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PROCESS FOR INHIBITING THE BLEACHING OF PHOTOGRAPHIC SILVER IMAGES

Roland G. Willis and Herbert E. Wabnitz, Jr., Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

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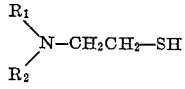
Int. Cl. G03c 5/32

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10 Claims

ABSTRACT OF THE DISCLOSURE

A photographic process for inhibiting the bleaching of photographically developed silver images such as silver sound track images which comprises treating such silver images with alkylaminoalkylenethiol bleach inhibitors such as those having the formula



wherein R_1 is an alkyl group or a cycloalkane group and R_2 is a hydrogen atom, a cycloalkane group or an alkyl group such that at least one of R_1 or R_2 has at least 3 carbon atoms and that the total number of carbon atoms in the bleach inhibitor molecule is 6 to 20 and preferably 8 to 16.

This invention relates to a process for treating photographically developed silver images with bleach inhibitors. In one aspect of the invention, silver sound track images on color photographic motion picture films are treated with a bleach inhibitor so that during the bleach processing step at least a portion of such sound track silver is retained.

Typical bleach inhibition processes for retaining sound silver on color film during color processing are described in Bevis et al. Ser. No. 100,608 and Bello et al. Ser. No. 100,609, both copending and filed Dec. 22, 1970, now U.S. Pats. 3,705,803 and 3,705,799, respectively.

It is an object of this invention to provide a new process for increasing the bleach resistance of photographically developed silver images.

It is another object of this invention to provide a new process for preparing silver sound tracks on color motion picture films.

These and other objects of the invention are accomplished with a photographic process which comprises treating a photographically developed silver image with an alkylaminoalkylenethiol bleach inhibitor and increasing the bleach resistance of such silver.

As used herein and in the appended claims, the term "bleach inhibitor" refers to an organic compound which, when dissolved in an aqueous solution at a concentration of 10^{-4} molar and mixed with an equal volume of a 0.05% w. aqueous gelatin solution containing a concentration of 3×10^{-3} molar silver metal particles of about 0.12 micron in diameter, which silver particles are prepared by contacting a silver nitrate solution with equal molar amounts of sodium citrate and ferrous sulfate (as described by Frens, "The Reversibility of Irreversible Colloids Ph. D. Thesis, University of Utrecht, Holland, 1968, page 27), inhibits bleaching for a minimum of 15 minutes when there is added to the mixture of silver particles

and bleach inhibitor one volume of the following bleach-fix bath:

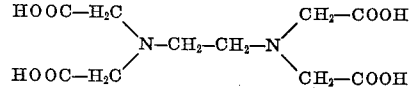
BLEACH-FIX BATH

NaFeEDTA* (13% Fe)	grams	6.0
Na_2SO_3	do	1.2
Na_4EDTA	gram	0.7
$(NH_4)_2S_2O_3$ (60% solution)	ml	20

Water to 1 liter.

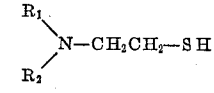
pH 6.68.

*EDTA—Ethylenediamine tetraacetic acid.



Bleach-fixing occurs when the mixture changes from dark brown to colorless. A control solution which contains no bleach inhibitor becomes colorless within four minutes.

A typical alkylaminoalkylenethiol bleach inhibitor of the type suitable for treating the silver in the sound track area of a motion picture film to lend bleach resistance to such silver has the formula



wherein R_1 is a hydrogen atom, a cycloalkane group or an alkyl group and R_2 is an alkyl group or a cycloalkane group (e.g., cyclohexyl), such that at least one of R_1 or R_2 is a group having at least 3 carbon atoms, the total number of carbon atoms in the bleach inhibitor molecule being 6 to 20, and preferably 8 to 16. In processing embodiments of the invention wherein the subject bleach inhibitor in solution is used to treat a motion picture film containing an overcoated auxiliary sound recording layer, such as described in the aforementioned copending Bello et al. application, the total number of carbon atoms in the bleach inhibitor molecule is preferably 9 to 16.

