United States Patent Office 3,705,800 Patented Dec. 12, 1972

3,705,800

NOVEL PHOTOGRAPHIC PROCESSING COMPOSITIONS AND IMPROVED PROCESSING USING SUCH COMPOSITIONS FOR PREPARING SILVER SOUND TRACKS

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No Drawing. Continuation-in-part of abandoned application Ser. No. 100,769, Dec. 22, 1970. This application Dec. 17, 1971, Ser. No. 209,404

Int. Cl. G03c 7/24, 5/44

U.S. Cl. 96—4 18 Claims

ABSTRACT OF THE DISCLOSURE

Improved photographic processing compositions for preparing silver sound tracks are provided which contain a silver bleach inhibitor and a diffusible onium salt. Also provided is an improved process for producing a silver sound track in an exposed photographic element having at least one silver halide emulsion layer which comprises developing the exposed element to form a picture record comprising silver and dye and a sound record comprising silver and bleaching and fixing the element to remove the silver of the picture record which improvement comprises selectively contacting the sound track record prior to bleaching with a mixture of a silver bleach inhibitor and a diffusible onium salt to retain at least a portion of the silver of the silver sound track during the bleaching.

This application is a continuation-in-part of my copending U.S. patent application Ser. No. 100,769 filed Dec. 22, 1970 and now abandoned.

This invention relates to photographic processes and more particularly to an improvement in the process of developing color film with a silver sound record.

A serious problem in providing color films with a silver sound track resides in preventing loss of density of the sound track during processing during the bleaching of the silver in the picture areas or of filter antihalation layers containing silver.

Previous methods of retaining the silver of the sound image have included (1) redeveloping the sound image only with a viscous developer after bleaching the film, (2) bleaching only the picture image area, (3) converting the silver of the image area to silver sulfide and (4) protecting the sound track with an adhesive tape or varnish. All of these approaches to the problem entail certain disadvantages such as critical concentrations of reactants, a number of treatments to one area only of the film, or the use of silver sulfide which has less absorbance of infrared radiation than silver, whereas most photocells in sound projectors are highly sensitive to infrared radiation.

It has been found that when a developed silver image is contacted with a silver bleach inhibitor subsequent to initial devolpment and prior to bleaching, the silver is rendered unbleachable. 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. This method is disclosed and claimed in copending application Bevis, Bello and Holtz, entitled Process for Preparing Color Film With Silver Sound Record Using Bleach Inhibitor, Ser. No. 100,608, filed Dec. 22, 1970, and the continuation-in-part thereof filed concurrently herewith.

It has also been found that when the sound track portion of the film is contacted with a quaternary ammonium salt subsequent to initial development and prior to color development and/or bleaching, the silver formed in the sound image portion of the film is rendered unbleachable.

This method is disclosed in Vogt U.S. Patent 3,243,295, issued Mar. 29, 1966.

However, when the silver images are bleached with very strong highly active bleaching solutions, the silver sound image protected by the above compounds is less than completely resistant to being bleached. It therefore appears desirable to provide an improved method for retaining the silver of the sound image during bleaching and fixing of color photographic elements having such sound images.

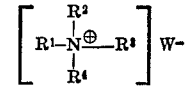
Accordingly, it is an object of my invention to provide an improved process of retaining silver sound images in color film as well as novel processing compositions for carrying out this process.

I have discovered that a substantial loss of density of the silver sound image during bleaching of photographic elements having such silver sound images can be prevented by selectively contacting the silver sound image subsequent to initial development and prior to bleaching with a mixture of a silver bleach inhibitor and a diffusible onium compound. The results obtained by the use of the mixture of the silver bleach inhibitor and the diffusible onium compound are well in excess of that obtained by the use of either compound alone. In other words, the results obtained by the use of the mixture are synergistic.

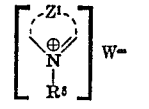
The process of the invention includes a treatment of just the sound track portion of the film to selectively retain the silver sound image in the sound track portion of the film.

A wide variety of diffusible onium compounds can be utilized in the present invention. Such onium compounds, that is, compounds that contain an organic cation, are diffusible in the hydrophilic organic colloids comprising photographic elements in the presence of alkaline processing compositions. Such onium compounds are typically quaternary ammonium compounds, quaternary phosphonium compounds or tertiary sulfonium compounds. The onium compounds can be used as hydroxides or as other types of salts such as halides. Typical suitable quaternary ammonium compounds have the formulas:

I.

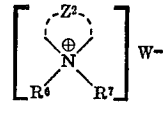


II.



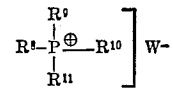
and

III.



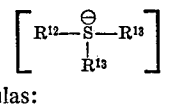
Typical suitable phosphonium compounds have the formula:

VI.



Typical suitable tertiary sulphonium compounds have the formula:

V.



In the above formulas:

R^1 to R^{14} are each organic radicals such as alkyl radicals having from 1 to 24 carbon atoms including

substituted alkyl radicals such as aralkyl radicals, or aryl radicals including substituted aryl radicals such as tolyl, phenyl and the like;

W^- is an anion including hydroxyl or an anion derived from an acid such as bromide, chloride, p-toluene sulfonate perchlorate or the like; and

Z^1 and Z^2 each represents the non-metallic atoms necessary to complete a heterocyclic ring generally having from 5 to 10 and preferably from 5 to 6 atoms in the heterocyclic nucleus such as carbon, nitrogen, oxygen, selenium and sulfur atoms to form such heterocyclic rings as pyridine, quinoline, benzoquinoline, oxazole, benzoxazole, selenazole, benzoselenazole, thiazole, benzothiazole, piperidine, naphthothiazole, imidazole, benzimidazole, naphthimidazole, naphthoxazole, naphthoselenazole, isoquinoline, pyrrole, pyrrolidine and the like, such heterocyclic rings being suitably substituted with such substituents as halogens, lower alkyl radicals and halo-lower alkyl radicals. A particularly useful class of onium compounds are the tetraalkyl quaternary ammonium compounds of Formula I wherein at least one of the alkyl groups is a straight chain radical composed of carbon and hydrogen containing from 12 to 18 carbon atoms and wherein X represents a halide.

Typical onium compounds and other materials that can be utilized in the present invention are listed below.

