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

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ABSTRACT OF THE DISCLOSURE

Novel photographic processing compositions for preparing silver auxiliary images and silver sound tracks are provided which contain a ballasted silver bleach inhibitor and a silver halide solvent. Also provided are improved processes for producing a silver auxiliary image or silver sound record in an exposed photographic element comprising a support having coated thereon at least one picture recording photographic silver halide layer and as the light sensitive layer outermost from the support an auxiliary image-recording silver halide layer which does not form an image upon image-forming exposure of the picture recording layer or layers which comprises (A) developing a picture record comprising silver and dye and an auxiliary or sound record comprising silver, (B) contacting the auxiliary layer which a ballasted silver bleach inhibitor to adsorb the bleach inhibitor onto at least the silver of the auxiliary layer and (C) removing the bleachable silver and the residual silver halide which improvement comprises carrying out step (B) in the presence of a silver halide solvent.

This application is a continuation-in-part of my copending U.S. patent application Ser. No. 100,776 filed Dec. 22, 1970, and now abandoned.

This invention relates to photographic film having an auxiliary metallic silver image. In one aspect, this invention relates to processing imagewise exposed color motion picture films having metallic silver sound tracks and to compositions useful in such processing.

Color photographic films having auxiliary metallic silver images are known. Color motion picture films having metallic silver sound tracks are also known. Typically, the color images are prepared by the three-color system of photography. In this well known system color images are formed from three subtractive dyes: a yellow dye to control blue light, magenta dye to control green light and a cyan dye to control red light. These dye images can be formed by various methods.

For example, a photographic record can be formed in a multilayer element having three color-forming units, each unit being sensitive to essentially a different primary color region of the visible spectrum. These color-forming units can contain photographic color couplers which form, upon coupling with oxidized aromatic primary amine color developing agent, subtractive dyes essentially complementary to a primary color region of the visible spectrum. Generally, the subtractive dyes formed are complementary in color to the sensitivity of the color-forming unit in which it is formed. Subsequent to dye formation, the developed silver and residual silver halide must be removed from the picture area. This is usually accomplished by bleaching and fixing or by bleach-fixing (single step bleaching and fixing).

Optical motion picture sound tracks are printed onto the same film on which the picture image is printed. The sound track itself can be comprised of dyes, dyes plus silver, silver compounds, silver plus other metals or silver alone. Due to the sensitivity of the photocell conventionally used to detect light passing through the optical sound track, the sound track must modulate electromagnetic radiation having a wavelength of about 700 to 900 nanometers (nm.). Subtractive dyes which form a picture image have regions of maximum absorption of from about 400 to 700 nm. and are relatively transparent to radiation in the 700 to 900 nm. region.

Since the picture image dyes do not absorb infrared radiation materials other than dyes have generally been used to form an optical sound track. Commonly used materials are metallic silver and silver sulfide.

As noted above, the developed silver and residual silver halide must be removed from the picture area of the color motion picture film subsequent to color image formation. At the same time, developed silver or a silver compound must be retained in the sound track area if the color motion picture film is to have a sound track which adequately modulates infrared radiation. A number of techniques have been devised to retain the silver of the sound track. For example, the sound track area can be covered with a varnish subsquent to the formation of the picture and sound track images and prior to silver bleaching. The varnish prevents diffusion of the bleaching solution into the sound track area. Subsequent to rehalogenation of the silver in the picture area, the varnish is removed with a suitable solvent and silver halide is removed from the entire film, reference being made to U.S. Pat. 1,973,463, issued Sept. 11, 1934. Another method of retaining the metallic silver sound track in negative-positive print films is to remove the residual silver halide by fixing the entire film subsequent to color development. The metallic silver is then converted to a fixable silver salt by bleaching both the sound track and picture areas. Subsequent to bleaching, the silver salt in the sound track area is reconverted to metallic silver by applying a viscous, highly active developer. The application of this developer to only the sound track area is accomplished by known striping methods. Subsequent to sound track redevelopment, the silver salt in the picture area is removed by fixing.

The disadvantage of these methods of preparing a silver sound track is the requirement of individual treatment to the sound track or picture record areas. Novel processes and novel photographic elements have been discovered which allow the preparation of silver sound tracks and auxiliary silver images in color photographic elements without individual treatment of any area of the film. These elements and processes are the invention of Bello and Holtz and are disclosed and claimed in copending application entitled Film and Process Using Bleach Inhibitor for Producing Color Film With Silver Sound Record, Ser. No. 100,609, filed Dec. 22, 1970, now abandoned, and the continuation-in-part thereof filed concurrently herewith. The novel elements of this copending application are provided with an auxiliary silver halide emulsion layer coated as the outermost light sensitive layer from the support and over the picture recording layers. Sound record exposure forms a latent sound record image in at least the auxiliary layer while picture record exposure causes no image to form in the auxiliary layer. The so-exposed element is then processed according to the disclosed novel process which comprises initial development of the latent image (to a silver image in reversal print films or a silver and dye image in negative-positive print films), contacting the auxiliary layer with a ballasted silver bleach inhibitor to to adsorb the bleach inhibitor onto at least the silver of the auxiliary layer, reversal exposure and development if necessary, and bleach-fixing or bleaching and fixing to remove the metallic silver not contacted with bleach inhibitor and the residual silver halide. The processed element comprises a picture record comprising dye and a sound record comprising silver.

This is possible because of the auxiliary layer of the element. During initial development, the unexposed silver halide in the picture area of the auxiliary layer is not developed while the latent sound image is developed to metallic silver. When the element is contacted with a ballasted silver bleach inhibitor, the bleach inhibitor diffuses into and through the auxiliary layer in those areas where metallic silver was developed (the sound track area) much faster than in those areas where only silver halide is present (the picture area) and thus only the silver of the sound track area is contacted with bleach inhibitor. This sound track silver is thus rendered unbleachable. The picture record silver in the underlying layers not having been contacted with bleach inhibitor remains bleachable and is subsequently bleached and fixed out.

Exposure of motion picture print films can be made through the support if the element does not have an antihalation layer but this increases the original-to-emulsion distance, causing loss of sharpness. Loss of sharpness also is caused by light scattering within the support material. Exposure is preferably made from the emulsion side of the element. This is done to reduce to a minimum the distance between the photographic emulsion and the original image and thereby improve sharpness. Since the method of Bello and Holtz requires the auxiliary silver halide layer be coated as the light sensitive layer outermost from the support, exposure of the underlying picture recording units is made through the auxiliary layer if exposure is made from the emulsion side of the element. The presence of silver halide in this layer causes some small amount of light scattering and thus some loss of picture sharpness. The greater the silver halide content of the auxiliary layer, the thicker the layer is and the thicker the layer the greater the loss of sharpness.

The reason the developed silver of the picture recording layers in the picture area is not contacted with bleach inhibitor is because the bleach inhibitor diffuses more slowly through the residual silver halide present in the picture area of the auxiliary layer than through the developed silver in the sound area of the auxiliary layer. As discussed in the referenced application, it is believed that the residual silver halide in the auxiliary layer exhibits a barrier-like effect to the diffusion of the bleach inhibitor into the hydrophilic colloid emulsion. The greater the silver halide content of the auxiliary layer, the thicker the layer is and the greater the length of time required for the bleach inhibitor to diffuse through the auxiliary layer and into the underlying picture recording layers. Since the bleach inhibitor diffuses through the auxiliary layer faster where developed silver is present than where residual silver halide is present, the bleach inhibitor, in the sound area, will have diffused not only into the auxiliary layer but also through it and into the underlying layers wherever developed silver is present if the bleach inhibitor can be left in contact with the photographic element for a sufficient length of time. This diffusion of the bleach inhibitor into the underlying layers in the sound area is desirable since, in this case, not all the silver forming the final sound track must be obtained from the auxiliary layer. When part of the silver of the sound track is obtained from the underlying layers the silver halide content of the auxiliary layer can be reduced allowing the layer to be made thinner thereby improving sharpness of the picture image for the reasons discussed above. There, however, is a point of compromise between reducing the silver halide content of the auxiliary layer to make it as thin as possible for maximum sharpness and yet having it thick enough to prevent diffusion of the bleach inhibitor into the underlying picture recording layers and retaining silver in these layers in the picture area.