Typical bleach inhibitors suitable for use in the invention include:

2-(n-octylamino)ethanethiol,
2-(n-butylamino)ethanethiol,
2-(cyclohexylamino)ethanethiol,
2-(n-decylamino)ethanethiol, etc.

In accordance with one embodiment of the invention, an exposed film having a silver auxiliary image or sound track is selectively contacted subsequent to initial development, and prior to bleaching of the film with an alkylaminoalkylenethiol silver bleach inhibitor in the area of the auxiliary image or sound track.

We have found that when a developed silver image is contacted with an alkylaminoalkylene bleach inhibitor subsequent to initial development and prior to bleaching, the silver is rendered unbleachable (i.e., not solubilized but photographic processing compositions containing such bleaches as alkali metal or ammonium thiocyanates and ferric ethylenediamine tetraacetic acid). Therefore, when only the sound track portion of a film having a silver

sound record is contacted with a silver bleach inhibitor, this silver sound record is rendered unbleachable. The silver in the picture area of the film not having been contacted with the bleach inhibitor remains bleachable. A color film having been so treated will upon bleaching and fixing comprise a picture record of dye images and a sound track record of silver images. Our invention, therefore, provides a method for retaining image silver in the sound track area of the film during subsequent processing treatments to the entire film such as bleaching out silver in any filter layers that can be present and in the picture image area of the film.

For negative-positive print films such a method offers the advantage of a single treatment to the silver sound record. Unlike the redevelopment processes presently used in the art, the film does not have to be fixed before bleaching. Subsequent to initial development the silver sound track record is contacted with a solution containing a silver bleach inhibitor. The film is then bleached and fixed or bleach-fixed. A reversal film is black and white developed followed by selective fixing of only the sound track area. The film is then reversal color developed. At this time the silver sound track record is contacted with a solution containing a silver bleach inhibitor. The entire film is then bleached and fixed or bleach-fixed. The processed films then comprise a color picture record and a silver sound record.

If desired, for example, to aid in silver recovery, print films can be fixed prior to bleach-fixing since silver is more easily recovered from fix solutions than from present bleach-fixing solutions. If this procedure is used, it is preferred that the sound record be contacted with the bleach inhibitor subsequent to the fixing treatment.

The present invention, therefore, provides a convenient single step method for retaining a silver sound record in a color motion picture film during removal of the silver of the picture record. The method is particularly convenient since it involves merely contacting the film with a solution containing a silver bleach inhibitor. The contacting procedure is not dependent upon critical concentrations, times or temperatures.

The selective treatment of only the sound track portion of the film can be accomplished by any convenient method. For example, the edge bearing the sound image can be passed through a bath containing the bleach inhibitor. A method particularly useful because many motion picture photofinishers have the necessary equipment is passing the sound area of the film under a roller (called a striping wheel) wet with a solution containing a bleach inhibitor.

Also our process includes processing photographic elements having imagewise exposed picture areas and image wise exposed sound track areas or auxiliary images comprising a support having coated thereon, on one surface, in order from the support, at least one picture recording photographic image or color-forming unit comprising at least one silver halide emulsion layer and an auxiliary or sound track image recording radiation sensitive silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units which comprises the following steps, including steps (B) and (C) in either sequence: (A) developing an auxiliary image record in the sound track areas comprising silver, (B) developing a picture record in the picture areas comprising silver and a nondiffusible dye, (C) contacting the auxiliary layer with an alkylaminoalkylenethiol silver bleach inhibitor as described herein to adsorb said bleach inhibitor onto at least the silver of the auxiliary layer and (D) removing the bleachable silver images in the picture areas remaining after steps (B) and (C) and the residual or undeveloped silver halide. Photographic elements suitable for use in such processes are described in the aforementioned copending Bello et al. application.

Particularly useful photographic elements suitable for use in the process of the invention are those used for preparing multicolor motion picture films having a silver sound track and comprised of a film support having coated thereon, on one surface, in order (1) a plurality (generally three) picture recording photographic image or color-forming units, each unit comprising one or more (generally one or two) silver halide emulsion layers which are so disposed and sensitized that each unit is essentially sensitive to a different primary color region of the visible spectrum and (2) an auxiliary sound track image recording radiation sensitive silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units. The auxiliary layer preferably contains a substantially colorless nondiffusible compound (e.g., a photographic coupler) which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye and which decreases the rate of diffusion of a ballasted silver bleach inhibitor through the auxiliary layer.

