is from 0.1 to 200 g. per liter of solution.

9. A bleach-fix bath according to claim 6 wherein the concentration of selenourea therein of the formula set forth in claim 6 or of selenouracil therein of the formula set forth in claim 6 is from 0.5 mg. to 1.5 g. per liter of the solution.

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