(I) Hexadecyltrimethyl ammonium bromide
(II) Trimethyllauryl ammonium chloride
(III) Trimethyl tall oil fatty ammonium chloride [1]
(IV) Trioctylpropyl ammonium bromide
(V) Tetrapentyl ammonium iodide
(VI) (2-chloroethyl)trimethyl ammonium chloride
(VII) Tetramethyl ammonium bromide
(VIII) Ethyltrimethyl ammonium iodide
(IX) Trimethyl coco ammonium chloride [2]
(X) Dodecyltrimethyl ammonium chloride
(XI) Trimethylphenyl ammonium chloride
(XII) Octadecyltrimethyl ammonium chloride
(XIII) Tetrahexyl ammonium iodide
(XIV) Dodecyltrimethyl ammonium sulfate
(XV) Dodecyltrimethyl ammonium phosphate
(XVI) 1-benzyl-2-picolinium bromide
(XVII) 1-(3-bromopropyl)-2-picolinium-p-toluenesulfonate
(XVIII) 1-phenethyl-2-picolinium bromide
(XIX) 1-γ-phenylpropyl-2-picolinium bromide
(XX) 2,4-dimethyl-1-phenethylpyridinium bromide
(XXI) 2,6-dimethyl-1-phenethylpyridinium bromide
(XXII) 5-ethyl-2-methyl-1-phenethylpyridinium bromide
(XXIII) α-Picoline-β-naphthoylmethyl bromide
(XXIV) 1-β-phenylcarbamoyloxyethyl-2-picolinium bromide
(XXV) Anhydro-1-(4-sulfobutyl)-2-picolinium bromide
(XXVI) 2-ethyl-1-phenethylpyridinium bromide
(XXVII) 1-[3-(N-pyridinium bromide)-propyl]-2-picolinium-2-toluenesulfonate
(XXVIII) 1-methyl-2-picolinium-p-toluenesulfonate
(XXIX) 1-phenethyl-2,4,6-trimethylpyridinium bromide
(XXX) 1-phenethyl-4-n-propylpyridinium bromide
(XXXI) 4-γ-hydroxypropyl-1-phenethylpyridinium bromide
(XXXII) 1-n-heptyl-2-picolinium bromide
(XXXIII) 2-isopropyl-1-phenethylpyridinium bromide
(XXXIV) Tetraphenylammonium bromide
(XXXV) Tetraethylammonium bromide
(XXXVI) N-ethylpyridinium bromide
(XXXVII) N,N-diethylpiperidinium bromide
(XXXVIII) Ethylene-bis-pyridinium bromide
(XXXIX) 1-phenethyl-3-picolinium bromide
(XL) Polyethylene oxide bis-pyridinium perchlorate
(XLI) 3-methyl-2-ethylisoquinolium bromide
(XLII) 3-methylisoquinolinium methyl-p-toluenesulfonate
(XLIII) 1-ethyl-2-methyl-3-phenethylbenzimidazolium bromide
(XLIV) 5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfobutyl)-benzimidazolium betaine
(XLV) Lauryldimethylsulfonium-p-toluenesulfonate
(XLVI) Nonyldimethylsulfonium-p-toluenesulfonate
(XLVII) Octadimethylsulfonium-p-toluenesulfonate
(XLVIII) Butyldimethylsulfonium bromide
(XLIX) Triethylsulfonium bromide
(L) Dodecyldimethylsulfonium-p-toluenesulfonate
(LI) Decyldimethylsulfonium-p-toluenesulfonate
(LII) Phenyldimethylsulfonium bromide
(LIII) Phenethyldimethylsulfonium bromide
(LIV) Tetraethylphosphonium bromide
(LV) Ethylene-bis-oxymethyltriethylphosphonium bromide
(LVI) Tetraphenylphosphonium bromide
(LVII) Phenethyltrimethylphosphonium bromide

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:

NaFeEDTA [1] (13% Fe)	g.. 6.0
Na_2SO_3	g.. 1.2
Na_4EDTA	g.. 0.7
$(NH_4)_2S_2O_3$ (60% solution)	ml.. 20

Water to 1 liter.
pH 6.68.

[1] 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.

We have found that organic compounds which exhibit particular utility as bleach inhibitors as defined above are thiol- and selenol-containing compounds such as mercapto- and selenol-substituted alkanoic acids, especially 2-mercapto-alkanoic acids, thiol- and selenol-substituted aryls, such as thiophenols and thionaphthols, thiol- and selenol-substituted heterocyclic compounds containing 5 to 6 atoms in the hetero ring, said ring containing at least one nitrogen atom such as mercaptobenzoxazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotriazoles, 1-phenyl-5-mercaptotetrazoles and mercaptoquinolines, thiocarboxylic acids and esters thereof such as thiobenzoic acid and xanthates such as potassium octyl xanthate.

In a preferred embodiment of our invention, the term "bleach inhibitor" refers to a compound of the following general formulae:

(VI) $R_a^{15}(A^{15})XR^{19}$

(VII) $R_a^{16}(A^{16})X—X(A^{17})R_a^{17}$

and

(VIII) $R_a^{18}(A^{18})X^{\ominus}Y^{\oplus}$

wherein:

a represents 0, 1, 2, 3, 4, 5 or 6;

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X represents a member selected from the group consisting of sulfur and selenium;