The auxiliary superposed sound track recording layer acts in conjunction with the bleach inhibitor to prevent bleaching of the silver in the sound track area while permitting bleaching of developed silver in the picture area of the photographic element. This layer can be comprised simply of a silver halide emulsion. The silver halide content of this layer can vary widely such as from 10 milligrams per square foot or less to 150 milligrams per square foot or more. The quantity of silver halide present in this auxiliary layer will have an effect upon the turbidity of the element and the sharpness of the image when viewed. For best results, it is thereofore preferred that the auxiliary layer contain from about 10 milligrams per square foot to 100 milligrams per square foot silver halide, and preferably from about 15 milligrams per square foot to about 75 milligrams per square foot. Particularly useful results are obtained when the auxiliary layer contains from about 20 to 40 milligrams per square foot silver halide.

The grain size of the silver halide of the auxiliary layer can vary widely. For example, the average grain size can range from about 0.05 micron or less to about 0.5 micron or greater. Preferably, the grain size is as small as possible without requiring such high intensity exposure in the sound record area that the underlying picture recording layers in the sound area are overexposed causing a loss of definition of the sound record. An average grain size of from about 0.05 micron to about 0.2 micron is preferred.

The alkylaminoalkylenethiol silver bleach inhibitor used in the present process is adsorbed onto the silver of the sound record after initial development and before bleaching the silver by contacting the sound track area of the film or the entire film if an auxiliary sound track layer is used with a solvent solution containing the bleach inhibitor. The solvent for the bleach inhibitor can be any solvent which will dissolve, alone or with other solvents, the bleach inhibitor and is compatible with hydrophilic colloid emulsions and the aqueous processing of these elements. Typical solvents are predominantly water but can be, for example, lower alkyl alcohols such as methanol, ethanol, isopropyl alcohol, butanol and the like.

The bleach inhibitor composition can be comprised of simply one or more bleach inhibitors in concentrations ranging from as little as 10^{-5} molar or less to 10^{-1} molar or more. Preferably, the concentration of bleach inhibitor ranges from about 10^{-4} to about 10^{-2} molar. The concentration of bleach inhibitor in the treatment compositions can vary depending upon the particular bleach inhibitor. For example, the concentration of bleach inhibitor can vary depending upon the hydrophilic nature of the bleach inhibitor. We have found that higher concentrations of the more hydrophilic bleach inhibitors often yield better results. On the other hand, less hydrophilic bleach inhibitors, e.g., those containing more carbon atoms as longer chain alkyls, often yield satisfactory results at lower concentrations.

The bleach inhibitor composition, if predominantly an aqueous solution, can contain, in addition to the bleach inhibitor, other compounds such as water-miscible organic solvents to aid in dissolving the other ingredients of the composition. The composition can also contain one or more compounds to produce a desired pH or to act as a buffering agent. The concentration of these compounds is determined by the quantity needed to achieve the desired result.

The pH of the aqueous bleach inhibitor composition can vary widely from mildly acidic of about pH 5 to strongly alkaline from about pH 12 or greater. Preferably the pH of the solution is from about pH 6 to strongly alkaline and most preferably is from about pH 8 to about pH 12.5.

In addition to the bleach inhibitor, the aqueous bleach inhibitor composition can contain one or more water-soluble silver halide solvents or fixing agents such as ammonium, sodium or potassium sulfite, thiosulfate or thiocyanate or dithiooctandiol. The concentration of silver halide solvent can vary widely depending generally upon the particular bleach inhibitor used and the photographic element to which the composition is applied. The silver halide solvents can be present in concentrations ranging from as little as 0.05% w. or less of the composition to 5% w. or more of the composition. Preferably, the amount of silver halide solvent is from about 0.1% w. to about 2% w. of the solution.