It, therefore, appears desirable to provide a method for preparing sound tracks using the process described which would allow the use of a photographic element having a very thin auxiliary layer.

Accordingly, it is an object of my invention to provide a new and improved method for preparing films having silver sound records or auxiliary silver images.

Another object of my invention is to provide novel processing compositions for the preparation of films having silver sound records or auxiliary silver images.

These and other objects can be attained by contacting an exposed film having an auxiliary sound recording layer subsequent to initial development and prior to bleaching of the film with a ballasted silver bleach inhibitor composition containing a silver halide solvent.

I have found that when a photographic element containing an auxiliary or sound recording layer of the type described above having subsequent to initial development residual silver halide in the picture area and a silver sound image in the sound area of the auxiliary layer is contacted with a ballasted silver bleach inhibitor composition containing a silver halide solvent, the rate of diffusion of the bleach inhibitor through the residual silver halide of the auxiliary layer is significantly decreased while the rate of diffusion of the bleach inhibitor through the developed silver in the auxiliary layer is unaffected or not decreased to the same extent. Thus, it will take as long for a bleach inhibitor to diffuse through a thinner auxiliary layer if the bleach inhibitor composition contains a silver halide solvent as it took to diffuse through a thicker auxiliary layer when the bleach inhibitor composition did not contain a silver halide solvent. Therefore, the auxiliary layer can have a reduced silver halide content allowing it to be thinner resulting in improved picture sharpness.

In one embodiment, my invention comprises an improved process for producing a picture record and an auxiliary silver image or sound record in an imagewise exposed photographic element, which element comprises a support having coated thereon, on one surface in order from the support at least one picture recording photographic image-forming unit comprising at least one silver halide emulsion layer (generally one or two) and coated thereover an auxiliary image or sound recording radiation sensitive silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording layer or layers, which process comprises (A) developing a picture record in the picture recording unit or units comprising silver and a nondiffusible dye and developing an auxiliary or sound record in the auxiliary layer comprising silver, (B) contacting the auxiliary layer with a ballasted silver bleach inhibitor to adsorb the bleach inhibitor onto at least the silver record in the auxiliary layer and (C) removing the belachable silver images remaining after step (B) and the residual silver halide wherein the improvement comprises carrying out step (B) in the presence of a silver halide solvent. The photographic elements processed according to my improved method preferably have a plurality (generally three) of picture recording photographic image-forming units comprising silver halide emulsion layers (generally one or two). This plurality of image-forming units are generally so disposed and sensitized such that each is essentially sensitive to a different primary color region of the visible spectrum. Preferably, these image-forming units are color-forming units containing nondiffusible photographic couplers capable of reacting with oxidized color developing agent to form nondiffusible subtractive dyes preferably complementary color to the sensitivity of the unit in which the coupler is incorporated.

The auxiliary layer of these elements is comprised of silver halide and a hydrophilic colloid such as gelatine as a vehicle for the silver halide. The quantity of silver halide can vary substantially but for the reasons stated above is kept to a minimum consistent with the purpose of the auxiliary layer. For example, the silver halide content, expressed as milligrams per square foot silver as silver halide, can range from as little as 10 mg./sq. ft. or less to as much as 100 mg./sq. ft. or more. For maximum sharpness of the picture images the silver halide content of the auxiliary layer is less than 50 mg./sq. ft. and preferably is from about 15 mg./sq. ft. to about 30 mg./sq. ft.

The average size of the silver halide grain can range 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 units 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.

In addition to silver halide, the auxiliary layer can and preferably does contain a substantially colorless nondiffusible compound which reacts with oxidized aromatic primary amine color developing agent. This compound can be a photographic coupler and can be the same as the colorless couplers of the picture recording units. Also, this compound decreases the rate of diffusion of a ballasted silver bleach inhibitor through the auxiliary layer. Compounds which have been found to be particularly useful for this last purpose are the well known 5-pyrazolone couplers, especially when the auxiliary layer is contacted with a bleach inhibitor composition having a pH of 10 or greater. The quantity of this compound which is added to the auxiliary layer should be an amount at least sufficient to consume that quantity of oxidized color developing agent which would be produced if all the silver halide in the auxiliary were developed to silver. As the silver halide content of the auxiliary layer is reduced the quantity of this compound which should be added to the layer is proportionately reduced.

In the above disclosures, it was stated that for maximum sharpness of the picture images when exposure is made through the auxiliary layer the auxiliary layer should be as thin as possible. Since the silver halide of the auxiliary layer is the principle cause of the light scattering which causes loss of sharpness and since the quantity of vehicle and other addenda of the auxiliary layer varies, to some degree, in proportion to the quantity of silver halide present in the auxiliary layer, the thickness of the auxiliary layer is readily expressed and compared in terms of the silver halide present. It can be seen that this manner of expressing the thickness of the auxiliary layer as a function of the silver halide content is appropriate since, for example, to double the silver halide content per square foot and yet maintain proper vehicle and addenda ratios would require coating the emulsion at approximately twice the thickness.

In another embodiment of my invention, novel photographic processing compositions are provided comprising a ballasted silver bleach inhibitor and a silver halide solvent.

The concentration of bleach inhibitor can range from as little as 10^{-5} molar or less to 10^{-1} 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 composition can vary depending upon the particular bleach inhibitor as discussed in the aforementioned Bello et al. application.

Any silver halide solvent is suitable for use in my novel processing composition. Examples of such silver halide solvents include inorganic salts having ammonium or alkali metals such as sodium or potassium ions as a cation, and sulfite, thiosulfate or thiocyanate ions as the anion. Suitable organic silver halide solvents include organic thioethers as disclosed in U.S. 3,271,157, thiosugars as disclosed in U.S. 3,220,838 and the like. The concentration of silver halide solvent in the composition can vary widely depending generally upon the particular bleach inhibitor used and the photographic element to which the composition is applied and can be determined by one skilled in the art according to the guidelines set forth below. Silver halide solvents can be present in a wide range of concentrations, typically ranging from as little as 0.05% weight or less of the compsition to 5% weight or more of the composition. Preferably, the amount of silver halide solvent is from about 0.1% weight to about 2% weight of the solution.

Since the silver halide solvent does exhibit a fixing property, it is readily apparent that the amount of silver halide solvent present in the bleach inhibitor composition should be at a minimum. If too much silver halide solvent is present it will fix out the silver halide from the auxiliary layer leaving the underlying silver images exposed to the bleach inhibitor. These silver images would then become contacted with bleach inhibitor which would not be subsequently bleached out. Therefore, the amount of silver halide solvent in the bleach inhibitor composition should be that amount which increases the barrier-like effectiveness of the auxiliary layer to a maximum and at the same time fixes out a minimum of silver halide.

The solvent for the present bleach inhibitor processing compositions can be any solvent which will dissolve alone or with other solvents, the bleach inhibitor and the silver halide solvent and is compatible with photographic silver halide emulsions, the supports for these emulsions and the aqueous processing of the emulsions. The solvent can be, for example, lower alkyl alcohol such as methyl alcohol, ethyl alcohol, isopropyl alcohol, isobutyl alcohol and the like. Preferably, however, the solvent is predominantly water.