R^{15}, R^{16}, R^{17} and R^{18} each represents a member selected from the group consisting of nitro; halo (e.g., chloro, bromo, fluoro, iodo); an alkyl group including substituted alkyl having from 1 to 22 carbon atoms, preferably having 1 to 16 carbon atoms such as alkyl (e.g., methyl, ethyl, propyl, cyclopropyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, pentyl, iso-amyl, tert-amyl, cyclopentyl, hexyl, cyclohexyl, cyclohexadiene, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl and the like), haloalkyl (e.g., fluoroalkyl, chloroalkyl, bromoalkyl, as for example, chlorooctyl, bromododecyl, fluorotetradecyl and the like), sulfoalkyl (e.g., sulfohexyl, sulfooctyl, sulfododecyl and the like), sulfatoalkyl (e.g., sulfatodecyl, sulfatotetradecyl and the like), alkylsulfonylalkyl (e.g., ethylsulfonylbutyl and the like), cyanoalkyl (e.g., cyanohexyl, cyanooctyl, cyanodecyl and the like), carboxyalkyl (e.g., carboxyhexyl, carboxydecyl, carboxyhexadecyl and the like), alkoxyalkyl (e.g., octoxyhexyl, butoxyhexyl, ethoxydecyl and the like), aryloxyalkyl (e.g., phenoxymethyl, phenoxyethyl and the like), alkoxyaralkyl (e.g., methoxyphenylmethyl, butoxyphenylhexyl and the like), acyloxyalkyl (e.g., benzoyloxyhexyl, acetoxybutyl and the like), alkoxycarbonylalkyl (e.g., butoxycarbonylhexyl and the like), aryloxycarbonylalkyl (e.g., phenoxycarbonylethyl, chlorophenoxycarbonylbutyl and the like), alkylamidoalkyl (e.g., hexanamidobutyl, octanamidopropyl and the like), arylamidoalkyl (e.g., phenylamidoethyl, methylphenylamidobutyl and the like) and the like; an aryl group including naphthyl and other fused ring aromatics and substituted aryl such as aryl (e.g., phenyl, naphthyl, anthracenyl, phenanthrenyl and the like), haloaryl (e.g., chlorophenyl, trichlorophenyl, dibromophenyl, fluorophenyl, chlorotolyl and the like), sulfoaryl (e.g., sulfophenyl and the like), sulfatoaryl (e.g., sulfatophenyl and the like), nitroaryl (e.g., nitrophenyl, dinitrophenyl and the like), cyanoaryl (e.g., cyanophenyl, cyanonaphthyl and the like), carboxyaryl (e.g., carboxyphenyl, dicarboxyphenyl and the like), alkaryl (e.g., tolyl, butylphenyl, decylphenyl, diethylphenyl, trifluoromethylphenyl and the like), aralkaryl (e.g., benzylphenyl, naphthylmethylphenyl and the like), alkoxyaryl (e.g., octoxyphenyl, methoxyphenyl and the like), aryloxyaryl (e.g., phenoxyphenyl, phenoxynaphthyl and the like), acyloxyaryl (e.g., benzoyloxyphenyl, acetyloxyphenyl and the like), alkoxycarbonylarlyl (e.g., ethoxycarbonylphenyl and the like), aryloxycarbonylaryl (e.g., phenoxycarbonylphenyl, methylphenoxycarbonylnaphthyl and the like), alkylamidoaryl (e.g., acetamidophenyl, amylamidophenyl, di-t-amylamidophenyl, hexanamidophenyl, heptanamidophenyl, octanamidophenyl, nonanamidophenyl, decanamidophenyl, undecanamidophenyl, dodecanamidophenyl, tridecanamidophenyl, tetradecanamidoaryl, pentadecanamidophenyl, heptafluorobutanamidophenyl, carboxycyclopentanacetamidophenyl and the like), cycloalkyliminosulfonylaryl (e.g., piperidinylsulfonylphenyl, acetidinylsulfonylphenyl, pyrrolidinylsulfonylphenyl, indolinylsulfonylphenyl and the like) and the like; a thio group containing 3 to 22 carbon atoms such as alkylthio (e.g., propylthio, hexylthio, octylthio, dodecylthio and the like), carboxyalkylthio (e.g., carboxybutylthio, carboxyhexylthio and the like), arylthio (e.g., phenylthio, naphthylthio, methylphenylthio and the like), alkylcarbonylalkylthio (e.g., methylcarbonylethylthio, butylcarbonylpropylthio and the like), alkylcarbonylarylthio (e.g., methylcarbonylphenylthio, hexylcarbonyltolylthio, benzylcarbonylphenylthio and the like), arylcarbonylarylthio (e.g., phenylcarbonylphenylthio and the like), arylcarbonylalkylthio (e.g., phenylcarbonylmethylthio and the like) and the like; an amido group containing from 4 to 22 carbon atoms such as alkylamido (e.g., hexanamido, heptanamido, octanamido, decanamido, heptafluorobutanamido and the like), arylamido (e.g., benzylamido and the like), alkarylamido (e.g., methylbenzylamido, butylbenzylamido, hexylbenzylamido, decylbenzylamido and the like), aralkylamido (e.g., phenacetamido, phenbutanamido, tolylhexanamido and the like), aryloxyalkylamido (e.g., phenoxyacetamido, naphthoxyacetamido, di-t-amylphenoxyacetamido and the like) and the like; a carbonyl group such as alkylcarbonyl (e.g., butylcarbonyl, heptylcarbonyl and the like), arylcarbonyl (e.g., phenylcarbonyl, naphthylcarbonyl and the like), alkoxycarbonyl (e.g., ethoxycarbonyl, butoxycarbonyl and the like), aryloxycarbonyl (e.g., phenoxycarbonyl, naphthoxycarbonyl and the like) and the like; a carbamoyl group such as alkylcarbamoyl (e.g., butylcarbamoyl, hexylcarbamoyl and the like), arylcarbamoyl (e.g., phenylcarbamoyl, naphthylcarbamoyl and the like) and the like; alkoxy (e.g., ethoxy, butoxy, octoxy, benzoxy and the like), and aryloxy (e.g., phenoxy, toluoxy and the like);

R^{19} represents a member selected from the group consisting of hydrogen and an acyl group having from 1 to 22 carbon atoms including aryloyl and alkanoyl groups (e.g., benzoyl, acetyl, propanoyl, benzothioyl, acetothioyl and the like);

$Y^{\oplus}$ represents a basic cation such as an alkali metal ion like sodium and potassium, ammonium and the like;

A^{15}, A^{16}, A^{17} and A^{18} each represents a member selected from the group consisting of a carbonyl group (>C=O); a thiocarbonyl group (>C=S); a carboxymethylene group (>CH—COOH); a carbocyclic ring containing 3 to 6 carbon atoms which can be part of a fused ring structure such as cycloalkylene (e.g., cyclopropylene, cyclobutylene, cyclopentylene and cyclohexylene), cycloalkenylene (e.g., cyclopropenylene, cyclobutenylene, cyclopentenylene, cyclopentadienylene, cyclohexenylene and cyclohexadienylene) and arylene (e.g., phenylene, naphthylene, anthrylene and the like); a 3 to 6 membered heterocyclic ring containing at least one carbon atom and from 1 to 5 atoms selected from the group consisting of nitrogen, oxygen, sulfur and selenium which ring can have other carbocyclic and heterocyclic rings fused to it such as oxirenyl, furanyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, oxazolyl, benzoxazolyl, isoxazolyl, benzisoxazolyl, oxadiazolyl, benzoxadiazolyl, 1,2-pyranyl, 1,4-pyranyl, 2(H)benzopyranyl, 4(H)benzopyranyl, dioxolyl, methylenedioxybenzene, 1,2-oxazinyl, 1,3-oxazinyl, 1,4-oxazinyl, morpholinyl, 1,3-oxathianyl, 1,4-oxathianyl, 1,2-dioxanyl, 1,3-dioxanyl, 1,4-dioxanyl, dioxanenyl, dioxadienyl, diazetyl, pyrrolyl, indolyl, isoindolyl, carbazolyl, pyrrocolinyl, acridinyl, phenanthridinyl, 2-imidazolinyl, 3-imidazolinyl, 4-imidazolinyl, pyridyl, pyridazinyl, cinnolinyl, phthalazinyl, quinoxalinyl, pyrimidinyl, pyrazolo-[3,4-d]pyrimidinyl, hypoxanthinyl, benzopyrimidinyl, pyrazinyl, quinoxalinyl, phthalazinyl, quinolinyl, isoquinolinyl, phenazinyl, phenoxazinyl, phenothiazinyl, purinyl, pteridinyl, 1,3,5-triazinyl, 1,2,4-triazinyl, 1,2,3-triazinyl, triazolyl, benzotriazolyl, tetrazolyl, triazinthionyl, 1(H)-azepinyl, piperidinyl, imidazolidinyl, quinolizidinyl, thienyl, benzothienyl, isobenzothienyl, dibenzothienyl, thiazolyl, benzothiazolyl, isothiazolyl, benzisothiazolyl, thiadiazolyl, benzothiazolyl, 1,2-dithiolyl, 1,3-dithiolyl, 1,3-oxathiolyl, thianthrinyl, thiamorpholinyl, 1,4-thianinyl, 1,4-dithanyl 1,4-dithiadienyl, selenazolyl, benzoselenazolyl, isoselenazolyl, benzisoselenazolyl, selenadiazolyl, benzoselenadiazolyl and the like; such that R^{15}, R^{16}, R^{17} and R^{18} do not represent a carbonyl group, a carbamoyl group or an amido group when A^{15}, A^{16}, A^{17} and A^{18} represent a carbonyl or thiocarbonyl and such that the grouping $R_a^{15}(A^{15})$, the grouping $R_a^{16}(A^{16})$, the grouping $R_a^{17}(A^{17})$ and the grouping $R^{18}(A^{18})$ each represents a moiety having a molecular weight of from 100 to 1,000 and preferably from 125 to 400 and preferably containing not more than one solubilizing group such as carboxy unless the grouping contains a hydrophobic moiety such as a long alkyl chain or an aryl group.