The temperature at which the bleach inhibitor can be brought into contact with the photographic element can vary widely but preferably is approximately the same temperature as the remainder of the processing solutions. For example, photographic processing temperatures typically range from about 20° C. or less to 60° C. or higher. Temperatures of about 25° C., 40° C. and 50° C. are suitable in high speed processing procedures.

The time the bleach inhibitor is in contact with the silver sound record prior to being brought into contact with another processing solution can vary widely. It typically ranges from as little as 5 seconds or less to 10 minutes or more. Preferably, the film is contacted with bleach inhibitor for about 30 seconds to about 5 minutes. The contact time for optimum results also can depend upon the hydrophilic nature of the bleach inhibitor and its rate of diffusion through the sound track layer.

The method of the invention is generally applicable to the production of sound track images in color films of any type in which dye images are formed or retained as a function of a developed latent silver halide image. Films of this type include those containing incorporated photographic couplers, a nondiffusible dye image being formed by reaction of a nondiffusible incorporated coupler with oxidized color developing agent resulting from development of the latent silver halide image. Also included are those not containing incorporated couplers such as disclosed in Mannes et al. U.S. Pat. 2,252,718, the latent silver halide image being developed with a coupler-developer composition and the nondiffusible dye image being formed from the reaction of the oxidized color developing agent and the coupler present in the coupler-developer composition. These films can be reversal print films or negative-positive print films. In one embodiment of the invention, an auxiliary light-sensitive silver halide sound track layer is coated over the color film as described above. Such color films preferably have three color forming units comprising silver halide emulsions capable of recording red, green or blue light. Phenolic or naphtholic couplers, 5-pyrazolone couplers and open-chain ketomethylene couplers that react with oxidized aromatic primary amine color developing agent to form cyan, magenta and yellow dye respectively are more generally used in concert with such red, green and blue light recording layers respectively.

The terms "picture record area" and "sound record area" and obviously analogous terms as used herein refer to areas of a motion picture film as these areas can be seen in a plane view. Along one or both edges of the film are sprocket perforations used to transport the film through motion picture printing and projecting apparatus. Occupying the major part of the area between the sprocket perforations or the perforations and the opposite edge and are the individual frames containing the picture record. A narrow strip extending lengthwise along the film contains the sound record. These two areas are referred to as the picture record area and the sound record area, respectively.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A multilayer color photographic motion picture negative-positive print film with a picture record area and a sound track record area and bearing on a transparent cellulose acetate film support three gelatino silver halide color-forming units sensitive to the blue, green and red regions of the visible spectrum and containing nondiffusible photographic couplers capable of forming nondiffusible yellow, magenta and cyan dye images when reacted with aromatic primary amino color developing agents, respectively, and outermost from the support an auxiliary gelatino silver halide (unsensitized) layer containing 25 mg./ft.^{2} silver as silver chlorobromide (having 80% molar chloride and 20% molar bromide) of about 0.1 micron average grain size and 45 mg./ft.^{2} magenta coupler 1 - (6-chloro-2,4-dimethylphenyl)-2-[α-(m-pentadecylphenoxy)-butyramido]-5-pyrazolone (U.S. Pat. 3,062,-653 at lines 10 to 20, column 4) is exposed for 1/25 second through a Wratten 18–A filter (transmits radiation of 300 to 400 nm.) to a step tablet in the sound track area, and for 1/100 second through a filter pack which results in a nearly neutral density exposure to a 21 step 0.15 Log E increment step tablet in the picture area and processed in the following baths:

(1) Prebath	sec.	10
(2) Wash	sec.	10
(3) Color developer	sec.	90
(4) Wash	sec.	10
(5) Stop bath	sec.	60
(6) Wash	sec.	30
(7) Bleach inhibitor bath	sec.	60
(8) Wash	sec.	15
(9) Bleach-fix	sec.	60
(10) Wash	sec.	60
(11) Stabilizer	sec.	10
Process temperature	° C.	38

The chemical composition of the processing baths is as follows:

(1) PREBATH

Borax ($Na_2B_4O_7 \cdot 10H_2O$)	g.	20
Sodium sulfate, desiccated	g.	100
Sodium hydroxide, 10% solution	ml.	10

Water to make 1 liter (pH 9.3).