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

The temperature at which the bleach inhibitor can be brought into contact with the auxiliary layer can vary widely, but preferably is approximately the same temperature as the remainder of the processing baths. For example, 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 ballasted silver bleach inhibitor composition is in contact with the auxiliary layer can vary widely. For example, the contact time can range from as little as 5 seconds or less to 10 minutes or more depending upon such factors as the silver halide content of the auxiliary layer, the particular bleach inhibitor being used and the contact temperature. Contact times of 30 seconds to 5 minutes have been found to be particularly useful.

My novel photographic processing compositions include not only those specified above as having certain concentration ranges which can be termed working concentrations, but also include more concentrated compositions which can be diluted with a solvent such as water to produce compositions having the above working concentration ranges.

As used herein and in the appended claims, the term "ballasted bleach inhibitor" refers to an organic compound which when in the form of a solution of the following composition:

Bleach inhibitor ------------------	moles--	1×10^{-2}
Water miscible solubilizer for bleach inhibitor ----------------------		As needed
Water to make 1 liter.		
pH adjusted to ------------------------		12

which is brought into contact for 15 seconds to 10 minutes at a temperature of 25° with a photographic element having two gelatino layers coated in a superposed relationship on one side of a support and having sound record and picture record areas in those layers, the underlying layer containing photographically developed silver in both areas and the outer layer containing in the sound track area silver photographically developed from silver halide of about 0.1 micron average grain size, coated at 140 mg. gelatin and 70 mg. silver per square foot, will prevent the bleaching of a sufficient amount of the silver in the sound record area to result in an infrared density of at least 1.20 measured at 900 nm. while not preventing substantially complete bleaching of the developed silver of the underlying layer in the picture when the element is treated for 90 seconds at a temperature of 25° C. with a photographic bleach-fix solution of the following composition:

NaFeEDTA[1] (13% Fe)	g	60
Na_2SO_3	g	12
NH_4SCN	g	12
Na_4EDTA[1]	g	7
Ammonium thiosulfate (60% solution)	ml	200
Water to 1 liter.		
pH		6.68

[1] EDTA—Ethylenediamine tetraacetic acid.

In conducting the above test, the contact time with the bleach inhibitor solution is selected to give highest sound record silver retention and lowest picture record silver retention, using the guidelines given above.

We have found that organic compounds which exhibit particular utility as ballasted bleach inhibitors as defined above are thio- and selenol-containing compounds which are substituted with or contain a hydrophobic moiety such as a medium to long alkyl chain. One function of this moiety is to act as a ballast to control the rate of diffusion of the ballasted bleach inhibitor into the hydrophilic colloid of the silver halide emulsion layer. Examples of such compounds are mercapto- and selenol-substituted alkanoic acids, especially 2-mercapto alkanoic acids, thio- and selenol-substituted aryls such as thiophenols, thionaphthols, alkyl- and alkyl-amidothiophenols and thionaphthols, ballasted thiol- and selenol-substituted heterocyclic compounds containing at least one nitrogen atom such as alkylamidomercaptobenzoxazoles, alkylamidomercaptobenzothiazoles, alkylamidomercaptobenzimidazoles, alkylamidomercaptothiadiazoles, alkylthiomercaptothiadiazoles, alkylamidomercaptotriazoles, 1-alkylamidophenyl-5-mercaptotetrazoles and mercaptoquinolines, alkylamido- and alkylmercaptoquinolines, ballasted thiocarboxylic acids and esters thereof such as alkyl- and alkylamidothiobenzoic acid.

Particularly useful bleach inhibitors that can be used in the invention have the following general formulae:

(I) $R^1_a{-}(A^1){-}XR^5$

(II) $R^2_a{-}(A^2){-}X{-}X{-}(A^3){-}R^3$

(III) $R^4_a{-}(A^4){-}X^{\ominus}Y^{\oplus}$

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^1, R^2, R^3 and R^4 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 and preferably having 5 to 18 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, cyclohexadienyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl 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), aralkyl (e.g., benzyl, phendodecyl, tolyldodecyl 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), alkoxycarbonylaryl (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, azetidinylsulfonylphenyl, 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); aryloxy (e.g., phenoxy, toluoxy and the like);

R^5 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^1, A^2, A^3 and A^4 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, benzisoxazoloyl 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-dioxolanyl, 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[3,4d]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, benzothiadiazolyl, 1,2-dithiolyl, 1,3-dithiolyl, 1,3-oxathiolyl, thianthrinyl, thiamorpholinyl, 1,4-thianyl, 1,4-dithanyl, 1,4-dithiadienyl, selenazolyl, benzoselenazolyl, isoselenazolyl, benzisoselenazolyl, selenadiazolyl, benzoselenadiazolyl and the like; such that R^1, R^2, R^3, and R^4 do not represent a carbonyl group, a carbamoyl group or an amido group $R^2_a(A^2)$, the grouping $R^3_a(A^3)$ and the grouping when A^1, A^2, A^3 and A^4 represent carbonyl or thiocarbonyl and such that the grouping $R^1_a(A^1)$, the grouping $R^2_a(A^2)$, the grouping $R^3_a(A^3)$ and the grouping $R^4_a(A^4)$ each represent a moiety having a molecular weight of from 125 to 1,000 and preferably from 175 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 and such that when A^1, A^2, A^3 and A^4 represent a carbocyclic or a heterocyclic ring said ring has attached to it a hydrophobic moiety such as the atoms necessary to complete a 5 to 6 membered carbocyclic or heterocyclic ring fused to said ring; an alkyl group having from 6 to 18 carbon atoms; an alkylamido group having from 6 to 18 carbon atoms and an aryl group such as phenyl, naphthyl and an alkylamidoaryl group having 6 to 18 carbon atoms in the alkyl moiety and the like or has attached to it a plurality of such hydrophobic moieties, the total effect of which is to impart similar hydrophobic character such as two alkylamido groups having 3 to 12 carbon atoms and two alkylamidoaryl groups having 3 to 12 carbon atoms in the alkyl moiety.

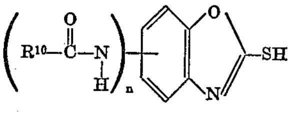
Many heterocyclic compounds having a molecular weight of less than 100 (exclusive of the mercapto group) such as those compounds shown in British Pat. 1,138,842 have been found not to be bleach inhibitors but rather bleach accelerators. Compounds of this type do not fall within the meaning of the term 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 I, II and III 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 LXIII and LXIV. Examples of compounds which can be treated to increase the number of acidic thiol groups are bleach inhibitors IX and X. Another example of thiol-forming compounds are disulfides (i.e., compounds of Formula II above) which cleave at the sulfur atoms to yield at least one thiol compound.

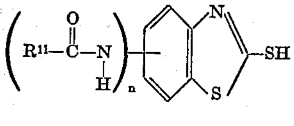
The acidity of the thiol and selenol groups can be imparted by the group to which these groups are attached (e.g., a heterocyclic or carbocyclic ring). Alternatively, other groups attached to the group having the thiol and selenol groups can impart acidity. For example, a carboxylic acid group on a carbon atom adjacent to the atom to which these groups are attached (e.g., 2-mercapto-lauric 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 general formulae exhibit particular utility as bleach inhibitors in the present invention:

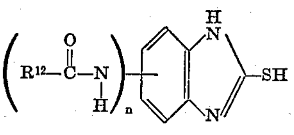
(IV) 2-mercaptobenzoxazoles



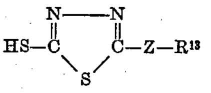
(V) 2-mercaptobenzothiazoles



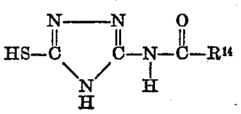
(VI) 2-mercaptobenzimidazoles



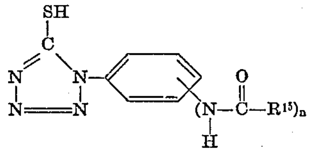
(VII) 2-mercaptothiadiazoles



(VIII) 2-mercaptotriazoles



(IX) 1-phenyl-5-mercaptotetrazoles



wherein:

R^{10}, R^{11}, R^{12} and R^{15} each represents an alkyl group having from 1 to 17 carbon atoms and preferably 5 to 12 carbon atoms;

R^{13} and ^{14} each represents an alkyl group of from 5 to 17 and preferably from 8 to 12 carbon atoms;

Z represents sulfur or the group —NHCO—; and

n represents 1 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:

(I) 2-mercaptolauric acid
(II) 4-octylthiobenzoic acid
(III) 2-naphthalenethiol
(IV) 4-butyl-2-naphthalenethiol
(V) 2-quinolinethiol
(VI) 4-quinolinethiol
(VII) 4-hexyl-2-quinolinethiol
(VIII) 5-pentyl-4-benzopyrimidinethiol
(IX) 3-(5-mercapto-1,2,4-triazol-3-ylthio)-propanoic acid
(X) 1-(5-mercapto-1,2,4-triazol-3-ylthio)-butan-2-one
(XI) 3-mercapto-4-phenyl-5-n-undecyl-1,2,4-triazole
(XII) 1-(3-octanamidophenyl)-5-mercaptotetrazole
(XIII) 1-(3-heptafluorobutramidophenyl)-5-mercaptotetrazole
(XIV) 1-{3-[2-(2,4-di-t-amylphenoxy)-acetamido]-phenyl}-5-mercaptotetrazole
(XV) 1-(4-methoxybenzyl)-5-mercaptotetrazole
(XVI) 1-[4-(1-piperidinylsulfonyl)-phenyl]-5-mercaptotetrazole
(XVII) 1-(3-trifluoromethylphenyl)-5-mercaptotetrazole
(XVIII) 1-(1-naphthyl)-5-mercaptotetrazole
(XIX) 1-(2-naphthyl)-5-mercaptotetrazole
(XX) 1-(3-pentanamidophenyl)-5-mercaptotetrazole
(XXI) 1-(3-hexanamidophenyl)-5-mercaptotetrazole
(XXII) 1-(3-heptanamidophenyl)-5-mercaptotetrazole
(XXIII) 1-(3-octanamidophenyl)-5-mercaptotetrazole
(XXIV) 1-(3-nonanamidophenyl)-5-mercaptotetrazole
(XXV) 1-(3-decanamidophenyl)-5-mercaptotetrazole
(XXVI) 1-(3-undecanamidophenyl)-5-mercaptotetrazole
(XXVII) 1-(3-dodecanamidophenyl)-5-mercaptotetrazole
(XXVIII) 1-(3-tridecanamidophenyl)-5-mercaptotetrazole
(XXIX) 1-(3-tetradecanamidophenyl)-5-mercaptotetrazole
(XXX) 1-(2,4-di-butanamidophenyl)-5-mercaptotetrazole
(XXXI) 1-(2,4-di-propanamidophenyl)-5-mercaptotetrazole
(XXXII) 1-(2,4,6-tri-acetamidophenyl)-5-mercaptotetrazole
(XXXIII) 2-mercapto-6-pentanamido-1,3-benzothiazole
(XXXIV) 2-mercapto-6-hexanamido-1,3-benzothiazole
(XXXV) 2-mercapto-6-heptanamido-1,3-benzothiazole
(XXXVI) 2-mercapto-6-octanamido-1,3-benzothiazole
(XXXVII) 2-mercapto-6-nonanamido-1,3-benzothiazole
(XXXVIII) 2-mercapto-6-decanamido-1,3-benzothiazole
(XXXIX) 2-mercapto-6-undecanamido-1,3-benzothiazole
(XL) 2-mercapto-6-dodecanamido-1,3-benzothiazole
(XLI) 2-mercapto-6-tridecanamido-1,3-benzothiazole
(XLII) 2-mercapto-6-tetradecanamido-1,3-benzothiazole
(XLIII) 2-mercapto-4,7-di-butanamido-1,3-benzothiazole
(XLIV) 2-mercapto-4,6,7-tri-acetanamido-1,3-benzothiazole
(XLV) 2-mercapto-5-hexanamido-1,3,4-thiadiazole

(XLVI) 2-mercapto-5-heptanamido-1,3,4-thiadiazole
(XLVII) 2-mercapto-5-octanamido-1,3,4-thiadiazole
(XLVIII) 2-mercapto-5-nonanamido-1,3,4-thiadiazole
(XLIX) 2-mercapto-5-decanamido-1,3,4-thiadiazole
(L) 2-mercapto-5-undecanamido-1,3,4-thiadiazole
(LI) 2-mercapto-5-dodecanamido-1,3,4-thiadiazole
(LII) 2-mercapto-5-tridecanamido-1,3,4-thiadiazole
(LIII) 2-mercapto-5-tetradecanamido-1,3,4-thiadiazole
(LIV) 2-pentylthio-5-mercapto-1,3,4-thiadiazole
(LV) 2-hexylthio-5-mercapto-1,3,4-thiazole
(LVI) 2-heptylthio-5-mercapto-1,3,4-thiadiazole
(LVII) 2-octylthio-5-mercapto-1,3,4-thiadiazole
(LVIII) 2-nonylthio-5-mercapto-1,3,4-thiadiazole
(LIX) 2-decylthio-5-mercapto-1,3,4-thiadiazole
(LX) 2-undecyl-5-mercapto-1,3,4-thiadiazole
(LXI) 2-dodecyl-5-mercapto-1,3,4-thiadiazole
(LXII) 2,4-dihexanamido-6-mercaptopyrimidine
(LXIII) 1-(1-phenyltetrazol-5-ylthio)-butan-3-one
(LXIV) 2-(1-phenyltetrazol-5-ylthio)-ethylphenylketone
(LXV) 3-decanamido-2-oxirenthiol
(LXVI) 5-(5-trichloropentanamido)-2-furanthiol
(LXVII) 6-(10-sulfodecyl)-2-benzofuranthiol
(LXVIII) 6-(8-sulfatooctyl)-3-isobenzofuranthiol
(LXIX) 4-butylsulfonylhexyl-1-dibenzofuranthiol
(LXX) 4-(7-cyanoheptyl)-2-oxazolthiol
(LXXI) 6-hexanamido-1,3-benzoxazol-2-thiol
(LXXII) 6-heptanamido-1,3-benzoxazol-2-thiol
(LXXIII) 6-octanamido-1,3-benzoxazol-2-thiol
(LXXIV) 6-nonanamido-1,3-benzoxazol-2-thiol
(LXXV) 6-decanamido-1,3-benzoxazol-2-thiol
(LXXVI) 6-undecanamido-1,3-benzoxazol-2-thiol
(LXXVII) 6-dodecanamido-1,3-benzoxazol-2-thiol
(LXXVIII) 5-octanamido-1,3-benzoxazol-2-thiol
(LXXIX) 5-decanamido-1,3-benzoxazol-2-thiol
(LXXX) 4,7-di-butanamido-1,3-benzoxaol-2-thiol
(LXXXI) 7-(4-butanamidobenzyl)-3-benzisoxazolthiol
(LXXXII) 4-propoxypentyl-2,1,3-oxadiazol-5-thiol
(LXXXIII) 4-phenoxybutyl-1,2,3-oxadiazol-5-thiol
(LXXXIV) 7-(7-hexylenebenzoate)-2,1,3-benzoxadiazol-4-thiol
(LXXXV) 7-(4-butyleneacetate)-1,2,3-benzoxadiazol-4-thiol
(LXXXVI) 4-(6-ethylhexanoate)-1,2-pyran-2-ylthiol
(LXXXVII) 4-(3-phenylhexanoate)-1,4-pyran-2-ylthiol
(LXXXVIII) 8-butanamidoethyl-2(H)-benzopyran-4-ylthiol
(LXXXIX) 8-phenamidobutyl-4(H)-benzopyran-2-ylthiol
(XC) 4-(2-ethyl-4-hexanamidophenyl)-dioxazol-2-ylthiol
(XCI) 4-(2-hexanamido-4-sulfatophenyl)-benzodioxazol-2-ylthiol
(XCII) 2-butyl-5-(2,4-dinitrophenyl)-1,2-oxazin-3-ylthiol
(XCIII) 4-(2-mercapto-1,3-oxazin-4-yl)-benzoic acid, butyl ester
(XCIV) 3-(4-benzylphenyl)-1,4-oxazin-5-ylthiol
(XCV) 4-(4-butoxyphenyl)-morpholin-3-ylthiol
(XCVI) 4-(4-phenoxyphenyl)-1,3-dioxolan-2-ylthiol
(XCVII) 5-hexanamido-6-(4-phenylenebutanoate)-1,3-oxathian-2-ylthiol
(XCVIII) 5-octanamido-6-(4-ethylbenzoate)-1,4-oxathian-2-ylthiol
(XCIX) 6-(4-phenylbenzoate)-1,2-dioxan-3-ylthiol
(C) 8-(2-mercapto-1,3-dioxanol-5-ylthio)-octanamido, n-butyl
(CI) 4-(2-mercapto-1,4-dioxanol-3-ylthiol)-benzamide, n-butyl
(CII) 2-(3-hexanamidophenylthio)-1,4-dioxin-3-ylthiol
(CIII) 4′-(5-mercapto-1,2,4-triazol-3-ylthiol)-4-butanamidoacetophenone
(CIV) 2-(5-mercapto-1,2,4-triazol-3-ylthiol)-4-butanamidoacetophenone
(CV) 4-(5-mercapto-1,2,4-triazol-3-ylthiol)-benzophenone

(CVI) 4-dodecanamido-1,2-diazet-3-ylthiol
(CVII) 1-(4-hexanamidobenzyl)-5-mercaptotetrazole
(CVIII) 2-(4-phenoxybutanamido)-5-mercapto-1,3,4-thiadiazole
(CIX) 1-(3-octanamidophenyl)-pyrrol-2-ylthiol
(CX) 1-ethyl-3-n-octylthio-indol-2-ylthiol
(CXI) 2-ethyl-3-octanamido-isoindol-1-ylthiol
(CXII) 1-methyl-4-hexyl-carbazol-2-ylthiol
(CXIII) 7-nonanamidopyrrocolin-3-ylthiol
(CXIV) 4-ethylacridin-2-ylthiol
(CXV) 5-butanamido-2-phenanthridinylthiol
(CXVI) 3-ethyl-4-heptanamido-2-imidazolin-2-ylthiol
(CXVII) 6-hexanamido-1,3-benzimidazol-2-thiol
(CXVIII) 6-heptanamido-1,3-benzimidazol-2-thiol
(CXIX) 6-octanamido-1,3-benzimidazol-2-thiol
(CXX) 6-nonanamido-1,3-benzimidazol-2-thiol
(CXXI) 6-decanamido-1,3-benzimidazol-2-thiol
(CXXII) 6-undecanamido-1,3-benzimidazol-2-thiol
(CXXIII) 6-dodecanamido-1,3-benzimidazol-2-thiol
(CXXIV) 4,7-di-n-butanamido-1,3-benzimidazol-2-thiol
(CXXV) 4,5,7-tri-acetamido-1,3-benzimidazol-2-thiol
(CXXVI) 5-octanamido-1,3-benzimidazol-2-thiol
(CXXVII) 5-decanamido-1,3-benzimidazol-2-thiol
(CXXVIII) 4-octanamido-2-pyridinylthiol
(CXXIX) 4-(3-hexanamidophenyl)-2-pyridazinylthiol
(CXXX) 3-(3-hexanamidophenyl)-pyrazin-2-ylthiol
(CXXXI) 3-butanamidoquinoxalin-2-ylthiol
(CXXXII) 1-octylphthalazin-4-ylthiol
(CXXXIII) 5-benzylamidophenylquinolin-2-ylthiol
(CXXXIV) 5-butylphenazin-2-ylthiol
(CXXXV) 5-methylphenoxyazin-2-ylthiol
(CXXXVI) 5-chlorophenothiazin-2-ylthiol
(CXXXVII) 5-n-decylthio-1,2,4-triazin-3-ylthio
(CXXXVIII) 5-(3-octanamidophenyl)-6-benzotriazolylthiol
(CXXXIX) 4-hexanamido-1(H)-azepin-2-ylthiol
(CXL) 1-(3-phenylpropyl)-2-piperidinylthiol
(CXLI) 1,3-dihexyl-2-imidazolidinylthiol
(CXLII) 2-octylthio-5-thienylthiol
(CXLIII) 5-hexanamido-2-benzothienylthiol
(CXLIV) 5-octylthio-2-thiazolylthiol
(CXLV) 5-hexanamido-1,2,3-benzothiadiazol-6-ylthiol
(CXLVI) 4-(3-decanamidophenyl)-1,3-dithiol-2-ylthiol
(CXLVII) 4-(3-octanamidophenyl)-1,3-oxathiol-2-ylthiol
(CXLVIII) 6-hexanamido-4-hexyl-3-thiamorpholinylthiol
(CXLIX) 5-butanamido-4-(4-phenylbutyl)-1,4-thianin-3-ylthiol
(CL) 4-(3-octanamidophenyl)-2-selenazolylthiol
(CLI) 5-benzamido-2-benzoselenazolylthiol
(CLII) 5-decanamido-3-benzoisoselenazolylthiol
(CLIII) 4-(3-hexanamidophenyl)-3-isoselenazolylthiol
(CLIV) 4-decanamido-2,1,3-selenadiazol-5-ylthiol
(CLV) 4-(3-hexanamidophenyl)-2,1,3-benzoselenadiazol-7-ylthiol
(CLVI) 2-naphthaleneselenol
(CLVII) 1-(2,4-di-n-butanamidophenyl)-tetrazol-5-ylselenol
(CLVIII) 1-(2,4,6-tri-acetamidophenyl)-tetrazolyl-5-ylselenol
(CLIX) 1-(3-hexanamidophenyl)-tetrazol-5-ylselenol
(CLX) 1-(3-heptanamidophenyl)-tetrazol-5-ylselenol
(CLXI) 1-(3-octanamidophenyl)-tetrazol-5-ylselenol
(CLXII) 1-(3-nonanamidophenyl)-tetrazol-5-ylselenol
(CLXIII) 1-(3-decanamidophenyl)-tetrazol-5-ylselenol
CLXIV) 1-(3-undecanamidophenyl)-tetrazol-5-ylselenol
(CLXV) 1-(3-dodecanamidophenyl)-tetrazol-5-ylselenol
(CLXVI) 4,7-di-tert-amylamido-1,3-benzoselenazol-2-ylselenol
(CLXVII) 4,5,7-tri-acetamido-1,3-benzoselenazol-2-ylselenol
(CLXVIII) 6-octanamido-1,3-benzoselenazol-2-ylselenol
(CLXIX) 6-nonanamido-1,3-benzoselenazol-2-ylselenol
(CLXX) 6-decanamido-1,3-benzoselenazol-2-ylselenol
(CLXXI) 6-undecanamido-1,3-benzoselenazol-2-ylselenol
(CLXXII) 6-dodecanamido-1,3-benzoselenazol-2-ylselenol
(CLXXIII) 5-octanamido-1,3,4-selenadiazol-2-ylselenol
(CLXXIV) 5-decanamido-1,3,4-selenadiazol-2-ylselenol
(CLXXV) 5-octanamido-1,3,4-thiadiazol-2-ylselenol
(CLXXVI) 5-decanamido-1,3,4-thiadiazol-2-ylselenol
(CLXXVII) 2-octylthio-1,3,4-thiadiazol-2-ylselenol
(CLXXVIII) 2-nonylthio-1,3,4-thiadiazol-2-ylselenol
(CLXXIX) 2-decylthio-1,3,4-thiadiazol-2-ylselenol
(CLXXX) 2-heptylthio-1,3,4-selenadiazol-2-ylselenol
(CLXXXI) 2-octylthio-1,3,4-selenadiazol-2-ylselenol
(CLXXXII) 2-decylthio-1,3,4-selenadiazol-2-ylselenol
(CLXXXIII) oxalic-bis-N-[3-(5-mercaptotetrazol-1-yl)-anilide]
(CLXXXIV) suberic-bis-N-[3-(5-mercaptotetrazol-1-yl)-anilide]
(CLXXXV) terephthalic-bis-N-[3-(5-mercaptotetrazol-1-yl)-anilide]
(CLXXXVI) disulfide,bis-1-(3-nonanamidophenyl)-tetrazol-1-yl
(CLXXXVII) disulfide,bis-1-(3-hexanamidophenyl)-tetrazol-1-yl
(CLXXXVIII) disulfide,bis-6-octanamido-1,3-benzothiazol-2-yl
(CLXXXIX) disulfide,bis-6-hexanamido-1,3-benzothiazol-2-yl
(CXC) disulfide,bis-5-hexanamido-1,3,4-thiadiazol-2-yl
(CXCI) disulfide,bis-5-nonanamido-1,3,4-thiadiazol-2-yl
(CXCII) disulfide,bis-2-heptylthio-1,3,4-thiadiazol-5-yl
(CXCIII) disulfide,bis-2-octylthio-1,3,4-thiadiazol-5-yl
(CXCIV) 1-(3-octanamidophenyl)-5-mercaptotetrazole, sodium salt
(CXCV) 1-(3-nonanamidophenyl)-5-mercaptotetrazole, potassium salt
(CXCVI) 2-octylthio-5-mercapto-1,3,4-thiadiazol, ammonium salt

The method of our invention is useful to prevent bleaching of sound records and auxiliary silver images by both bleach compositions and bleach-fix compositions. Bleach compositions contain only an oxidizing agent and oxidize the metallic silver to a silver salt which is subsequently removed by treatment with a silver halide solvent. Bleach-fixing compositions contain both an oxidizing agent and a silver halide solvent and accomplish removal of developed silver in one step.

A further understanding of my improved method of processing photographic elements having an auxiliary image-forming layer can be had by referring to the drawing in the Bello et al. application referred to above. This drawing depicts diagrammatically and sequentially the processing of one embodiment of the novel photographic element of that invention 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 in the composition of the bleach inhibitor composition.

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

EXAMPLE 1

Three multilayer color photographic motion picture negative-positive print films 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, respectively, and over the color-forming units outermost from the support one of the following auxiliary gelatino silver halide layers—

Film:	Contents
A	25 mg./sq. ft. silver as silver chlorobromide of about 0.2 micron average grain size and containing 80 mole percent chloride and 20 mole percent bromide and 113 mg./sq. ft. gelatine.
B	As in A plus 46 mg./sq. ft. magenta coupler 1 - (6-chloro-2,4-dimethylphenyl) - 3 - [α - (m - pentadecylphenoxy) - butyramido]-5-pyrazolone and 23 mg./sq. ft. tricresyl phosphate as coupler solvent.
C	As in B except without coupler solvent.

are exposed through a step exposure object in the sound track area and through a Wratten 2B, 0.25R, 0.20M and 0.10 neutral density filter pack to a step exposure object in the picture area and processed as follows:

(1) Prebath	15 sec.
(2) Wash	Do.
(3) Color develop	8 min.,45 sec.
(4) Wash	15 sec.
(5) Stop bath	2 min.
(6) Wash	1 min.
(7) Bleach inhibitor bath	Do.
(8) Wash	Do.
(9) Bleach-fix	2 min.
(10) Wash	6 min.
(11) Stabilizer	15 sec.
Process temperature	24° C.

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.	

(3) COLOR DEVELOPER

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

(5) STOP BATH

Acetic acid, glacial ml	24.5
Sodium bisulfite g	6.4
Water to make 1 liter.	

(7) BLEACH INHIBITOR BATH

Series 1

	G.
Trisodium phosphate, dodecahydrate	19.0
1-(3-nonanamidophenyl)-5-mercaptotetrazole	0.4
Sodium thiocyanate (as silver halide solvent if specified)	2.0
Water to make 1 liter.	
pH adjusted to 12.1.	

Series 2

	G.
Trisodium phosphate, dodecahydrate	19.0
1-(3-nonanamidophenyl)-5-mercaptotetrazole	0.4
Sodium sulfite (as silver halide solvent if specified)	10.0
Water to make 1 liter.	
pH adjusted to 12.1.	

(9) BLEACH-FIX

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.	

(11) STABILIZER

	Ml.
Formaldehyde (37% w. solution)	20
Octylphenoxy polyethoxy ethanol (Triton X–100)	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 is measured at 900 nm. on a densitometer in the step of maximum density. The picture record area silver density is measured in a similar manner at the tenth step exposure. The results shown in Table I below demonstrate the advantage of incorporating a silver halide solvent in the bleach inhibitor bath.

TABLE I

		Silver density ($D_{max.}$)			
		Without silver halide solvent		With silver halide solvent	
Bleach inhibitor series	Film	Picture	Sound	Picture	Sound
1	A	0.88	1.96	0.04	2.00
1	B	0.38	1.98	0.05	1.90
1	C	0.58	1.95	0.05	1.86
2	A	0.88	1.96	0.04	2.18
2	B	0.38	1.98	0.05	2.08
2	C	0.58	1.95	0.14	1.96

The above results demonstrate that the effectiveness of the auxiliary layer to prevent the diffusion of the bleach inhibitor into the underlying picture recording layers in the picture record area and thereby prevent the bleaching of silver in these layers is markedly increased by the incorporation of a silver halide solvent into the bleach inhibitor bath. Similar results are obtained when other silver solvents such as sodium thiosulfate and 1,8-dihydroxy-3,6-dithiaoctane are substituted for the above silver halide solvents. These results demonstrate that it is advantageous to use a bleach inhibitor bath containing silver halide solvent. When the above films are exposed to a multicolor image as well as a sound track record and processed as above using bleach inhibitor baths containing a silver halide solvent motion picture film having a yellow, magenta and cyan picture record substantially free of silver and an excellent sound record comprised of silver are obtained.

EXAMPLE 2

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 as in Example 1 and over the color-forming units outermost from the support an unsensitized auxiliary gelatino silver halide layer containing 113 mg./ft.^{2} gelatin, 25 mg./sq. ft. silver as silver chlorobromide (80/20) of about 0.1 micron average grain size and 45 mg./sq. ft. magenta coupler of Example 1, film *b* and 23 mg./sq. ft. tricresyl phosphate as coupler solvent is exposed for $\frac{1}{25}$ second through a Wratten 18A filter (transmits radiation of 300 to 400 nm.) to a step tablet in the sound track area and for $\frac{1}{100}$ second through a filter pack comprised of 0.10R, 0.30M, 1.00 neutral density and Wratten 2B filters to a 21 step 0.15 log E increment step tablet in the picture area and processed as follows:

(1) Prebath	15 sec.
(2) Wash	Do.
(3) Color develop	8 min., 45 sec.
(4) Wash	15 sec.
(5) Stop bath	2 min.
(6) Wash	1 min.
(7) Bleach inhibitor	As indicated below.
(8) Wash	1 min.
(9) Bleach-fix	2 min.
(10) Wash	6 min.
(11) Stabilizer	10 sec.
Process temperature	24° C.

The chemical composition of baths 1, 3, 5, 9 and 11 are the same as the correspondingly numbered baths of Example 1. The composition of bath 7 is shown below:

(7) BLEACH INHIBITOR BATH

1-(3-nonanamidophenyl)-5-mercaptotetrazole	g	0.4
Sodium hydroxide	g	8.0
Sodium thiocyanate	g	2.0
Water	ml	400
Methanol	ml	600

The silver densities of the picture record and sound track record areas are measured in the same manner as in Example 1. The results are set forth in Table II.

TABLE II

Bleach inhibitor treatment time	Silver density	
	Picture	Sound
2 minutes	0.06	1.15
3 minutes	0.06	2.11

The above results demonstrate that satisfactory results are obtained when the bleach inhibitor composition is predominantly non-aqueous. When the above film is exposed to a multicolor image and a sound track record and processed as above, motion picture films having a yellow, magenta and cyan dye picture record substantially free of silver and an excellent sound record comprised of silver are obtained.

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. A photographic processing composition comprising a ballasted silver bleach inhibitor and a silver halide solvent.

2. A photographic processing composition comprising an aqueous solution containing a ballasted silver bleach inhibitor and a silver halide solvent.

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

(I) $R^1_a\text{-}(A^1)\text{-}XR^5$

(II) $R^2_a\text{-}(A^2)\text{-}X\text{—}X\text{-}(A^3)\text{-}R^3_a$ and

(III) $R^4_a\text{-}(A^4)\text{-}X^{\ominus}Y^{\oplus}$

wherein:

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

X represents sulfur or selenium;

R^1, R^2, R^3 and R^4 each represents 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 or an aryloxy group;

R^5 represents hydrogen or an acyl group;

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

A^1, A^2, A^3 and A^4 each represents a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring or 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^1, R^2, R^3 and R^4 do not represent a carbonyl group, a carbamoyl group or an amido group when A^1, A^2, A^3 and A^4 represent a carbonyl group or a thiocarbonyl group and such that the grouping $R^1_a\text{-}(A^1)\text{-}$, the grouping $R^2_a\text{-}(A^2)\text{-}$, the grouping $R^3_a\text{-}(A^3)\text{-}$ and the grouping $R^4_a\text{-}(A^4)\text{-}$ each represents a moiety having a molecular weight of from 125 to 1,000 and such that when A^1, A^2, A^3 and A^4 represent a carbocyclic ring or a heterocyclic ring, each said carbocyclic or heterocyclic ring being substituted with a hydrophobic moiety, and a silver halide solvent.

4. The photographic processing composition of claim 3 wherein the grouping $R^1_a\text{-}(A^1)\text{-}$, the grouping $R^2_a\text{-}(A^2)\text{-}$, the grouping $R^3_a\text{-}(A^3)\text{-}$ and the grouping $R^4_a\text{-}(A^4)\text{-}$ each represents a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, said ring containing at least one nitrogen atom and X represents sulfur.

5. The photographic processing composition of claim 4 wherein the grouping $R^1_a\text{-}(A^1)\text{-}$, the grouping $R^2_a\text{-}(A^2)\text{-}$, the grouping $R^3_a\text{-}(A^3)\text{-}$ and the grouping $R^4_a\text{-}(A^4)\text{-}$ each represents a member selected from the group consisting of an alkylamidobenzoxazole nucleus, an alkylamidobenzothiazole nucleus, an alkylamidobenzimidazole nucleus, an alkylamidothiadiazole nucleus, an alkylthiothiadiazole nucleus, an alkylamidobenzotriazole nucleus and a 1-alkylamidophenyltetrazole nucleus.

6. The photographic processing composition of claim 5 wherein the silver halide solvent is 1,8-dihydroxy-3,6-dithiaoctane.

7. The photographic processing composition of claim 5 wherein the silver halide solvent is selected from the group consisting of inorganic salts having a cation selected from the group consisting of ammonium, sodium and potassium ions and an anion selected from the group consisting of sulfite, thiocyanate and thiosulfate ions.

8. A photographic processing composition having a pH of about 8 to 12.5 comprising an aqueous solution containing 10^{-5} to 10^{-11} moles per liter 1-(3-nonanamidophenyl)-5-mercaptotetrazole and 0.05% weight to 5% weight sodium thiocyanate.

9. In the process of producing a picture record and an auxiliary silver image record in an imagewise exposed photographic element which element comprises a support having coated thereon, on one surface in order from the support, (1) a picture recording photographic image-forming unit comprising at least one silver halide emulsion layer and (2) an auxiliary layer comprising image-recording radiation sensitive silver halide which does not form an image upon image-forming exposure of said picture recording unit which process comprises (A) developing a picture record in said picture recording unit comprising silver and a nondiffusible dye and developing an auxiliary image record in said auxiliary layer comprising silver, (B) contacting said auxiliary layer with a ballasted silver bleach inhibitor to adsorb said bleach inhibitor onto at least the silver record in said auxiliary layer and (C) removing the bleachable silver images remaining after step (B) and the residual silver halide, the improvement which comprises carrying out step (B) in the presence of a silver halide solvent.

10. In the process of producing a picture record and a silver sound record in an imagewise exposed photographic element which element comprises a support having coated thereon, on one surface in order from the support, (1) a picture recording photographic image-forming unit comprising at least one silver halide emulsion layer and (2) an auxiliary layer comprising image-recording radiation sensitive silver halide which does not form an image upon image-forming exposure of said picture recording unit which process comprises (A) developing a picture record in said picture recording unit comprising silver and a nondiffusible dye and developing a sound record in said auixilary layer comprising silver, (B) contacting said auxiliary layer with a ballasted silver bleach inhibitor to adsorb said bleach inhibitor onto at least the silver record in said auxiliary layer and (C) removing the bleachable silver images remaining after step (B) and the residual silver halide, the improvement which comprises carrying out step (B) in the presence of a silver halide solvent.

11. The improvement of claim **10** wherein said ballasted silver bleach inhibitor has a formula selected from the group consisting of:

(I) $R^1{}_a(A^1)XR^5$

(II) $R^2{}_a(A^2)X{-}X(A^3)R^3{}_a$ and

(III) $R^4{}_a(A^4)X^{\ominus}Y^{\oplus}$

wherein:

a represents 0, 1, 2, 3, 4, 5 or 6;
X represents sulfur or selenium;
R^1, R^2, R^3 and R^4 each represents 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 or an aryloxy group;
R^5 represents hydrogen or an acyl group;
$Y^{\oplus}$ represents a basic cation;
A^1, A^2, A^3 and A^4 each represents a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring or 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^1, R^2, R^3 and R^4 do not represent a carbonyl group, a carbamoyl group or an amido group when A^1, A^2, A^3 and A^4 represent a carbonyl group or a thiocarbonyl group and such that the grouping $R^1{}_a(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a moiety having a molecular weight of from 125 to 1,000 and such that when A^1, A^2, A^3 and A^4 represent a carbocyclic ring or a heterocyclic ring, each said carbocyclic or heterocyclic ring being substituted with a hydrophobic moiety.

12. The improvement of claim **11** wherein the grouping $R^1{}_a(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, said ring containing at least one nitrogen atom and wherein X represents sulfur.

13. The improvement of claim **11** wherein the grouping $R^1{}_a(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a member selected from the group consisting of an alkyamidobenzoxazole nucleus, an alkylamidobenzothiazole nucleus, an alkylamidobenzimidazole nucleus, an alkylamidothiadiazole nucleus, an alkylthiothiadiazole nucleus, an alkylamidobenzotriazole nucleus and a 1-alkylamidophenyltetrazole nucleus.

14. The improvemen tof claim **13** wherein the silver halide solvent is 1,8-dihydroxy-3,6-dithiaoctane.

15. The improveemnt of claim **13** wherein the silver halide solvent is selected from the group consisting of inorganic salts having a cation selected from the group consisting of ammonium, sodium and potassium ions and an anion selected from the group consisting of sulfite, thiocyanate and thiosulfate ions.

16. In the process of producing a picture record and a silver sound track record in an imagewise exposed photographic element which element comprises a support having coated thereon, on one surface in order from the support, (1) a plurality of picture recording photographic image-forming units comprising 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 layer comprising image-recording radiation sensitive silver halide which does not form an image upon image-forming exposure of said picture recording units which process comprises (A) developing a picture record in said picture recording units comprising silver and a nondiffusible dye and developing a sound track record in said auxiliary layer comprising silver, (B) contacting the auxiliary layer with a ballasted bleach inhibitor to adsorb said bleach inhibitor onto at least the silver of the auxiliary layer and (C) removing the bleachable silver images remaining after step (B) and the residual silver halide, the improvement which comprises carrying out step (B) in the presence of a silver halide solvent.

17. The improvement of claim **16** wherein each said picture recording photographic image-forming unit contains a nondiffusible photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye complementary in color to the sensitivity of the unit in which it is incorporated.

18. The improvement of claim **17** wherein said ballasted silver bleach inhibitor has a formula selected from the group consisting of:

(I) $R^1{}_a(A^1)XR^5$

(II) $R^2{}_a(A^2)X{-}X(A^3{}_a)R^3{}_a$ and

(III) $R^4{}_a(A^4)X^{\ominus}Y^{\oplus}$

wherein:

a represents 0, 1, 2, 3, 4, 5 or 6;
X represents sulfur or selenium;
R^1, R^2, R^3 and R^4 each represents 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 or an aryloxy group;
R^5 represents hydrogen or an acyl group;
$Y^{\oplus}$ represents a basic cation;
A^1, A^2, A^3 and A^4 each represents a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring or 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^1, R^2, R^3 and R^4 do not represent a carbonyl group, a carbamoyl group or an amido group when A^1, A^2, A^3 and A^4 represent a carbonyl group or a thiocarbonyl group and such that the grouping $R^1{}_a(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a moiety having a molecular weight of from 125 to 1,000 and such that when A^1, A^2, A^3 and A^4 represent a carbocyclic ring or a heterocyclic ring, each said carbocyclic or heterocyclic ring being substituted with a hydrophobic moiety.

19. The improvement of claim **18** wherein the grouping $R^1{}_a(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a heteocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, said ring containing at least one nitrogen atom and wherein X represents sulfur.

20. The improvement of claim **18** wherein the grouping $R_{1a}(A^1)$, the grouping $R^2{}_a(A^2)$, the grouping $R^3{}_a(A^3)$ and the grouping $R^4{}_a(A^4)$ each represents a member selected from the group consisting of an alkylamidobenzoxazole nucleus, an alkylamidobenzothiazole nucleus, an alkylamidobenzimidazole nucleus, an alkylamidothiadiazole nucleus, an alkylthiothiadiazole nucleus, an alkylamidobenzotriazole nucleus and a 1-alkylamidophenyltetrazole nucleus.

21. The improvement of claim **20** wherein the silver halide solvent is 1,8-dihydroxy-3,6-dithiaoctane.

22. The improvement of claim **20** wherein the silver halide solvent is selected from the group consisting of inorganic salts having a cation selected from the group consisting of ammonium, sodium and potassium ions and an anion selected from the group consisting of sulfite, thiocyanate and thiosulfate ions.

23. In the process of producing a picture record and a silver sound track record in an imagewise exposed photographic element which element comprises a support having coated thereon, on one surface in order from the support, (1) a plurality of picture recording photographic color-forming units comprising 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 contains a nondiffusible photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusible dye complementary in color to the sensitivity of the unit in which it is incorporated and (2) an auxiliary layer comprising image-recording radiation sensitive silver halide which does not form an image upon image-forming exposure of said picture recording units which process comprises (A) developing a picture record in said picture recording units comprising silver and nondiffusible dyes and developing a sound track record in said auxiliary layer comprising silver, (B) contacting said auxiliary layer with 1-(3-nonanamidophenyl)-5-mercaptotetrazole to adsorb said compound onto at least the silver of the sound track record in said auxiliary layer and (C) removing the bleachable silver images remaining after step (B) and the residual silver halide, the improvement which comprises carrying out step (B) in the presence of sodium thiocyanate.

24. In the process of producing a picture record and an auxiliary silver record in a photographic element exposed to picture and auxiliary exposures, said element comprising a support having coated on one side of the support, in order:

(1) a picture-recording photographic image-recording unit comprising at least one silver halide emulsion layer for recording a picture record in response to said picture exposure; and,

(2) an auxiliary image-recording unit comprising a radiation sensitive silver halide emulsion layer for recording an auxiliary silver record in response to said auxiliary exposure;

which process comprises:

(A) developing a silver record of said auxiliary exposure, at least a portion of said auxiliary silver record being in said auxiliary image-recording unit;

(B) developing a picture record of said picture exposure in said picture-recording unit, said picture record comprising silver and a nondiffusible dye, essentially all of the silver of said picture record being in said picture-recording unit;

(C) bleaching said silver picture record and removing residual silver salts from said picture-recording unit and said auxiliary layer; and,

(D) contacting said silver halide emulsion layer of said auxiliary unit, prior to said bleaching, with a ballasted silver bleach inhibitor to adsorb said bleach inhibitor onto at least a portion of said auxiliary silver record to prevent substantial removal of said auxiliary silver record during step (C);

the improvement in said step (D) which comprises contacting said silver halide emulsion layer of said auxiliary unit with the combination of a silver halide solvent and said bleach inhibitor.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,705,802 Dated December 12, 1972

Inventor(s) John L. Baptista

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

Column 9, lines 54-55, delete "$R^2_a\{A^2\}$, the grouping $R^3_a\{A^3\}$ and the grouping";

Column 18, line 2, (Claim 3), "R" should read ---R^2---;

Column 18, line 52 (Claim 8), "10^{-11}" should read ---10^{-1}---.

Signed and sealed this 10th day of July 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

Rene Tegtmeyer
Acting Commissioner of Patents