Many heterocyclic compounds having a molecular weight of less than 100 (exclusive of the mercapto group)

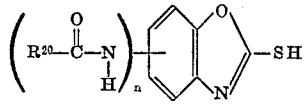
such as those compounds shown in British Patent 1,138,842 have been found not to be bleach inhibitors but rather bleach accelerators. Compounds of this type do not fall within the meaning of the term bleach inhibitor as defined herein.

In a more preferred embodiment of our invention, the bleach inhibitor is an organic compound or the salt of an organic compound as defined in Formulae VI, VII and VIII above having an acidic thiol or selenol, or having a group capable of forming such a compound prior to or subsequent to being brought into contact with a photographic element. For example, such thiol and selenol precursors can form the thiol or selenol group upon hydrolysis. Examples of precursors which form acidic thiol bleach inhibitors are bleach inhibitors XCI and XCII. Another example of thiol forming compounds is disulfides (i.e., compounds of Formula VI above) which cleave at the sulfur atoms to yield at least one thiol compound.

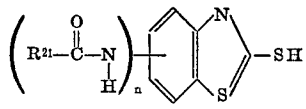
The acidity of the thiol and selenol groups can be imparted by the group to which these groups are attached (e.g., a heterocyclic or carbocyclic ring). Alternatively, other groups attached to the group having the thiol and selenol groups can impart acidity. For example, a carboxylic acid group on a carbon atom adjacent to the atom to which these groups are attached (e.g., 2-mercaptoluric acid) imparts the desired acidity. Other electron withdrawing groups (e.g., nitro and halo) can also impart acidity to the thiol and selenol groups.

Compounds having the following formulae exhibit particular utility as bleach inhibitors:

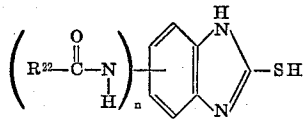
(A) 2-mercaptobenzoxazoles



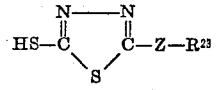
(B) 2-mercaptobenzothiazoles



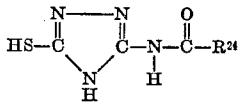
(C) 2-mercaptobenzimidazoles



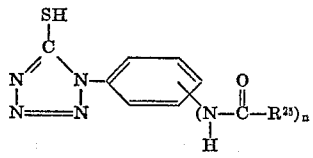
(D) 2-mercaptothiadiazoles



(E) 2-mercaptotriazoles



(F) 1-phenyl-5-mercaptotetrazoles



wherein:

R^{20}, R^{21}, R^{22} and R^{25} each represents an alkyl group having from 1 to 17 carbon atoms and preferably 5 to 10 carbon atoms;

R^{23} and R^{24} each represents an alkyl group having from 5 to 17 and preferably from 8 to 12 carbon atoms;

Z represents sulfur or the group —NHCO—;

n represents 0 to 5 and preferably 1.

The following list of compounds are typical sulfur and selenium compounds which function as bleach inhibitors in the present invention:

(LVIII) 4-hexanamidothiobenzoic acid
(LIX) 2-mercaptolauric acid
(LX) n-Butylthiobenzoic acid
(LXI) 4-octylthiobenzoic acid
(LXII) 2-naphthalenethiol
(LXIII) 4-quinolinethiol
(LXIV) 2,3-quinoxalinedithiol
(LXV) 5-ethyl-4-benzopyrimidinethiol
(LXVI) 3-mercapto-5-phenyl-1,2,4-triazole
(XLVII) 3-(5-mercapto-1,2,4-triazol-3-ylthio)-propanoic acid
(LXVIII) 1-(3,5-di-pentanamidophenyl)-5-mercaptotetrazole
(LXX) 1-(3-acetamidophenyl)-5-mercaptotetrazole
(LXXI) 1-phenyl-5-selenoltetrazole
(LXXII) 1-phenyl-5-mercaptotetrazole
(LXXIII) 1-{3-[2-(2,4-di-t-amylphenoxy)-acetamido]-phenyl}-5-mercaptotetrazole
(LXXIV) 1-[4-(1-piperidinylsulfonyl)-phenyl]-5-mercaptotetrazole
(LXXV) 1-(1-naphthyl)-5-mercaptotetrazole
(LXXVI) 1-(3-pentanamidophenyl)-5-mercaptotetrazole
(LXXVII) 1-(3-nonanamidophenyl)-5-mercaptotetrazole
(LXXVIII) 1-(3-tetradecanamidophenyl)-5-mercaptotetrazole
(LXXIX) 2-nonanamido-6-mercaptopurine
(LXXX) 2-mercapto-1,3-benzoxazole
(LXXXI) 2-mercapto-1,3-benzothiazole
(LXXXII) 2-mercapto-6-pentanamido-1,3-benzothiazole
(LXXXIII)-2-mercapto-6-nonanamido-1,3-benzothiazole
(LXXXIV) 2-mercapto-5-pentanamido-1,3,4-thiadiazole
(LXXXV) 2-mercapto-5-nonanamido-1,3,4-thiadiazole
(LXXXVI) 2-mercapto-5-tetradecanamido-1,3,4-thiadiazole
(LXXXVII) 2-pentylthio-5-mercapto-1,3,4-thiadiazole
(LXXXVIII) 2-octylthio-5-mercapto-1,3,4-thiadiazole
(LXXXIX) 2-dodecyl-5-mercapto-1,3,4-thiadiazole
(XC) 2,4-diamino-6-mercaptopyrimidine
(XCI) 2-(1-phenyltetrazol-5-ylthio)-butan-3-one
(XCII) α-(1-phenyltetrazol-5-ylthio)-ethyl-phenylketone
(XCIII) 3-decyl-2-oxirenthiol
(XCIV) 5-(5-trichloropentyl)-2-furanthiol
(XCV) 6-(10-sulfodecyl)-2-benzofuranthiol
(XCVI) 6-(8-sulfatoocyl)-3-isobenzofuranthiol
(XCVII) 4-butylsulfonylhexyl-1-dibenzofuranthiol
(XCVIII) 4-(7-cyanoheptyl)-2-oxazolthiol
(XCIX) 1,3-benzoxazol-2-thiol
(C) 6-pentanamido-1,3-benzoxazol-2-thiol
(CI) 6-nonanamido-1,3-benzoxazol-2-thiol
(CII) 5-pentanamido-1,3-benzoxazol-2-thiol
(CIII) 8-(3-mercapto-4-isoxazolyl)-octanoic acid
(CIV) 7-benzyl-3-benzisoxazolthiol
(CV) 4-propoxypentyl-2,1,3-oxadiazol-5-thiol
(CVI) 7-(2-ethylenebenzoate)-2,1,3-benzoxadiazol-4-thiol
(CVII) 4-(6-ethylhexanoate)-1,2-pyran-2-ylthiol
(CVIII) 4-(3-phenylpropanoate)-1,4-pyran-2-ylthiol
(CIX) 8-butanamidoethyl-2(H)-benzopyran-4-ylthiol
(CX) 4-(2-ethyl-4-sulfophenyl)-dioxazol-2-ylthiol
(CXI) 5-(2,4-dinitrophenyl)-1,2-oxazin-3-ylthiol
(CXII) 4-(4-butoxyphenyl)-morpholin-3-ylthiol
(CXIII) 4-(4-phenoxyphenyl)-1,3-dioxolan-2-ylthiol
(CXIV) 6-(4-phenylenebutanoate)-1,3-oxathian-2-ylthiol
(CXV) 6-(4-phenylbenzoate)-1,2-dioxan-3-ylthiol
(CXVI) 4'-(5-mercapto-1,2,4-triazol-3-ylthiol)-acetophenone

(CXVII) 4-(5-mercapto-1,2,4-triazol-3-ylthiol)-benzophenone
(CXVII) 4-decyl-1,2-diazet-3-ylthiol
(CXVIII) 1-(3-octanamidophenyl)-pyrrol-2-ylthiol
(CXIX) 1-ethyl-3-n-octylthio-indol-2-ylthiol
(CXX) 2-ethyl-3-butyl-isoindol-1-ylthiol
(CXXI) 1-methyl-4-ethyl-carbazol-2-ylthiol
(CXXII) 7-butanamidopyrrocolin-3-ylthiol
(CXXIII) 4-ethylacridin-2-ylthiol
(CXXIV) 2-phenanthridinylthiol
(CXXV) 3-ethyl-4-butanamido-2-imidazolin-2-ylthiol
(CXXVI) 1,3-benzimidazol-2-thiol
(CXXVII) 6-acetamido-1,3-benzimidazol-2-thiol
(CXXVIII) 6-nonanamido-1,3-benzimidazol-2-thiol
(CXXIX) 4-butyl-2-pyridinylthiol
(CXXX) 4-(3-hexanamidophenyl)-2-pyridazinylthiol
(CXXXI) 7-methylhypoxanthin-6-ylthiol
(CXXXII) 3-(3-hexanamidophenyl)-pyrazin-2-ylthiol
(CXXXIII)-3-butylquinoxalin-2-ylthiol
(CXXXIV) 1-methylphthalazin-4-ylthiol
(CXXXV) 5-benzylamidophenylquinolin-2-ylthiol
(CXXXVI) 5-butylphenazin-2-ylthiol
(CXXXVII) 5-methylphenoxyazin-2-ylthiol
(CXXXVIII) 5-chlorophenothiazin-2-ylthiol
(CXXXIX) 5-n-decylthio-1,2,4-triazin-3-ylthiol
(CXL) 5-(3-octanamidophenyl)-6-benzotriazolylthiol
(CXLI) 4-butyl-1(H)-azepin-2-ylthiol
(CXLII) 1-(3-phenylpropyl)-2-piperidinylthiol
(CXLIII) 1,3-dihexyl-2-imidazolidinylthiol
(CXLIV) 2-octylthio-5-thienylthiol
(CXLV) 5-hexanamido-2-benzothienylthiol
(CXLVI) 4-(3-hexanamidophenyl)-1,3-dithiol-2-ylthiol
(CXLVI) 4-(3-octanamidophenyl)-1,3-oxathiol-2-ylthiol
(CXLVII) 4-hexyl-3-thiamorpholinylthiol
(CXLVIII) 4-(4-phenylbutyl)-1,4-thianin-3-ylthiol
(CXLIX) 4-(3-octanamidophenyl)-2-selenazolylthiol
(CL) 5-benzamido-2-benzoselenazolylthiol
(CLI) 5-acetamido-3-benzoisoselenazolylthiol
(CLII) 4-(3-hexanamidophenyl)-3-isoselenazolylthiol
(CLIII) 2-naphthaleneselenol
(CLIV) 1-(3-pentanamidophenyl)-tetrazol-5-ylselenol
(CLV) 1-(3-nonanamidophenyl)-tetrazol-5-ylselenol
(CLVI) 6-octanamido-1,3-benzoselenazol-2-ylselenol
(CLVII) 5-pentanamido-1,3,4-selenadiazol-2-ylselenol
(CLVIII) 5-octanamido-1,3,4-thiadiazol-2-ylselenol
(CLIX) 2-decylthio-1,3,4-thiadiazol-2-ylselenol
(CLX) 2-decylthio-1,3,4-selenadiazol-2-ylselenol
(CLXI) oxalic-bis-N-[3-(5-mercaptotetrazol-1-yl)-anilide]
(CLXII) disulfide, bis-1-(3-nonanamidophenyl)-tetrazol-1-yl
(CLXIII) disulfide, bis-5-nonanamido-1,3,4-thiadiazol-2-yl
(CLXIV) 1-(3-octanamidophenyl)-5-mercaptotetrazole, sodium salt
(CLXV) 1-(3-nonanamidophenyl)-5-mercaptotetrazole, potassium salt
(CLXVI) 2-octylthio-5-mercapto-1,3,4-thiadiazol, ammonium salt

The combination of onium salt and silver bleach inhibitor are brought into contact with the sound track portion of the film in the form of a solution. The solvent can be any solvent which will dissolve alone or with other solvents, the onium salts and the silver bleach inhibitors, and is compatible with hydrophilic colloid silver halide emulsions, the supports for these emulsions, and the aqueous processing of such emulsions. The solvent can be for example, lower alkyl alcohol such as methyl alcohol, ethyl alcohol, isopropyl alcohol and the like, but is preferably predominantly aqueous.

The concentration of onium salts in the solution can vary widely and typically range from about 1% weight to 15% weight and preferably from about 5% weight to about 10% weight.

The concentration of silver bleach inhibitor in the solutions can also vary widely and typically range from about 0.1% weight to about 3% weight and preferably range from about 0.5% weight to about 2% weight.

In addition to the onium salt and the silver bleach inhibitor, the solution can also contain a silver halide solvent such as an alkali metal or ammonium thiosulfate, thiocyanate or sulfite or mixtures of these compounds. As a result, the residual silver halide in the sound track area is fixed out at the same time the silver image is protected against subsequent bleaching. However, silver halide solvent can be omitted from the solution.

The process of the invention is generally applicable to the production of silver auxiliary or sound track images in color film. Typically, the color film is comprised of one or more (generally three) color-forming units, each unit comprising one or more (generally one or two) silver halide emulsion layers. The color-forming units can be of the type which do not contain incorporated photographic couplers. In this event, the photographic element is processed in the presence of a coupler-developer composition. This composition contains both a diffusible aromatic primary amine color developing agent and a diffusible photographic coupler. The oxidized color developing agent resulting from the development of a latent silver halide image reacts with the diffusible photographic coupler to produce a nondiffusible dye at the site of development. The process, however, is particularly useful for color films of the type having color-forming units containing incorporated couplers. This type of film is developed in the presence of an aromatic primary amine color developing agent. The oxidized color developing agent resulting from the development of the latent silver halide image in this type of film reacts with the incorporated coupler at the site of development to produce a nondiffusible dye. The photographic couplers whether contained in a coupler development composition or incorporated into the color-forming units are well known to those skilled in the photographic art. For example, 5-pyrazolone couplers are typically used to produce magenta dye images, phenolic, including naphtholic, couplers are typically used to produce cyan dye images and open-chain ketomethylene couplers are typically used to produce yellow dye images. The above films can either be negative-positive print films or reversal print films.

The auxiliary silver image record or sound track record can be comprised of either silver or silver plus a dye. The record is comprised of silver if the film is the reversal film and is comprised of silver and a dye if the film is a negative-positive print film. Since the treatment of the auxiliary silver image record or silver sound track record is subsequent to initial development and prior to color development and/or bleaching, the auxiliary or sound track image to which the film is exposed is a negative image which will result in a positive image upon initial development.

The sound track image can be either a variable density sound track or a variable area sound track. The auxiliary silver image record can be of any image which one wishes to retain in some part of the film. For example, the auxiliary silver image can be a synchronizer signal printed in the sound track area to accomplish such purposes as the changing of slides in a multimedia program or to accomplish any other such purpose as one can wish to associate with motion picture films.

The treatment of the sound track to prevent subsequent bleaching of the silver therein is accomplished subsequent to initial development and in the case of reversal films prior to color development. In the case of negative-positive print films the sound track treatment is prior to bleaching.

In the case of reversal films, reversal development of the residual silver halide in the sound track must not

occur. This is because that even though the silver developed during reversal development will not have been treated to prevent its subsequent bleaching, dyes will form wherever reversal development takes place. These dyes, particularly the cyan dye, will interfere with the quality of sound track obtained. To prevent reversal development of the residual silver halide in the sound track the picture area can be fogged with light rather than by using a chemical fogging agent. Alternatively, the onium salt-silver bleach inhibitor solution can contain sufficient silver halide solvent to fix out the residual silver halide in the sound track area. In this case, the film can be treated with a chemical fogging agent prior to or concurrent with reversal development.

The application of the onium salt-silver bleach inhibitor solution to only the sound track area of the film can be accomplished in any convenient manner such as passing the edge of the film bearing the sound image through a bath containing the onium salt and the bleach inhibitor or by passing the area of the film under a roller which is wet with the solution containing these compounds.

The length of time the sound track portion of the film is contacted with this processing solution can be varied considerably and depends to some extent on the concentration of the compounds in the solution. Especially good results are obtained with contact times of 5 to 10 seconds in baths containing about 50 to 150 grams per liter ammonium salt and about 5 to 20 grams per liter of silver bleach inhibitor. However, contact times can range up to 5 to 10 minutes or more if needed. The contact times and relative concentrations of the compounds in the solution can be adjusted as desired.

The improved process of this invention is useful in preventing the bleaching of the silver sound image by strong bleaching solutions such as acid or alkaline ferricyanide solutions and dichromate solutions which are used to convert silver in color photographic films to salts soluble in fixing solutions. This process is particularly useful in preventing bleaching by very strong bleaching solutions such as those which contain 15 to 25% weight of the bleaching compound such as the ferricyanide or dichromate compound. These strong bleaching solutions are designed for use in high speed processing to rapidly convert the silver to a soluble silver salt.

The process of this invention provides a highly convenient method for retaining silver image in the sound track area of a color film. It requires but one separate treatment of the sound track portion of the film and allows obtaining the metallic silver sound track in a color reversal film from a negative sound original.

A further understanding of my improved method of processing photographic elements can be had by referring to the drawing in the Bevis et al. application referred to hereinabove, and which drawing is incorporated herein by reference. This drawing depicts diagrammatically and sequentially the processing of a photographic element shown in cross-sectional view to produce a color picture record and a silver sound record. The processing is according to the novel method of that invention and differs from my improved method of processing only in the composition of the bleach inhibitor composition.

The following example is included for a further understanding of the invention, it being understood that other bleach inhibitors and onium salts as described above can similarly be utilized.

A multilayer color photographic motion picture reversal print film with a picture record area and a sound track record area and bearing on a transparent cellulose acetate film support, in order from the support, a photographic color-forming unit primarily sensitive to the red region of the visible spectrum comprising a gelatino silver halide emulsion layer containing a nondiffusible cyan-forming phenolic coupler, a photographic color-forming unit primarily sensitive to the green region of the visible spectrum comprising a gelatino silver halide emulsion layer containing a nondiffusible magenta dye forming 5-pyrazolone coupler, a yellow filter layer, and a photographic color-forming unit primarily sensitive to the blue region of the visible spectrum comprising a gelatino silver halide emulsion layer containing a nondiffusible yellow dye forming open-chain ketomethylene coupler is exposed to a multicolor picture record multi-step test object and a sound record negative multi-step test object and processed as follows:

Bath	Time	Temperature, ° C.
1. Prehardener	2 minutes, 30 seconds	35
2. Neutralizer	30 seconds	35
3. First developer	2 minutes, 15 seconds	38
4. First stop	30 seconds	35
5. Wash	do	38
6. Sound track bath	10 seconds	38
7. Wash	30 seconds	38
8. Color develop	2 minutes, 30 seconds	43
9. Second stop	30 seconds	35
10. Wash	do	38
11. Bleach	1 minute, 30 seconds	35
12. Fix	do	35
13. Wash	1 minute	38
14. Stabilize	30 seconds	35

The chemical composition of the above processing baths is as follows:

(1) Prehardener:

Water	ml	800.0
p-toluenesulfinic acid (sodium salt)	g	1.0
Succinaldehyde, bis, bisulfite	g	8.5
Magnesium sulfate, heptahydrate	g	257.0
Sodium sulfate	g	75.0
Sodium bromide	g	2.0
Sodium acetate	g	15.0
Formalin (37% by volume aqueous formaldehyde solution)	ml	27.0
Glacial acetic acid	ml	2.4
N - methyl benzothiazolium-p-toluene sulfonate	g	.03

Water to 1.0 liter.

(2) Neutralizer:

Water	ml	800.0
Hydroxylamine sulfate	g	18.0
Sodium bromide	g	17.0
Glacial acetic acid	ml	10.0
Sodium hydroxide	g	6.8
Sodium sulfate	g	50.0

Water to 1.0 liter.

(3) First developer:

Water	ml	800.0
Sodium tetraphosphate	g	2.0
Sodium bisulfite	g	8.0
1-phenyl-3-pyrazolidone	g	.35
Sodium sulfite	g	37.0
Hydroquinone	g	5.5
Sodium carbonate (anhydrous)	g	28.2
Sodium thiocyanate	g	1.38
Potassium iodide (0.1% by weight aqueous solution)	ml	13.0
Sodium bromide	g	1.30

Water to 1.0 liter.

(4 and 9) First and second stop bath:

Water	ml	800.0
Glacial acetic acid	ml	30.0
Sodium hydroxide	g	1.65

Water to 1.0 liter.

(6) Sound track bath:

Hexadecyl trimethyl ammonium bromide	g	100.0
1-phenyl-5-mercaptotetrazole	g	10.0
Ammonium thiosulfate (60% solution)	ml	170.0

Water to 1.0 liter.

(8) Color developer:

Water	ml	800.0
Nitrilo (trimethylene phosphonic acid) sodium salt	ml	3.0
Benzyl alcohol	g	4.5
Sodium sulfite	g	7.5
Trisodium phosphate·$12H_2O$	g	36.0
Sodium bromide	g	0.9
Potassium iodide (0.1% w. solution)		
Sodium hydroxide		
Citrazinic acid	g	1.5
4-amino-3-methyl-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sesquisulfate monohydrate	g	11.0
Ethylenediamine	g	3.0
Water to 1.0 liter.		

(11) Ferricyanide bleach:

Water	ml	800.0
Sodium bromide	g	43.0
Sodium ferrocyanide (decahydrate)	g	245.0
Potassium persulfate	g	67.0
Borax ($Na_2B_4O_7·5H_2O$)	g	1.0
Carbowax 1540	g	3.6
Water to 1.0 liter.		

(12) Fixing bath:

Water	ml	800.0
EDTA (disodium salt)	g	0.5
Sodium thiosulfate (pentahydrate)	g	204.0
Sodium sulfite	g	10.0
Disodium phosphate	g	15.0
Water to 1.0 liter.		

(14) Stabilizing bath:

Renex 30, Atlas Chemical (a polyethylene ether alcohol)	ml	0.14
Formalin (37% w. solution)	ml	6.0
Water to 1.0 liter.		

The step 6 sound track bath is applied to only the sound track area of the film. Because the sound track bath contained a silver halide solvent, reversal fogging was accomplished with a chemical fogging agent in the color developer. Silver densities are measured at 900 nm. on a densitometer at D_{max}. The silver density of the sound track of a film processed as above is 1.57. The silver density of the sound track of a film processed as above except omitting the 1-phenyl-5-mercaptotetrazole from the sound track bath is 1.18. The silver density of the sound track of a film processed as above except omitting the hexadecyl trimethyl ammonium bromide from the sound track bath is 0.08. When the above film is processed as above except that the sound track bath contains other onium salts and other silver bleach inhibitors, similar results are obtained. When the above film is exposed to a multicolor image and a negative sound record and processed as above, films are obtained having yellow, magneta and cyan picture records substantially free of silver and excellent silver sound records.

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.

I claim:

1. In the process of producing a picture record and an auxiliary silver image record in an imagewise 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 a nondiffiusible dye and an auxiliary image record comprising silver and bleaching and fixing the element to remove the silver of the picture record, the improvement which comprises contacting the silver of the auxiliary image but not the silver of the picture record prior to bleaching with a mixture of a silver bleach inhibitor and a diffusible onium salt to retain at least a portion of the silver of the auxiliary image record during said bleaching.

2. The improvement of claim **1** wherein said onium salt is a quaternary ammonium salt.

3. The improvement of claim **2** wherein said silver bleach inhibitor has an acidic thiol or selenol group and wherein said quaternary ammonium salt is a tetraalkyl quaternary ammonium salt.

4. The improvement of claim **3** wherein said silver bleach inhibitor is a mercapto alkanoic acid, a thioaryl or a mercapto-substituted heterocyclic compound containing 5 to 6 atoms in the ring, said ring containing at least one nitrogen atom.

5. The improvement of claim **4** wherein said silver bleach inhibitor is a mercaptobenzoxazole, a mercaptobenzothiazole, a meracaptobenzimidazole, a mercaptothiadiazole, a mercaptotriazole or a 1-phenyl-5-mercaptotetrazole.

6. In the process of producing a color picture record and a silver sound track record in an imagewise exposed photographic element having at least one silver halide emulsion which comprises developing said exposed element to form a picture record comprising silver and a nondiffusible dye and a sound track record comprising silver and bleaching and fixing the element to remove the silver of the picture record, the improvement which comprises contacting the silver of the sound track record but not the silver of the picture record prior to bleaching with a mixture of a silver bleach inhibitor and an onium compound which retains at least a portion of the silver of the sound track record during said bleaching.

7. The improvement of claim **6** wherein said silver bleach inhibitor has a formula selected from the group consisting of:

(VI) $R_a^{15}—(A^{15})—XR^{19}$

(VII) $R_a^{16}—(A^{16})—X—X—(A^{17})—R_a^{17}$

and

(VIII) $R_a^{18}—(A^{18})—X^{\ominus}Y^{\oplus}$

wherein:

a represents 0, 1, 2, 3, 4, 5 or 6;

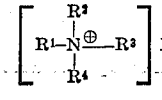
X represents a member selected from the group consisting of sulfur and selenium;

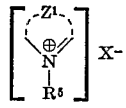
R^{15}, R^{16}, R^{17} and R^{18} each represents a member selected from the group consisting of nitro, halo, an alkyl group, an aryl group, a thio group containing from 3 to 22 carbon atoms, an amido group containing from 4 to 22 carbon atoms, a carbonyl group, a carbamoyl group, an alkoxy group and an aryloxy group;

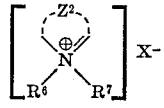
R^{19} represents a member selected from the group consisting of hydrogen and an acyl group;

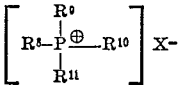
$Y^{\oplus}$ represents a basic cation;

A^{15}, A^{16}, A^{17} and A^{18} each represents a member selected from the group consisting of a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring and a 3 to 6 membered heterocyclic ring containing at least one carbon atom and at least one heteroatom selected from the group consisting of nitrogen, oxygen, sulfur and selenium such that R^{15}, R^{16}, R^{17} and R^{18} do not represent a carbonyl group, a carbamoyl group or an amido group when A^{15}, A^{16}, A^{17} and A^{18} represent a carbonyl group or a thiocarbonyl group and such that the grouping $R_a^{15}—(A^{15})—$, the grouping $R_a^{16}—(A^{16})—$, the grouping $R_a^{17}—(A^{17})—$ and the grouping $R_a^{18}—(A^{18})—$ each represents a moiety having a molecular weight of from 100 to 1,000 and wherein said onium salt has a formula selected from the group consisting of:

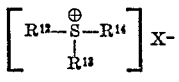
I. 

II. 

III. 

IV. 

and

V. 

wherein R^1 to R^{14} each represents alkyl or aryl, X^- represents an anion and Z^1 and Z^2 each represents the nonmetallic atoms necessary to complete a heterocyclic ring containing 5 to 6 atoms in the heterocyclic ring, said atoms being selected from the group consisting of carbon, nitrogen, oxygen, selenium and sulfur.

8. The improvement of claim **7** wherein the grouping R_a^{15}—(A^{15})—, R_a^{16}—(A^{16})—, R_a^{17}—(A^{17})— and the grouping R_a^{18}—(A^{18})— represent a member selected from the group consisting of a benzoxazole nucleus, a benzothiazole nucleus, a benzimidazole nucleus, a thiadiazole nucleus, a triazole nucleus and a 1-phenyltetrazole nucleus and said onium salt is a tetraalkyl quaternary ammonium salt.

9. In a process of producing a color picture record and a silver sound track record in an imagewise exposed photographic element having a plurality of superposed picture recording photographic image-forming units comprising at least one silver halide emulsion layer which process comprises developing said exposed element to form a picture record comprising silver and a nondiffusible dye and a sound track record comprising silver and bleaching and fixing the element to remove the silver of the picture record, the improvement which comprises contacting the silver of the sound track record but not the silver of the picture record prior to bleaching with a mixture of a silver bleach inhibitor and an onium compound to retain at least a portion of the silver of the sound record during said bleaching.

10. The improvement of claim **9** wherein said silver bleach inhibitor is selected from the group consisting of a mercaptoalkanoic acid, a thioaryl and a mercapto-substituted heterocyclic compound containing from 5 to 6 atoms in the ring, said ring containing at least one nitrogen atom and wherein said onium compound is a tetraalkyl quaternary ammonium salt.

11. The improvement of claim **10** wherein said picture recording photographic image-forming units contain in each of said units at least one nondiffusing photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye essentially complementary in color to the sensitivity of the emulsion in which it is incorporated.

12. In the process of producing a color picture record and a silver sound track record in an exposed photographic element having a plurality of picture recording photographic units comprising at least one silver halide emulsion layer which process comprises developing said exposed element to form a picture record comprising silver and a nondiffusible dye and a sound track record comprising silver, the improvement which comprises contacting the silver of the sound track record but not the silver of the picture record prior to bleaching with an aqueous solution of hexadecyltrimethyl ammonium bromide and 1-phenyl-5-mercaptotetrazole.

13. A photographic processing composition comprising a silver bleach inhibitor and an onium salt.

14. A photographic processing composition comprising an aqueous solution containing a silver bleach inhibitor and an onium salt.

15. A photographic processing composition comprising a silver bleach inhibitor having a formula selected from the group consisting of:

(VI) $R_a^{15}(A^{15})XR^{19}$

(VII) $R_a^{16}(A^{16})X—X(A^{17})R_a^{17}$

and

(VIII) $R_a^{18}(A^{18})X\ominus Y\oplus$

wherein:

a represents 0, 1, 2, 3, 4, 5 or 6;

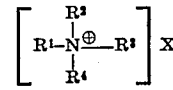
X represents a member selected from the group consisting of sulfur and selenium;

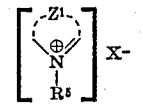
R^{15}, R^{16}, R^{17} and R^{18} each represents a member selected from the group consisting of nitro, halo, an alkyl group, an aryl group, a thio group containing from 3 to 22 carbon atoms, an amido group containing from 4 to 22 carbon atoms, a carbonyl group, a carbamoyl group, and alkoxy group and an aryloxy group;

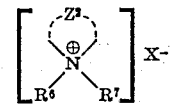
R^{19} represents a member selected from the group consisting of hydrogen and an acyl group;

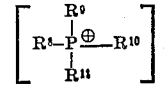
$Y\oplus$ represents a basic cation;

A^{15}, A^{16}, A^{17} and A^{18} each represents a member selected from the group consisting of a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring and a 3 to 6 membered heterocyclic ring containing at least one carbon atom and at least one heteroatom selected from the group consisting of nitrogen, oxygen, sulfur and selenium such that R^{15}, R^{16}, R^{17} and R^{18} do not represent a carbonyl group, a carbamoyl group or an amido group when A^{15}, A^{16}, A^{17} and A^{18} represent a carbonyl group or a thiocarbonyl group and such that the grouping $R_a^{15}(A^{15})$, the grouping $R_a^{16}(A^{16})$, the grouping $R_a^{17}(A^{17})$ and the grouping $R_a^{18}(A^{18})$ each represents a moiety having a molesular weight of from 100 to 1,000 and an onium salt having a formula selected from the group consisting of:

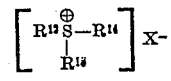
I. 

II. 

III. 

IV. 

and

V. 

wherein R^1 to R^{14} each represents alkyl or aryl, X^- represents an anion and Z^1 and Z^2 each represents the nonmetallic atoms necessary to compete a heterocyclic ring containing from 5 to 6 atoms in the heterocyclic ring, said atoms being selected from the group consisting of carbon, nitrogen, oxygen, selenium and sulfur.

16. A photographic processing composition of claim 15 wherein the grouping $R_a^{15}(A^{15})$, the grouping $R_a^{16}(A^{16})$, the grouping $R_a^{17}(A^{17})$ and the grouping $R_a^{18}(A^{18})$ each represents a heterocyclic nucleus containing 5 to 6 atoms in the heterocyclic ring, said ring containing at least one nitrogen atom, X represents sulfur and said onium salt is a tetraalkyl quaternary ammonium salt.

17. A photographic processing composition comprising a silver bleach inhibitor, and onium salt and a silver halide solvent.

18. A photographic processing composition having a pH of about 6 to 8 comprising an aqueous solution containing 0.1% weight to 3% weight 1-phenyl-5-mercaptotetrazole and 5% weight to 15% weight hexadecyl trimethylammonium bromide.

References Cited

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J. TRAVIS BROWN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—60 R, 39

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,705,800 Dated December 12, 1973

Inventor(s) William S. Lane

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

Column 17, line 9, the first "and" should be ---an---.

Signed and sealed this 10th day of July 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

Rene Tegtmeyer
Acting Commissioner of Patents