(3) COLOR DEVELOPER

	G.
Sodium hexametaphosphate	2
Sodium sulfite, desiccated	4
2-amino-5-diethylamino-toluenemonohydrochloride	3
Sodium carbonate, monohydrate	20
Potassium bromide	2

Water to make 1 liter (pH 10.65).

(5) STOP BATH

Acetic acid, glacial	ml.	24.5
Sodium bisulfite	g.	6.4

Water to make 1 liter (pH 3.76).

(7) BLEACH INHIBITOR BATH (BATH A)

Trisodium phosphate ---------- g--	19.1
2-(n-octylamino)ethanethiol ---------- ml--	1.0
Water to make 1 liter.	
pH adjusted to 12.1.	

(9) BLEACH-FIX BATH

Hydrochloric acid, conc. ---------- ml--	9.2
Sodium sulfite ---------- g--	12
Ammonium iron EDTA (1.56 molar solution) -ml--	92
Ammonium thiosulfate (60% solution ------ml--	200
Water to make 1 liter (pH 6.).	

(11) STABILIZER

	Ml.
Formaldehyde (37% w. solution) ----------	20
Octylphenoxypolyethoxyethanol ----------	0.6
Water to make 1 liter.	

The bleach inhibitor bath is applied to the entire element. The silver density of the sound track record area after processing as measured at 900 nm. on a densitometer had a density of about 2.5 in the tenth step. The picture record area silver density is measured in a similar manner at the tenth step of the step exposure had a density of about 0.04.

EXAMPLE 2

A photographic element as described in Example 1 is exposed and processed as described in Example 1 except 1 ml. of 2-(cyclohexylamino)ethanethiol is substituted for the 2-(n-octylamino)ethanethiol in the Bleach Inhibitor Bath and the bleach inhibiting time wa-s 20 seconds. After processing, the silver density at the tenth step in the sound track record area was about 1.6 and the silver density at the tenth step in the picture record area was about 0.04.

EXAMPLE 3

Strips of a multilayer color photographic motion picture negative-positive print film with a picture record area and a sound track record area and bearing three gelatino silver halide color forming units sensitive to the blue, green and red regions of the visible spectrum and having nondiffusible photographic couplers capable of forming nondiffusible yellow, magneta and cyan dye images when reacted with aromatic primary amino color developing agents, respectively, are sensitometrically exposed in both picture and sound areas as in Example 1 and processed as follows:

(1) Prebath ----------	15 sec.
(2) Wash ----------	Do.
(3) Color develop ----------	9 min.
(4) Stop bath ----------	2 min.
(5) Wash ----------	1 min.
(6) Remove surface water ----------	Air blast.
(7) Bleach inhibitor application ----------	40 sec.
(8) Bleach-fix ----------	2 min.
(9) Wash ----------	6 min.
(10) Stabilize ----------	10 sec.
(11) Dry.	
Process temperature ----------	24° C.

The chemical composition of the above baths is as follows:

(1) PREBATH

Borax ($Na_2B_4O_7 \cdot 10H_2O$) ----------g--	20
Sodium sulfate, desiccated ----------g--	100
Sodium hydroxide, 10% solution ----------ml--	10
Water to make 1 liter.	

(3) COLOR DEVELOPING COMPOSITION

	G.
Sodium hexametaphosphate ----------	2
Sodium sulfite, desiccated ----------	4
2-amino-5-diethylaminotoluene, monohydrochloride -	3
Sodium carbonate, monohydrated ----------	20
Potassium bromide ----------	2
Water to make 1 liter.	

(4) STOP BATH

Acetic acid, glacial ----------ml--	24.5
Sodium bisulfite ----------g--	6.4
Water to make 1 liter (pH 3.76).	

(7) BLEACH INHIBITOR BATH

"Gantrez" AN 169 (a copolymer of maleic anhydride and methyl vinyl ether sold by GAF Corporation) ----------	5 g.
Trisodium phosphate, dodecahydrate ----------	19 g.
Bleach inhibitor ----------	As indicated below.
Water ----------	To make 1 liter.
pH ----------	Adjusted to 12.1.

(8) BLEACH-FIX BATH

Hydrochloric acid, conc. ----------ml--	9.2
Sodium sulfite ----------g--	12
Ammonium iron salt of ethylenediamine tetraacetic acid (1.56 molar solution) ----------ml--	92
Ammonium thiosulfate (60% solution) ------ml--	200
Water to make 1 liter.	

(10) STABILIZING BATH

	Ml.
Formaldehyde (37% w. solution) ----------	20
Octylphenoxy polyethoxy ethanol ----------	9.6
Water to make 1 liter.	

The bleach inhibitor bath is applied to the sound track area of the film only for a period of 2 minutes.

The following bleach inhibitors can be individually utilized in the Bleach Inhibitor Bath at a concentration of 5 grams per liter to inhibit the bleaching of silver in the sound track record area during the Bleach-Fix Bath (processing step 8) to retain at least 75% of the sound track silver:

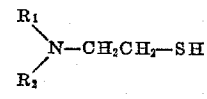
(a) 2-(cyclohexylamino)ethanethiol
(b) 2-(n-octylamino)ethanethiol
(c) 2-(n-butylamino)ethanethiol
(d) 2-(n-decylamino)ethanethiol

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

We claim:

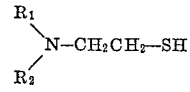
1. In a photographic process which comprises treating a photographically developed silver image with a bleach inhibitor and increasing the bleach resistance of said silver, the improvement wherein said bleach inhibitor is an alkylaminoalkylenethiol; said alkylaminoalkylenethiol containing from 6 to 20 carbon atoms and having at least one alkyl group containing at least 3 carbon atoms.

2. In a photographic process which comprises treating a photographically developed silver image with a bleach inhibitor and increasing the bleach resistance of said silver, the improvement wherein said bleach inhibitor has the formula:



wherein R_1 is an alkyl group or a cycloalkane group and R_2 is a hydrogen atom, a cycloalkane group or an alkyl group, such that at least one of R_1 or R_2 has at least 3 carbon atoms and the total number of carbon atoms in said bleach inhibitor is 6 to 20.

3. In the process of producing a picture record and a silver sound track record in an exposed photographic element having at least one silver halide emulsion layer which comprises developing said exposed element to form a picture record comprising silver and dye and a sound track record comprising silver, and bleaching and fixing the element to remove the silver of said picture record, selectively contacting said sound track record prior to bleaching with a silver bleach inhibitor which retains at least a portion of the silver of said sound track record during said bleaching, the improvement which comprises using a bleach inhibitor having the formula:



wherein R_1 is an alkyl group or a cyclohexyl group, and R_2 is a hydrogen atom or an alkyl group, such that at least one of R_1 or R_2 has at least 3 carbon atoms and the total number of carbon atoms in said bleach inhibitor is 6 to 20.

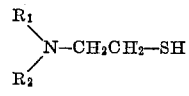
4. In the process of producing a color picture record and a silver sound track record on an exposed photographic element having a plurality of superposed, differently sensitized silver halide layers which comprises developing said exposed element to form a picture record comprising silver and dye and a sound track record comprising silver, bleaching and fixing the element to remove the silver of the picture record; the improvement which comprises selectively contacting the silver image of the sound track record prior to bleaching with an aqueous bleach inhibitor composition comprising 2-(n-octylamino) ethanethiol.

5. In the process of producing a color picture record and a silver sound track record on an exposed photographic element having a plurality of superposed, differently sensitized silver halide layers which comprises developing said exposed element to form a picture record comprising silver and dye and a sound track record comprising silver, bleaching and fixing the element to remove the silver of the picture record; the improvement which comprises selectively contacting the silver image of the sound track record prior to bleaching with an aqueous bleach inhibitor composition comprising 2-(n-butylamino) ethanethiol.

6. In the process of producing a color picture record and a silver sound track record on an exposed photographic element having a plurality of superposed, differently sensitized silver halide layers which comprises developing said exposed element to form a picture record comprising silver and dye and a sound track record comprising silver, bleaching and fixing the element to remove the silver of the picture record; the improvement which comprises selectively contacting the silver image of the sound track record prior to bleaching with an aqueous bleach inhibitor composition comprising 2-(cyclohexylamino)ethanethiol.

7. In the process of producing a color picture record and a silver sound track record on an exposed photographic element having a plurality of superposed, differently sensitized silver halide layers which comprises developing said exposed element to form a picture record comprising silver and dye and a sound track record comprising silver, bleaching and fixing the element to remove the silver of the picture record; the improvement which comprises selectively contacting the silver image of the sound track record prior to bleaching with an aqueous bleach inhibitor composition comprising 2-(n-decylamino)ethanethiol.

8. In the process of producing a picture record and a silver sound track record in an imagewise exposed photographic element comprising a support having coated on one side of said support in order, (1) a picture recording photographic image-forming unit comprising at least one silver halide emulsion layer and (2) a sound track image recording radiation sensitive silver halide emulsion layer, said picture recording unit being capable of recording imagewise exposure without exposing said sound track image recording layer, including steps (B) and (C) in either sequence: (A) developing a sound track record comprising silver, (B) developing a picture record in the picture areas comprising silver and a nondiffusible dye, (C) contacting said sound track layer with a silver bleach inhibitor to adsorb said bleach inhibitor onto the silver of said sound track layer and (D) removing the bleachable silver images in the picture areas remaining after steps (B) and (C) and the residual silver halide; the improvement which comprises using a bleach inhibitor having the formula:



wherein R_1 is an alkyl group or a cyclohexyl group and R_2 is a hydrogen atom or an alkyl group, such that at least one of R_1 or R_2 has at least 3 carbon atoms and the total number of carbon atoms in said bleach inhibitor is 8–16.

9. In the process of producing a picture record and a silver sound track record in a photographic element having imagewise exposed picture areas and imagewise exposed sound track areas comprising a transparent support having coated on one side of said support in order, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer which contains at least one photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye and (2) an auxiliary sound recording radiation sensitive silver halide emulsion layer, said picture recording unit being capable of recording imagewise exposure without exposing said auxiliary layer, said auxiliary layer containing a colorless nondiffusible compound which reacts with oxidized aromatic primary amine color developing agent which comprises the following steps, including steps (B) and (C) in either sequence: (A) developing a sound track record in the sound track areas comprising silver, (B) developing a picture record in the picture areas comprising silver and a nondiffusible dye, (C) contacting said auxiliary layer with a silver bleach inhibitor to adsorb said bleach inhibitor onto at least the silver of the auxiliary layer and (D) removing the bleachable silver images in the picture areas remaining after steps (B) and (C) and the residual silver halide; the improvement which comprises using as said bleach inhibitor 2-(n-octylamino)ethanethiol.

10. In the process of producing a picture record and a silver sound track record in a photographic element having imagewise exposed picture areas and imagewise exposed sound track areas comprising a transparent support having coated on one side of said support in order, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer which contains at least one photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye and (2) an auxiliary sound recording radiation sensitive silver halide emulsion layer, said picture recording unit being capable of recording imagewise exposure without exposing said auxiliary layer, said auxiliary layer containing a colorless nondiffusible compound which reacts with oxidized aromatic primary amine color developing agent which comprises the following steps, including steps (B) and (C) in

either sequence: (A) developing a sound track record in the sound track areas comprising silver, (B) developing a picture record in the picture areas comprising silver and a nondiffusible dye, (C) contacting said auxiliary layer with a silver bleach inhibitor to adsorb said bleach inhibitor onto at least the silver of the auxiliary layer and (D) removing the bleachable silver images in the picture areas remaining after steps (B) and (C) and the residual silver halide; the improvement which comprises using as said bleach inhibitor 2-(cyclohexylamino)ethanethiol.

References Cited

UNITED STATES PATENTS

3,243,295 3/1966 Vogt ---------- 96—4

NORMAN G. TORCHIN, Primary Examiner

R. L. SCHILLING, Assistant Examiner

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96—60

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,749,572 Dated July 31, 1973

Inventor(s) Roland G. Willis and Herbert E. Wabnitz, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 14, "6." should read ---6.5---;

Column 7, line 35, "wa-s" should read ---was---.

Signed and sealed this 27th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents