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C. F. HOLTZ

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FILM CONTAINING BLEACH-INHIBITOR-RELEASING COMPOUNDS AND
PROCESS FOR PREPARING SILVER AUXILIARY AND SOUND RECORDS
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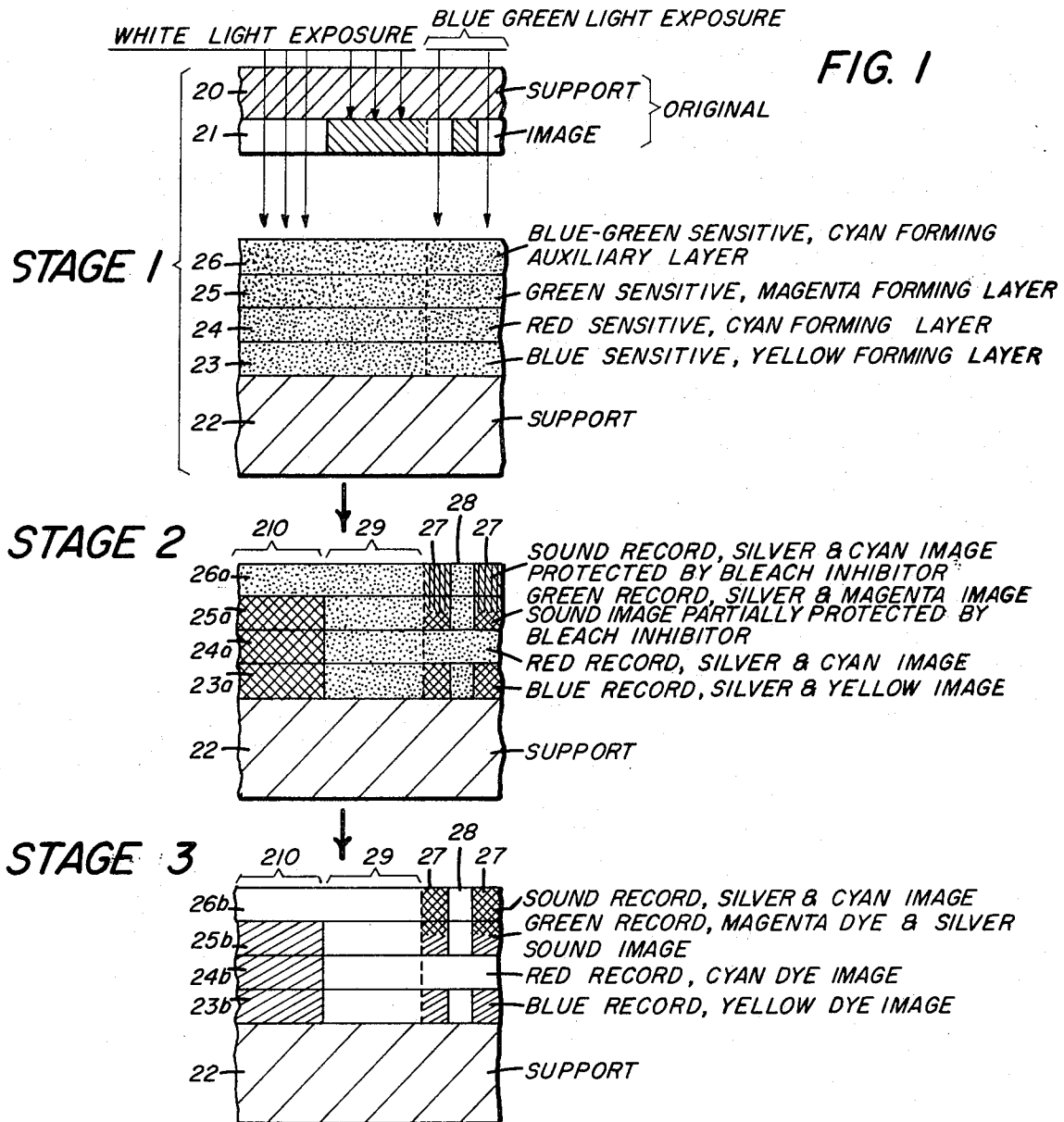
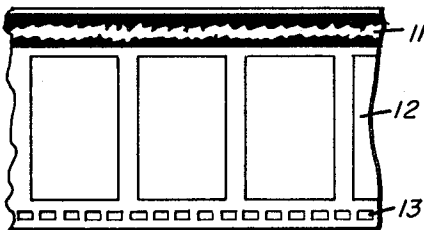


FIG. 2



CARL F. HOLTZ
INVENTOR.

BY *James R. Lufkin*

ATTORNEY

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FILM CONTAINING BLEACH-INHIBITOR-RELEASING COMPOUNDS AND PROCESS FOR PREPARING SILVER AUXILIARY AND SOUND RECORDS

Carl F. Holtz, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.

Continuation-in-part of abandoned application Ser. No. 100,610, Dec. 22, 1970. This application Dec. 17, 1971, Ser. No. 209,450

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64 Claims

ABSTRACT OF THE DISCLOSURE

Processes and elements are provided for forming separate silver and dye image records, the element comprising a support having coated thereon a picture recording photographic unit comprising at least one silver halide emulsion layer and an auxiliary silver image-producing silver halide emulsion layer, and the process including (1) forming dye and a first silver image in said picture recording unit; (2) reacting the silver halide in said auxiliary layer with a photographic developing agent to form a second silver image and oxidized photographic developing agent; and (3) bleaching and fixing the photographic element to remove the residual silver halide and the first silver image while retaining the second silver image. In accordance with the invention, the auxiliary layer contains at least one nondiffusing compound which releases a ballasted silver bleach inhibitor upon reaction with the oxidized developing agent.

This application is a continuation-in-part of my co-pending U.S. patent application Ser. No. 100,610 filed December 22, 1970 and now abandoned.

This invention relates to color photographic films having an auxiliary metallic silver image. In one aspect, this invention relates to color motion picture films having metallic silver sound tracks and more particularly to color photographic elements and processes useful in preparing such motion picture films.

Color photographic films having auxiliary metallic silver images are known. See, for example, French Pat. 912,605. Color motion picture films having silver sound tracks are well 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, a 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, color images can be produced by the dye-bleach process. This process uses a film which has incorporated therein, in three separate layers, each sensitive to a primary color region of the visible spectrum, a preformed subtractive dye which is capable of being destroyed in proportion to the silver formed upon development of a latent photographic image.

Another method of preparing a three-color record by the subtractive dye process is to photographically record an image in a photographic element having three photographic silver halide layers in a superposed relationship to each other, each layer being sensitive to essentially one primary color region of the visible spectrum. These photographic silver halide layers can contain photographic color couplers which form, upon coupling with oxidized aromatic primary amine color developing agent, subtractive dyes essentially complementary to the primary color regions of the visible spectrum. These photographic silver halide layers, can, alternatively, not contain photographic color formers; the color image then being produced by

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processing in a coupler-developer composition to form nondiffusible subtractive dyes. Subsequent to dye image formation the developed silver and the 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 was printed. Optical sound tracks can be of the variable density or variable area types. The sound track itself can be comprised of dyes, dyes plus silver, silver compounds, silver plus other metals or silver alone. The photocell used almost universally to detect light passing through an optical sound track is of such nature that it is most sensitive to electromagnetic radiation of a wavelength greater than 700 nanometers (nm.) with a peak sensitivity at about 800 nm. The subtractive dyes which form the picture image have regions of maximum absorption from 400 to 700 nm. Consequently, these dyes are nearly transparent to infrared radiation and have very little modulating effect upon this radiation to which the photocell is most sensitive.

Silver produced as a result of the chemical reduction of a latent silver halide image is uniformly opaque to the full spectrum of radiation ranging from ultraviolet through visible into the infrared region and acts as an excellent modulator for infrared radiation to which currently used optical photocells are most sensitive. Silver compounds such as silver sulfide and silver toned with metals such as gold are also more opaque than image dyes to infrared radiation. It can thus be seen it is preferable that optical sound records in color motion picture films be comprised of substances other than subtractive image dyes. The presence of subtractive dyes in addition to the other substances, however, is not objectionable.

As noted above, the developed silver and the residual silver halide must be removed from the picture area of a 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 the preferred sound track. A number of techniques have been devised to retain silver in the sound track area of color motion picture films during bleaching and fixing of the silver and residual silver halide in the picture area. For example, the sound track area can be covered with a varnish subsequent to formation of the picture and sound track images and prior to silver and silver halide removal. 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 from the entire film with a suitable solvent and silver halide is removed, reference being made to U.S. Pat. 1,973,463, issued Sept. 11, 1934 and U.S. Pat. 2,113,329, issued Apr. 5, 1938.

A currently used method of retaining metallic silver in the sound track area is to print the picture and sound track images in the photographic silver halide element and develop the latent image to metallic silver. In print films the residual silver halide is removed by fixing the entire film. In reversal films only the sound track area is fixed followed by color reversal development. At this point, both types of film have a sound track of metallic silver free from residual silver halide. The metallic silver is then converted to a fixable silver salt by bleaching both the sound track and picture areas. In the sound track area, the silver salt is reconverted to metallic silver by applying a viscous, highly active developer, for example, by known striping techniques. Subsequently, the silver salt in the picture area is removed by fixing.

Another method of preventing the removal of the silver sound track is to treat the silver metal with a solution which produces a gold tone. This gold-toned silver metal is not removed upon bleaching and fixing, reference being made to U.S. Pat. 2,263,019, issued Nov. 18, 1941.

Still another method is to stripe the sound track area of the film with a quaternary ammonium salt which renders the silver metal unbleachable, reference being made to U.S. Pat. 3,243,295, issued Mar. 29, 1966.

Still another method of retaining silver metal in the sound track area is to prepare a photographic multilayer element which forms a dye in the upper layer during chromogenic development which dye is reducible to a leuco dye which can reduce silver ions in solution to silver metal. The developed sound area is striped with water and passed through a sulfur dioxide gas atmosphere where the gas is absorbed only in the moistened sound track area. The absorbed gas reduces the dye to a leuco dye. The film is then passed through an ammonia-silver nitrate solution where the leuco dye reduces silver ions to silver metal which is deposited in the film, reference being made to U.S. Pat. 2,286,747, issued June 16, 1942.

Alternatively, the silver in the sound track area can be converted to compounds or complexes which resist the bleaching of the silver. For example, silver or silver halide can be converted to silver sulfide prior to bleaching. The sulfide is not converted to a flexible silver salt by bleaching and thus remains as silver sulfide following fixing, reference being made to U.S. Pat. 2,143,787, issued Jan. 10, 1939. The treatment solution can contain both sulfiding and iodizing compounds which also convert the silver to a compound, which is not removed upon bleaching and fixing, reference being made to U.S. Pat. 2,258,976, issued Oct. 14, 1941.

Still another method of preparing a sound track is to coat a separate layer on the back of the film support. Each of the two sides to the film is processed without contacting the other side with the processing solutions, for example, by floating the film on the surface of the solution, reference being made to U.S. Pat. 2,235,033, issued Mar. 18, 1941.

The above techniques refer to only a small number of the patented or known methods or refinements for producing silver or silver complex sound tracks in color motion picture films.

The disadvantage of all methods known today is the requirement of separate treatment of a portion of the film at least once during processing. The method most commonly used today involves the use of a striping device which applies a narrow bead of reagent to the sound track area. In order to use a striping device the film must be taken out of the processing solutions and dried by passing between ringer-type rollers or between squeegees. The film is then passed through the striping device which, in one form, comprises a rotating wheel dipping into a viscous processing solution which is then applied by the wheel in the form of a bead on the edge of the film. The conditions under which this striping process is performed are critical. For example, the striping wheel is only 0.094 inch wide for 16 millimeter film. If the striping wheel picks up an insufficient amount of processing composition, too little will be applied to the film and an inferior sound track can result. If the striping wheel picks up too much processing solution, the bead applied to the film will be too wide and can cover part of the picture area. In this event silver will be retained in the picture area degrading the color image in those areas. Another problem with this type of striping technique is that if the film is vibrated in some manner, the viscous processing composition can flow into the picture area with the same result. Although the striping technique has been refined throughout the years, the conditions under which this process is performed are still so critical that a small amount of error inevitably occurs. Sometimes the error can be corrected by partially reprocessing the film. On other occasions the film is ruined

and must be discarded. Whatever the result of error arising from the striping process and even though the amount of film affected by such error amounts to only a fraction of a percent of the film processed, these errors are economically costly.

It has been found that when a developed silver image is contacted with a silver bleach inhibitor subsequent to initial development 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 the invention of Bevis, Bello and Holtz and is disclosed and claimed in a copending application entitled Process for Preparing Color Film With Silver Sound Record Using Bleach Inhibitor, Ser. No. 100,608 filed Dec. 22, 1970, now abandoned, and the continuation-in-part thereof filed concurrently herewith. Although this method of producing sound tracks represents a significant advance over previously known methods since it involves a single application to the sound track area of a solution, the concentration, temperature and contact time of which are not critical, it still requires separate treatment of the sound track area of the film.

It has also found that certain of the silver bleach inhibitors used in the invention of Bevis et al. can be used for the preparation of silver sound tracks in novel photographic elements by novel processes which are the invention of Bello and Holtz and which are disclosed and claimed in a 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 layer coated outermost from the support and over the picture recording layers. This layer is of such photographic speed or spectral sensitivity or both that no image forms in the layer during picture image-forming exposure of the underlying picture recording layers. Sound record exposure of the novel element is by the necessary wavelength of radiation and of sufficient intensity to form a latent sound record image in at least the auxiliary layer. The so exposed element is then processed according to the disclosed novel process which comprises initial development of the latent image (either to a silver image in reversal print films or a silver and dye image in negative-positive print films), contacting the surface of the entire film with a bleach inhibitor composition, reversal development if necessary and bleach-fixing or bleaching and fixing. The processed element is comprised of a picture record which includes dye and a sound record which includes silver. The use of the novel element and process offers the advantage that at no point in the processing of the element must the sound record or picture record areas of the element be given individual treatment. This is possible because of the auxiliary layer of the element. In the picture record area of the element, the auxiliary layer is not exposed. During initial development the silver halide in this area of this layer does not develop to metallic silver. However, in the sound record area a latent image is formed and is developed to metallic silver. When the element is contacted with bleach inhibitor composition 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). As a result of this differential rate of diffusion of bleach inhibitor through the silver and silver halide of the auxiliary layer, only the silver of the sound record area is contacted with bleach inhibitor and is protected from the bleaching action of the bleach or bleach-fix solutions. Because the bleach inhibitor diffuses more slowly through silver halide, the picture record silver in the underlying layers is not contacted

with bleach inhibitor and remains bleachable. It is, therefore, subsequently bleached and fixed out.

Although this second method represents a significant advance in producing silver sound tracks in color motion picture films, it requires one treatment step (the bleach inhibitor bath step) for the production of the sound track which is not required for the production of the picture record. This process, therefore, requires a processing machine with more processing tanks and is therefore more expensive. It also requires a longer processing time.

Thus, it appears desirable to provide a method by which a silver sound record or auxiliary silver image can be produced in a color photographic film which avoids the need for extra processing steps. In brief, it is desired to produce a high quality silver sound track by a process which requires a minimum of processing steps.

Accordingly, it is an object of my invention to provide a novel method of preparing silver auxiliary images and sound records in color photographic films.

It is a further object of my invention to provide a novel method of preparing silver sound tracks in color motion picture films by simple processing techniques.

It is still a further object of my invention to provide silver sound tracks in color motion picture films by novel processing methods which do not require separate treatment steps for sound track preparation.

It is an object of my invention to provide novel photographic elements for the preparation of silver auxiliary images and sound records in color photographic films.

It is a further object of my invention to provide novel photographic elements for the preparation of silver sound tracks in color motion picture films by simple processing techniques.

It is still a further object of my invention to provide novel photographic elements for the preparation of silver sound tracks in color motion picture films by processing methods which do not require separate treatment steps for sound track preparation.

Other objects will become apparent from the following specification and the appended claims.

These and other objects can be attained by (A) the use of our novel multilayer photographic elements and (B) our novel methods of processing the novel multilayer photographic elements.

In accordance with this invention, processes and elements are provided for forming separate silver and dye image records, the element comprising a support having coated thereon a picture recording photographic unit comprising at least one silver halide emulsion layer, and an auxiliary silver image-producing silver halide emulsion layer, and the process including (1) forming dye and a first silver image in said picture recording unit; (2) reacting the silver halide in said auxiliary layer with a photographic developing agent to form a second silver image and oxidized photographic developing agent; and (3) bleaching and fixing the photographic element to remove residual silver halide and the first silver image while retaining the second silver image. The processes and elements of the invention feature, in the auxiliary layer, at least one nondiffusing compound which releases a ballasted silver bleach inhibitor upon reaction with the oxidized developing agent. Such compounds are referred to herein as "BIR compounds."

The preferred method of processing exposed photographic elements of the type described below comprises (A) developing the element with aromatic primary amine color developing agent to form a picture record comprising silver and a non-diffusible dye in the picture recording unit or units and an auxiliary image record comprising silver in the auxiliary layer. The oxidized aromatic primary amine color developing agent imagewise reacts with a bleach-inhibitor-releasing compound in the auxiliary layer to release a ballasted silver bleach inhibitor which inhibits bleaching of silver in the auxiliary image record area. Subsequent to development (B) the residual silver

halide and the bleachable silver remaining after step (A) are removed by bleaching and fixing while the silver in the auxiliary layer is retained to form the auxiliary silver image record.

The preferred photographic elements of this invention comprise a support having coated thereon (1) a picture recording photographic unit comprising one or more (generally one or two) silver halide emulsion layers and (2) an image-recording auxiliary photographic silver halide emulsion layer which does not form an image-forming exposure of the picture recording units. The auxiliary layer contains at least one nondiffusing compound which forms a ballasted silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent. In an especially preferred embodiment, the picture recording unit contains a nondiffusing photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a dye. The dye thus formed preferably is complementary in color to the primary sensitivity and color of light recorded in the emulsion in which it is incorporated. The nondiffusing compound in the auxiliary layer can be a photographic color coupler.

Particularly useful photographic elements of the invention are those used for preparing multicolor motion picture films having a silver sound track and comprising a transparent support having coated thereon a plurality (generally three) picture recording photographic units, each unit comprising one or more (generally one or two) silver halide emulsion layers which are so disposed and sensitized that each photographic unit is essentially sensitive to a different primary color region of the visible spectrum and an auxiliary silver image or silver sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording layers. The auxiliary layer contains at least one nondiffusing compound which forms a silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent. In a preferred embodiment, each picture recording layer contains a nondiffusing photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a dye. The dye that is formed in each layer preferably is complementary in color to the sensitivity of the emulsion in which it is incorporated.

The novel photographic elements can have, in addition to the plurality of picture recording units and the auxiliary layer, a yellow filter layer. The picture recording units and the yellow filter layer are then so disposed and sensitized such that each picture recording unit is essentially sensitive to a different region of the visible spectrum.

The picture recording layers of my novel element are used to form subtractive dye images of the picture to be recorded. The layers can form colors complementary to the color to which they are sensitive. For example, the blue sensitive layer can form a yellow dye image, the red sensitive layer can form a cyan dye image and the green layer can form a magenta dye image. Alternatively, these layers can be falsely sensitized, i.e., they can form colors not complementary to the color to which they are sensitive. If so desired, the layers can be used to form a dye or a mixture of dyes which appear to have a neutral density.

The novel elements can be used either in the negative-positive system of photography or the reversal system of photography.

In order to form subtractive dyes, the photographic elements can be processed in the presence of photographic color formers. Preferred photographic color formers are referred to as couplers. In the well known three color system of subtractive color photography, 5-pyrazolone couplers are typically used to form magenta dyes, phenolic couplers including naphtholic couplers are used to form cyan dyes and open-chain ketomethylene couplers are typically used to form yellow dyes.

The photographic element can have layers which do not contain incorporated couplers. In this case, the ex-

posed element can be processed in the presence of a coupler developing composition. This coupler-developer composition contains both diffusible photographic developing agents such as the aromatic primary amines and diffusible photographic color couplers. The oxidized photographic developing agent couples with the diffusible color coupler to form a non-diffusible dye at the site of photographic silver halide development. Suitable color couplers which can be used in coupler-developer compositions are shown in U.S. Pats. 2,252,718; 2,252,243 and 2,950,970.

Preferably, the couplers are nondiffusible and are incorporated into the picture recording silver halide layers. Exposed elements are then processed in the presence of an aromatic primary amine color developing agent, such as the well known p-phenylenediamines. The oxidized color developing agent resulting from the reduction of that latent silver halide image couples with the incorporated coupler to form a nondiffusible dye. Examples of nondiffusible photographic couplers which can be incorporated into the picture recording silver halide emulsion layers of my novel photographic element are the pyrazolone couplers shown in U.S. Pats. 2,343,702; 2,369,489; 2,436,130; 2,600,788; 3,006,759; 3,062,653; 3,311,476 and 3,419,391 and Belgian Pat. 698,354, the phenolic couplers shown in U.S. Pats. 2,367,531; 2,423,730; 2,474,293; 3,311,476; 3,419,390; 3,458,315 and 3,476,563 and the open-chain ketomethylene couplers shown in U.S. Patents 2,206,142; 2,346,130; 2,728,658 and 3,408,149. The layers can also contain other couplers such as development-inhibitor-releasing couplers such as are shown in U.S. Pat. 3,227,554.

This invention is not limited to photographic elements and processes wherein photographic color couplers are utilized to form dye images; rather, it is useful in any photographic system wherein first and second silver images are formed, and it is desired to selectively remove the first silver image, e.g., by bleaching and fixing, while retaining a second silver image.

The auxiliary layer of the photographic element is used only to record the auxiliary image, e.g., a sound track image. This layer can be coated anywhere in the element. For example, it can be coated as the light sensitive layer closest to the support or alternatively it can be coated as a light sensitive layer outermost from the support. In addition, it can be coated between two of the picture recording units or it can be coated between a picture recording unit and a filter layer if the element contains filter layers. For reasons that will become apparent, latent images of the picture record should not be formed in the auxiliary layer. Depending upon the arrangement of the picture recording units and auxiliary layers and filter layers, if any, various methods of exposure can be utilized to achieve exposure while at the same time not exposing the auxiliary layer to the picture images. For example, with the auxiliary layer as the light sensitive layer closest to the support and with a removable, e.g., bleachable, filter layer between the auxiliary layer and the picture recording units, the picture recording layers can be exposed from the emulsion side of the support and auxiliary layer exposed through the support. Alternatively, with the auxiliary layer as the light sensitive layer outermost from the support and with a removable filter layer between the auxiliary layer and the underlying picture recording layers, picture exposure can be through the support and auxiliary image exposure can be from the emulsion side. Generally however, it is desirable to expose all layers from the emulsion side. Selective exposure of the auxiliary and picture recording layers is attained in this case because of the photographic speed or spectral sensitivity or both of this layer. For example, the auxiliary layer can be sensitized to radiation to which the picture recording layers are at least partially insensitive such as infrared radiation and exposure is then made through the appropriate filters. Sensitization to the region of relatively equal minimum sensitivity between two of the picture recording layers is

still another alternative. Examples are those regions between the blue and green sensitive layers or the green and red sensitive layers of a color film having three color-forming units, each primarily sensitive to a different primary region of the visible spectrum. In addition to or instead of the spectral sensitization, the auxiliary layer can be of a different photographic speed. For example, the auxiliary layer can be unsensitized, i.e., it has only the native silver halide sensitivity to ultra-violet and near blue radiation. In this case, the auxiliary layer should be slower than the blue sensitive layer such that it is not exposed upon exposure of the blue sensitive picture recording layer. Alternatively, the auxiliary layer can be sensitized to one of the primary color regions of the visible spectrum. Again, the auxiliary layer should be slower than the picture recording layer of corresponding spectral sensitivity. Photographic elements having certain of these spectral sensitivity and photographic speed relationships are the invention of Baptista and Smith and are disclosed and claimed in a copending application entitled Novel Photographic Element and Process, Ser. No. 100,614, filed Dec. 22, 1970.

The silver halide content of the auxiliary layer can vary widely, typical coverages being from about 20 milligrams of silver as silver halide per square foot or less to 150 milligrams per square foot or more. The quantity of silver halide in this auxiliary layer will have an effect upon the turbidity of the element and the sharpness of the image when viewed. It is, therefore, preferred that the auxiliary layer contain from about 25 milligrams per square foot to 100 milligrams per square foot silver as silver halide and especially from about 30 milligrams per square foot to about 75 milligrams per square foot. Particularly useful auxiliary layers contain from about 35 to about 75 milligrams per square foot silver as silver halide.

The grain size of the silver halide of the auxiliary layer can vary widely. For example, the average silver halide grain size typically ranges from about 0.05 micron or less to about 0.5 micron or greater. Particularly, when the auxiliary layer is used only to record the sound image in a motion picture film, the grain size desirably is as small as possible without requiring such high intensity exposure in the sound record area that the picture recording layers in the sound area are over-exposed causing loss of definition in the sound record. An average grain size of from about 0.05 micron to about 0.2 micron is preferred.

The silver halide emulsions used in the auxiliary layer can be negative developing out emulsions or they can be fogged direct-positive emulsions. They can comprise silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide or mixtures thereof.

Particularly good results are obtained when the auxiliary layer of the reversal print film comprises a fogged direct-positive silver halide emulsion of the type described by Illingsworth et al. in French Pat. 1,520,821. Such fogged direct-positive emulsions are uniformly fogged and therefore contain a latent image throughout. This latent image is then destroyed in direct proportion to exposure. Upon development in conventional black and white developers, a reversal image is formed, the density of which is in inverse proportion to the exposure received, i.e., greatest density is found in the areas of no exposure and least density is found in areas of greatest exposure. The use of such a direct-positive emulsion is highly desirable for preparing a silver sound track in reversal print films since the sound track can be printed from a negative master rather than from a positive master. It is generally considered by those skilled in the art of preparing sound tracks that sound tracks obtained from negative masters are superior in quality to those obtained from positive masters. The use of the fogged direct-positive silver halide emulsions in the auxiliary layer of reversal print films of this invention therefore allows the obtaining of the higher quality negative sound track.

The silver covering power of the auxiliary silver image recording layer of reversal motion picture print film can be increased by the imagewise retention of silver derived from an adjacent silver halide layer whose reduction to silver is independent of exposure. Preferably, the auxiliary layer is a direct positive emulsion and the adjacent silver halide layer is a fogged or unfogged Lippman emulsion layer.

Also, direct-positive silver halide emulsions that form latent images predominantly inside the silver halide grains as described by Davey et al. in U.S. Patent 2,592,250 can be used in the auxiliary layer. Such internal image-forming emulsions are processed in the presence of a fogging developer such as one containing a hydrazine compound. The silver halide emulsion comprising the color-forming units with such auxiliary layers are likewise of the internal image-forming type if direct-positive color images are desired. picture record area of the auxiliary layer must be flashed to prevent development of the silver halide present there and consequent release of the bleach inhibitor which would prevent bleaching of this developed silver.

As described above, the auxiliary photographic silver halide emulsion layer contains at least one nondiffusing compound which imagewise forms a silver bleach inhibitor upon reaction with oxidized developing agent.

Preferably, this nondiffusible compound in the auxiliary layer is a photographic coupler substituted in the coupling position with a moiety capable of coupling off upon reaction of the coupler with oxidized aromatic primary amine color developing agent. This coupled-off moiety is then capable of forming a silver bleach inhibitor. These bleach-inhibitor-releasing couplers, referred to herein as "BIR" couplers, as well as other useful bleach-inhibitor-releasing compounds that are not couplers, are more fully described below.

Preferably, a scavenger for oxidized developing agent, such as hydroquinone (e.g., dioctylhydroquinone) or a photographic coupler, is incorporated in the auxiliary layer. As used herein, the word "scavenger" refers to any compound which reacts with oxidized developing agent to prevent the wandering of such oxidized agent away from a site of development, and does not release bleach inhibitor. If the oxidized color developing agent should wander away from the site of development, it can react with a color coupler at some other location, for example, in one of the picture recording units in the film to produce a dye. The production of this dye at a location away from the site of color development would cause false coloration of the developed image. It can thus be seen that it is desirable that the auxiliary layer contain at least that quantity of oxidized developing agent scavenger and BIR compound which would be required to react with all the oxidized color developing agent that would result from a development of all silver halide in the auxiliary layer. This amount can readily be determined by one skilled in the art.

In general, the quantity of bleach-inhibitor-releasing (BIR) compound necessary to react with all the oxidized color developing agent which would be produced upon complete development of the silver halide in the auxiliary layer would be more than quantity necessary to release sufficient bleach inhibitor to fully protect the developed silver from the bleach. Certain of the bleach inhibitors, if present in a quantity in excess of that amount necessary to fully protect the developed silver from bleaching, can cause adverse effects, such as interference with fixing, development inhibition, undesired reaction with oxidized color developing agent or diffusion to developed silver which should not be protected by bleach inhibitor. Therefore, it is desirable that the auxiliary layer contain approximately that quantity of BIR compound which will release sufficient bleach inhibitor moiety to substantially fully protect all the developed silver of the sound track record. This quantity of BIR compound represents a quantity less than that needed to react with all the oxidized color developing agent resulting from development

of all the silver halide in the auxiliary layer. For these reasons, it is therefore desirable to incorporate an oxidized developing agent scavenger, such as a non-BIR competing coupler, into the auxiliary layer in addition to the BIR compound. The combined amount of the scavenger and BIR compound should be present in at least the quantity necessary to react with all the oxidized color developing agent that will be produced by developing all the silver halide in the auxiliary layer. Typically, the ratio of the scavenger (e.g., non-BIR coupler) to the BIR compound will be one to several times the quantity of BIR compound incorporated. For example, the quantity of scavenger in the auxiliary layer often is four to ten times the quantity of BIR compound in this layer. As a further example, generally about 100% of the developed silver can be retained if approximately 0.01 to 0.03 millimoles of ballasted silver bleach inhibitor is released during development of an auxiliary layer comprising about 70 milligrams per square foot silver as silver halide of about 0.1 micron average grain size. The quantity of ballasted silver bleach inhibitor which must be released to retain about 100% of the developed silver which has been developed from silver halide of other grain sizes can readily be determined by one skilled in the art.

When the BIR compound is a coupler, the oxidized developing agent scavenger and the competing coupler can be, but need not be, the same type of coupler as the BIR coupler. For example, if the BIR coupler is a 5-pyrazolone coupler, the competing coupler can also be a 5-pyrazolone or another type of coupler, such as a phenolic or open-chain ketomethylene coupler. It can thus be seen that the dyes produced from the reaction of the BIR and competing couplers need not be of similar hue. This is because the silver of the auxiliary layer is not bleached out and consequently absorbs all colors of light to yield a neutral rendition of the auxiliary image or sound track. These dyes can be diffusible if they are washed out of the element without substantially staining any part of either the sound track or picture record areas. Otherwise, the dyes so formed from the BIR coupler and the competing coupler should be non-diffusible.

When an oxidized developing agent scavenger is used, its rate of reactivity is preferably about the same as the rate of reactivity of the BIR compound with the oxidized color developing agent. This "matching" of reactivity with oxidized color developing agent is to insure the release of the proper amount of bleach inhibitor. If the scavenger is less reactive than the BIR compound, most of the BIR compound will react with the oxidized color developing agent before the scavenger reacts. In this event, most of the bleach inhibitor will be released early in the development step when there is very little developed silver to which the bleach inhibitor can become adsorbed. If the scavenger is more reactive than the BIR coupler, nearly all of the silver halide will have to be developed before the BIR compound will react with oxidized color developing agent to release a bleach inhibitor. Therefore, unless there is nearly complete exposure and development of the silver halide in the auxiliary layer the developed silver will not be protected by bleach inhibitor and will be removed during subsequent bleaching and fixing operations. Thus, it can be seen that it is desirable to have a mixture of BIR compound and scavenger (e.g., non-BIR coupler) in the auxiliary layer and that the BIR compound and the scavenger should react at a generally similar rate with oxidized color developing agent. Preferably, the scavenger is a competing coupler which forms a non-diffusible cyan dye which absorbs at least some radiation longer than about 700 nm., thereby contributing to the infrared density provided by the auxiliary silver image.

The incorporation of the BIR compound and the scavenger in the auxiliary layer can be accomplished by a variety of known techniques. One of these techniques involves the use of organic solvents known as coupler sol-

vents. These coupler solvents can be of the low boiling or water soluble type which are removed from the emulsion by evaporation or washing following dispersion of the coupler and solvent in the emulsion. Alternatively, they can be of the high boiling, organic, crystalloidal type which remain incorporated in the emulsion. A description of the low boiling coupler solvents and the methods by which they can be used to disperse photographic couplers is found in Vittum et al., U.S. Pat. 2,801,170, particularly at column 2, lines 3 to 32. Also, refer to U.S. Pat. 2,861,170; Fierke et al. U.S. Pat. 2,801,171, particularly at column 10, lines 33 to 51. High boiling, organic, crystalloidal coupler solvents are those which are substantially water-insoluble, having a low molecular weight and a high boiling point (above about 175° C. at atmospheric pressure). Examples of this type of solvent include those shown in Fierke, U.S. Pat. 2,801,171 at column 10, lines 22 to 32; Julian, U.S. Pat. 2,949,360 at column 2, lines 3 to 18 and Jelley et al., U.S. Patent 2,322,027, column 4, line 45 through column 6, line 6.

The selection of other addenda such as sensitizing dyes and the method of their incorporation in the silver halide emulsion of the auxiliary layer can be made by one skilled in the art who wishes to tailor the auxiliary emulsion for particular purposes and needs.

Gelatin or any other conventional photographic hydrophilic colloids can be used as the vehicle for the silver halide in the auxiliary layer or in the silver halide emulsion layer comprising the picture recording layers.

The preferred method of processing multilayer photographic elements having at least one picture recording photographic unit comprising one or more silver halide emulsion layers and an image recording auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units and which contains a compound which forms a silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent comprises (A) developing the element with aromatic primary amine color developing agent to form a picture record comprising silver and a nondiffusible dye in the picture recording layer and a silver auxiliary or sound record in the auxiliary layer, oxidized aromatic primary amine color developing agent reacting with the bleach inhibitor precursor compound in the auxiliary layer to imagewise release silver bleach inhibitor, and (B) removing the residual silver halide and the bleachable silver remaining after step (A) by bleaching and fixing while retaining silver in the auxiliary layer to form the silver auxiliary image or sound record.

The processing of these elements can be carried out using available processing equipment such as the presently used continuous processing apparatus widely available. Processing temperatures can vary widely. Suitable processing temperatures include those which are now used for processing other conventional types of film. These temperatures typically range from about 20° C. or less to 60° C. or higher. Temperatures of about 25° C. to 40° C. and 50° C. are suitable in high speed processing procedures.

As was stated above, the auxiliary layer is of such photographic speed or spectral sensitivity or both that an image is not formed in the auxiliary layer upon image-forming exposure of the picture recording units. The auxiliary image exposure can be made prior to, concurrent with, or subsequent to, picture image exposure. The auxiliary image exposure is such that the auxiliary or sound image is recorded in at least the auxiliary layer. Subsequent to exposure, the element is processed as described above.

Although the present photographic elements are particularly suited for the preparation of color motion picture films having a silver sound record, the elements are also well adapted to the preparation of any color photographic film having an auxiliary silver image. Since the

element is particularly adapted for the preparation of silver sound records, the general processing sequence and the method by which the auxiliary silver images are retained in color photographic films will be described as it pertains to the preparation of color motion pictures having silver sound records.

Subsequent to exposure, the photographic element is developed with a photographic developing agent, preferably an aromatic primary amine color developing agent. The photoelement can be reversal developed by first developing with a black and white developer and thereafter color developing the remaining undeveloped fogged silver halide. The silver halide is reduced to metallic silver by the color developing agent which is oxidized in the process. The oxidized color developing agent produced in the auxiliary layer reacts with the incorporated photographic couplers present there. If the photographic coupler with which the oxidized color developing agent reacts is a competing coupler, it merely produces a dye. The BIR compound reacts with oxidized developing agent to form a bleach inhibitor which becomes adsorbed to the developed silver. In the picture recording units, assuming that they contain incorporated photographic couplers, the oxidized color developing agent produced by developing a latent image present there reacts with the incorporated couplers to form nondiffusible dyes. Upon completion of the development step, the picture recording units comprise silver plus nondiffusible dyes and the auxiliary layer comprises silver (and dye if nondiffusible dye formed during development) having adsorbed to it the bleach inhibitor. When the element is contacted with a bleach-fix composition or bleach composition, all the developed silver which is not protected by the bleach inhibitor is converted to a fixable salt and removed from the element. In the auxiliary layer, wherever silver develops a bleach inhibitor is released and becomes adsorbed to the developed silver. The silver is thus protected by the bleach inhibitor and is rendered substantially unbleachable in the process and is not removed from the element. Subsequent to bleaching and fixing or bleach-fixing the photographic element comprises nondiffusible dyes in the picture recording units and silver (and dye if nondiffusible dye formed during development) in the auxiliary layer.

The bleach inhibitor formed from the moiety released from the bleach-inhibitor-releasing compound during development can be either nondiffusible or moderately diffusible. If it is nondiffusible it does not migrate substantially away from the site of development and becomes adsorbed only to the silver at the site of development. In this event, only the silver developed in the auxiliary layer will be protected by the bleach inhibitor and this silver will be the only silver remaining in the film subsequent to bleaching and fixing. However, if the bleach inhibitor is moderately diffusible it can migrate away from the site of development and become adsorbed to the developed silver elsewhere in the film. Because photographic silver halide layers in color films are extremely thin relative to the other dimensions of the film, most significant migration is interlayer migration rather than lateral migration within a given layer. Thus, if the bleach inhibitor is moderately diffusible it would diffuse out of the auxiliary layer and into the layers above and below the auxiliary layer. If there is developed silver present in these adjacent layers the bleach inhibitor will become adsorbed to this silver and it will be rendered unbleachable also.

As described above, the addition of the auxiliary layer to a multilayer photographic element increases the turbidity of the element and causes some loss of sharpness of the picture images when exposure is made through the auxiliary layer. This is because of light scattering by the silver halide grains of the auxiliary layer. The greater the silver halide content of this layer, the greater the light scattering and consequently the greater the loss of sharpness. Thus, for picture sharpness considerations, the silver halide content of the auxiliary layer should be reduced.

However, reducing the silver halide content of the auxiliary layer reduces the silver density of the developed sound track and a point is finally reached where the density is insufficient to give excellent results throughout the life of the film. At this point it is still possible to obtain additional improvements in picture sharpness by further decreasing the silver halide content of the auxiliary layer. The requisite silver density needed for the sound track can be obtained in this case if the sound track exposure is such that the picture recording units adjacent to the auxiliary layer are exposed and the bleach inhibitor formed during development is moderately diffusible so that it can diffuse into these adjacent picture recording units and become adsorbed to the silver developed there. Subsequent to bleaching and fixing the element will contain a picture record comprising dye and substantially free of silver and a sound record comprising silver in the auxiliary layer as well as in the adjacent picture recording units.

Typically, color photographic elements have coated between each photographic unit an interlayer. These interlayers often contain compounds which will react with oxidized color developing agent. These compounds are generally referred to as oxidized color developing agent scavengers and are incorporated into the interlayers to prevent the wandering of oxidized color developing agent from the site of development in one layer into an adjacent layer where the agent can react with an incorporated coupler there to produce false coloration. Examples of such scavenger compounds include octylhydroquinone, dioctylhydroquinone, p-aminophenols, hydrazines, ascorbic acid derivatives and other compounds such as are shown in U.S. Pats. 2,403,721; 2,675,314; 2,356,486; 2,360,290; 2,701,197; 2,704,713; 2,728,659; 2,732,300 and 2,735,765. It has been found that the moderately diffusible bleach inhibitors can migrate through interlayers containing these scavenger compounds into adjacent silver halide emulsion layers and become adsorbed to the silver developed there as described above.

Typical processing sequences for exposed photographic elements having picture recording and auxiliary silver image or sound recording layers as described above are set forth below.

The processing of an exposed negative-positive system photographic element containing incorporated couplers in the picture recording layers is according to the following sequence:

- (1) Color development
- (2) (A) Bleach-Fix or (B) Bleach and Fix

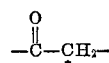
An exposed photographic element containing incorporated couplers can be reversal processed according to the following procedure:

- (1) Black and white development
- (2) Stop bath
- (3) Color development of remaining undeveloped fogged silver halide
- (4) Stop bath
- (5) (A) Bleach-Fix or (B) Bleach and Fix

If the reversal print film is to be used to prepare a motion picture film having a silver sound track the auxiliary layer must be fogged in the picture area so that it will be completely developed during the black and white development. This is done to prevent any development and consequently bleach inhibitor formation in the picture area of the auxiliary layer during color development since it is not desired to retain any silver in the picture area of the film.

The preferred BIR compounds are couplers which, exclusive of the bleach inhibitor moiety, can be any radical which has an active site capable of reacting with oxidized aromatic primary amine color developing agent and which can be substituted in this active site with a bleach inhibitor forming moiety and which retains its reactivity to the

oxidized color developing agent when so substituted. Many radicals are suitable for this purpose. Particularly useful radicals are radicals of photographic couplers such as 5-pyrazolone coupler radicals, phenolic coupler radicals including alpha-naphtholics and open-chain ketomethylene coupler radicals, such coupler radicals reacting with oxidized aromatic primary amine color developing agent to generally form magenta, cyan and yellow dyes, respectively. These couplers are substituted in the coupling position with a bleach inhibitor forming moiety to form a BIR compound or in this case a BIR coupler. The coupling position of photographic couplers is well known to those skilled in the art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position, the phenolic coupler radicals couple at the carbon atom in the 4-position and the open-chain ketomethylene coupler radicals couple at the carbon atom forming the methylene moiety (e.g.,



* denoting the coupling position).

As used herein and in the appended claims, the terms "nondiffusible bleach-inhibitor-releasing (BIR) compound" refers to a compound which, when incorporated in a fogged gelatin silver chlorobromide (the halide being about 80 molar chloride and 20 molar bromide) emulsion coated on a cellulose triacetate film support at a silver coverage of 140 mg. gelatin and 70 mg. silver per square foot, said emulsion also containing an oxidized developing agent scavenger which has substantially the same reactivity with oxidized developing agent as the BIR compound, the total amount of said BIR compound and said scavenger being sufficient to react with essentially all the oxidized developing agent resulting from developing essentially all the silver halide, and said emulsion is developed with the color developer solution described in Example 1 below to produce a silver image and oxidized developing agent, said BIR compound being present in an amount sufficient to react with the oxidized developing agent to form about .005 to .1 millimole per square foot of a ballasted bleach inhibitor which prevents bleaching of a sufficient amount of the developed silver to provide an infrared density of at least 0.80 measured at 900 nm. when the developed silver is treated for 90 seconds at a temperature of 25° C. with the following bleach-fix composition:

NaFeEDTA ¹ (13% Fe)	g--	60
Na ₂ SO ₃	g--	12
NH ₄ SCN	g--	12
Na ₄ EDTA ¹	g--	7
Ammonium thiosulfate (60% solution)	ml--	200
Water to 1 liter.		

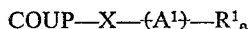
¹ EDTA—Ethylenediamine tetraacetic acid.

In conducting the above test, the weight ratio of competing coupler and BIR compound is regulated so that the optimum amount of bleach inhibitor will be released.

We have found that organic compounds which exhibit particular utility as ballasted bleach inhibitors as defined above are thiol- 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 silver bleach inhibitor within the hydrophilic colloid silver halide emulsion layers of the element. Examples of such compounds are mercapto- and selenol-substituted alkanolic acids, especially 2-mercapto alkanolic acids, thiol- and selenol-substituted ballasted aryls such as alkyl- and alkylamidothiophenols and thionaphthols, ballasted thiol- and selenol-substituted heterocyclic compounds containing at least one nitrogen atom such as alkylamidomercaptobenzoxazoles, alkylamidobenzothiazoles, alkylamidomercaptobenzimidazoles, alkyl-

amidomercaptothiadiazoles, alkylthiomercaptothiadiazoles, alkylamidomercaptotriazoles, 1-alkylamidophenyl-5-mercaptopotriazoles and ballasted mercaptoquinolines such as alkylamido- and alkylmercaptoquinolines, ballasted thiocarboxylic acids such as alkyl- and alkylamido-thiobenzoic acid.

Particularly useful bleach-inhibitor-releasing (BIR) couplers that can be used in the invention have the following general formula:



wherein:

COUP represents a photographic coupler moiety that reacts with oxidized aromatic primary amine color developing agent to form a dye:

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

X represents sulfur or selenium attached in the coupling position of the COUP moiety;

R¹ 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 8 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, cyclohexadiene, 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., sulfatoethyl, sulfatododecyl, sulfatotetradecyl and the like), alkylsulfonylalkyl (e.g., ethylsulfonylbutyl and the like), cyanoalkyl (e.g., cyanoethyl, cyanoctyl, cyanododecyl and the like), carboxyalkyl (e.g., carboxyethyl, carboxydecyl, carboxyhexadecyl and the like), aralkyl (e.g., benzyl, phenyl, cyclohexyl, tolyl, dodecyl and the like), alkoxyalkyl (e.g., octoxyethyl, butoxyethyl, ethoxydecyl and the like), aryloxyalkyl (e.g., phenoxyethyl, phenoxyethyl and the like), alkoxyaralkyl (e.g., methoxyphenylmethyl, butoxyphenylmethyl and the like), acyloxyalkyl (e.g., benzoyloxyethyl, acetoxybutyl and the like), alkoxyaralkyl (e.g., butoxyphenylmethyl and the like), aryloxyaralkyl (e.g., phenoxycarbonylphenyl, chlorophenoxycarbonylphenyl 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, phenoxy-naphthyl and the like), acyloxyaryl (e.g., benzoyloxyphenyl, acetyloxyphenyl and the like), alkoxyaralkaryl (e.g., ethoxyphenylphenyl and the like), aryloxyaralkaryl (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, carboxy cyclopentanacetamidophenyl and the like), cycloalkylimino-sulfonylaryl (e.g., piperidinylsulfonylphenyl, azetidinyl-

5 sulfonylphenyl, 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), aralkoxyalkylamido (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 aryl-
30 oxy (e.g., phenoxy, toluoxy and the like);

35 A¹ represents a member selected from the group consisting of a carbonyl group ($>C=O$); 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., cyclopropenylenylene, cyclobutenylene, cyclopentenylene, cyclopentadienylenylene, cyclohexenylenylene and cyclohexadienylenylene) and arylene (e.g., phenylene, naphthylene, anthrylene and the like); and a 3 to 10 and preferably 5 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 oxirenene, 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-oxazinylyl, 1,3-oxazinylyl, 1,4-oxazinylyl, morpholinyl, 1,3-dioxolanyl, 1,3-oxathianyl, 1,4-oxathianyl, 1,2-dioxanyl, 1,3-dioxanyl, 1,4-dioxanyl, dioxanenylyl, dioxadienylyl, diazetylyl, pyrrollyl, indolyl, isoindolyl, carbazolyl, pyrrocolinyl, acridinyl, phenanthridinyl, 2-imidazolinylyl, 3-imidazolinylyl, 4-imidazolinylyl, pyridyl, pyridazinyl, cinnolinylyl, phthalazinyl, quinoxalinylyl, pyrimidinyl, pyrazolo[3,4-d]pyrimidinyl, hypoxanthinyl, benzopyrimidinyl, pyrazinyl, quinoxalinylyl, phthalazinyl, quinolinylyl, isoquinolinylyl, phenazinyl, phenoxazinyl, phenothiazinyl, purinyl, pyridinyl, 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-thianinyl, 1,4-dithaninyl, 1,4-dithiadienyl, selenazolyl, benzoselenazolyl, isoselenazolyl, benzisoselenazolyl, selenadiazolyl, benzoselenadiazolyl and the like; such that R¹ does not represent a carbonyl group, a carbamoyl group or an amido group when A¹ represents carbonyl or thiocarbonyl and such that the grouping R¹-(A¹) represents a moiety having a molecular weight

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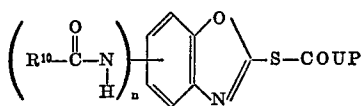
of from 125 to 1,000 and preferably from 175 to 400 and preferably containing not more than one solubilizing group such as carboxy unless the grouping contains a hydrophobic moiety such as a long alkyl chain or an aryl group and such that when A¹ represents a carbocyclic or a heterocyclic ring, said 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 8 to 18 carbon atoms; an alkylamido group having from 8 to 18 carbon atoms and an aryl group such as phenyl, naphthyl and an alkyl-amidoaryl group having 8 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 alkyl-amido groups having 3 to 12 carbon atoms and two alkyl-amidoaryl groups having 3 to 12 carbon atoms in the alkyl moiety. Preferably, the grouping A¹_a—A¹—X— does not react with oxidized aromatic color developing agent.

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.

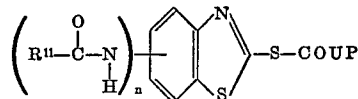
In a preferred embodiment of our invention, the BIR coupler releases a bleach inhibitor-forming moiety which is an organic compound or the salt of an organic compound as defined in formula COUP—X—A¹—R¹ above having an acidic thiol or selenol. The acidity of the thiol and selenol groups can be imparted 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 formulae exhibit particular utility as bleach-inhibitor-releasing couplers in the present invention:

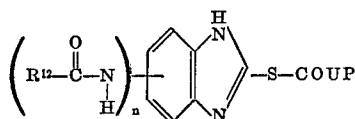
(A) 2-mercaptobenzoxazoles



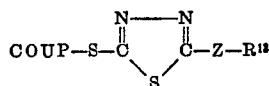
(B) 2-mercaptobenzothiazoles



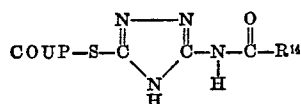
(C) 2-mercaptobenzimidazoles



(D) 2-mercaptothiadiazoles

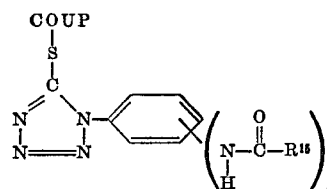


(E) 2-mercaptotriazoles



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(F) 1-phenyl-5-mercaptotetrazoles



wherein:

R¹⁰, R¹¹, R¹² and R¹³ represents an alkyl group having from 1 to 17 carbon atoms and preferably 8 to 12 carbon atoms;

R¹³ and R¹⁴ represents an alkyl group having from 5 to 17 carbon atoms and preferably 8 to 12 carbon atoms;

Z represents sulfur or the group —NHCO—;

n represents 1 to 5 and preferably 1 and

COUP represents a photographic coupler substituted in its coupling position with the thio radical.

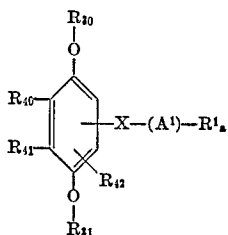
The following list of compounds are typical of the bleach-inhibitor-releasing couplers useful in the present invention:

- (I) 1-hydroxy-4-[1-(3-decanamidophenyl)-tetrazol-5-ylthio]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (II) 1-hydroxy-4-(5-decanamido-1,3,4-thiadiazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (III) 1-hydroxy-4-(5-decanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (IV) 1-hydroxy-4-(5-nonanamido-1,3-benzoxazol-2-ylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide
- (V) 1-hydroxy-4-(5-nonanamido-1,3-benzothiazol-2-ylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide
- (VI) α-(pivalyl)-α-(5-nonanamido-1,3,4-triazol-2-ylthio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide
- (VII) 1-hydroxy-4-(4-nonanamidodiazet-3-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (VIII) 1-hydroxy-4-(4-dodecanamido-1,3-pyrimidin-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (IX) 1-hydroxy-4-(1-carboxy-4-decanamidocyclohexylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide
- (X) 1-hydroxy-4-(4-dodecanamidocyclohexen-1-ylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide
- (XI) α-(pivalyl)-α-(4-nonanamidophenylthio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide
- (XII) α-(pivalyl)-α-(dodecanoic acid-2-ylthio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide
- (XIII) 1-hydroxy-4-(4-octylbenzoylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XIV) 1-hydroxy-4-(5-decylthio-1,3,4-thiadiazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XV) α-(pivalyl)-α-(benzophenone-4-thio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide
- (XVI) 1-hydroxy-4-(5-decylcarbamoyl-1,3-benzimidazol-2-ylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide
- (XVII) 1-hydroxy-4-(6-decyloxy-1,3-benzoxazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XVIII) α-(pivalyl)-α-(5-phenoxy-1,3-benzothiazol-2-ylthio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide
- (XIX) 1-[4-[α-(3-pentyldecylphenoxy)-butyramido]-phenyl]-3-ethoxy-4-(5-nonanamido-1,3,4-thiadiazol-2-ylthio)-5-pyrazolone
- (XX) 1-hydroxy-4-[1-(3-decanamidophenyl)-tetrazol-5-ylseleno]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide

- (XXI) 1-hydroxy-4-(5-octanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XXII) 1-hydroxy-4-(5-nonanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XXIII) 1-hydroxy-4-(5-undecanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XXIV) 1-hydroxy-4-(5-dodecanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide
- (XXV) 1-(2,4,6-trichlorophenyl)-3-{3-[α -(2,4-di-tert-amylphenoxy)acetamido]benzamido}-4-[1-(3-decanamidophenyl)-tetrazol-5-ylthio]-5-pyrazolone
- (XXVI) α -{3-[α -(2,4-di-tert-amylphenoxy)butyramido]-benzoyl}- α -[1-(3-nonanamidophenyl)-tetrazol-5-ylthio]-2-methoxyacetanilide
- (XXVII) 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-[1-(3-undecanamidophenyl)-tetrazol-5-ylthio]-5-pyrazolone
- (XXVIII) 4-[1-(3-decanamidophenyl)tetrazol-5-ylthio]phenol
- (XXIX) 5-methoxy-2-[α -(3-n-pentadecylphenoxy)butyramido]-4-[1-(3-octanamidophenyl)-tetrazol-5-ylthio]-phenol
- (XXX) 1-{4-[α -(2,4-di-tert-amylphenoxy)butyramido]-phenyl}-3-(1-pyrrolidine)-4-[1-(3-decanamidophenyl)-tetrazol-5-ylthio]-5-pyrazolone
- (XXXI) α -benzoyl- α -[1-(3-decanamidophenyl)-tetrazol-5-ylthio]acetophenone
- (XXXII) 1-phenyl-3-octadecylamino-4-[1-(3-decanamidophenyl)-tetrazol-5-ylthio]-5-pyrazolone
- (XXXIII) 1-hydroxy-4-[1-(3-nonanamidophenyl)-tetrazol-5-ylthio]-3',5'-di-carbomethoxy-2-naphthanilide
- (XXXIX) α -(2-furoyl)- α -[1-(3-dodecanamidophenyl)-tetrazol-5-ylthio]-3,5-disulfoacetanilide dipotassium salt

The bleach-inhibitor-releasing couplers used in the invention are known compounds or similar to known compounds and can be prepared by one skilled in the art by known methods. For example, the synthesis methods illustrated for the preparation of thioether couplers in Barr et al. U.S. Pat. 3,227,554, issued Jan. 4, 1966 can be utilized.

Also useful in the practice of this invention are the non-diffusible bleach-inhibitor-releasing (BIR) hydroquinones. As used herein, the term "hydroquinone" includes naphthoquinones and substituted hydroquinones. The preferred BIR hydroquinones contain a hydrophobic group linked to the aromatic nucleus through a thio (—S—) or seleno (—Se—) group to a hydroquinone. They release an acidic thiol or selenol upon reaction with oxidized developing agent (black-and-white or, preferably, aromatic primary amine color developing agents, such as those described by Mees and James, *The Theory of the Photographic Process*, pages 278–311, published by the MacMillan Co., 1966). The preferred BIR hydroquinone have the following formula:



wherein X, A¹ and R^{1a} have the meanings given above; R₃₀ and R₃₁ each represents hydrogen or an alkaline split-

- table masking group, such as an acyl group, e.g., acetyl, mono-, di- or trichloroacetyl, mono-, di- or trifluoroacetyl, perfluoroacetyl (e.g., butyryl), pyruvyl, alkoxalyl, nitrobenzoyl, cyanobenzoyl, etc.; R₄₀, R₄₁ and R₄₂ each represents hydrogen; an alkyl group including substituted alkyl as described in the definition of R¹, or, R₄₀ and R₄₁, taken together, represent the atoms to complete a fused benzene ring. Particularly useful BIR hydroquinones are listed below:
- 5 2,3-dimethyl-5-[1-(3-nonanamidophenyl)-tetrazol-5-ylthio]hydroquinone
- 10 2,3-dimethyl-5-(5-decanamido-1,3,4-thiadiazol-2-ylthio)hydroquinone
- 3-butyl-5-(5-decanamido-1,3-benzimidazolyl-2-ylthio)hydroquinone
- 15 3-octyl-5-(5-nonanamido-1,3-benzothiazol-2-ylthio)hydroquinone
- 2,3-dimethyl-5-(1-carboxy-4-decanamidocyclohexylthio)hydroquinone
- 20 2,3-diethyl-5-(4-dodecanamidocyclohexen-1-ylthio)hydroquinone
- 2,3-diethyl-5-[1-(3-decanamidophenyl)tetrazol-5-ylseleno]hydroquinone

The BIR hydroquinones are related to the thio-substituted development inhibitors described in Barr U.S. Pat. 3,364,022 issued Jan. 16, 1968, and can be prepared by procedures similar to those described by Barr.

Other bleach-inhibitor-releasing compounds which can be utilized in the practice of this invention are described in British Pat. 1,224,555, complete specification published Mar. 10, 1971, and corresponding Belgian Pat. 713,448 of Apr. 18, 1968, wherein the —S—Y group of the structural formula shown on page 2 of the British patent is replaced with the group —X—(A¹)—R^{1a}, defined above.

The method of this invention is useful to prevent the bleaching of sound records by both bleach compositions and bleach-fix compositions. Bleach compositions contain, for example, potassium dichromate or potassium ferricyanide as the oxidizing agent. Bleach-fix compositions are those which contain an oxidizing agent such as an iron salt of EDTA and a silver halide solvent. In a bleach-fix composition, the silver is oxidized to a silver salt which is then removed from the film all in a single solution. Bleach compositions, however, only oxidize the silver to a silver salt. This silver salt and residual silver halide are subsequently removed by treatment with a separate fixing bath.

In general, bleaching compositions are more vigorous oxidizing compositions than bleach-fix compositions. For this reason it is preferred that the bleach inhibitor moiety formed during color development be less hydrophilic if the picture record silver is to be oxidized with a bleach composition. Examples of such compounds are those which are substituted with a more hydrophobic moiety such as a longer fatty chain.

The method of the invention is also applicable to the production of silver sound records and films in which dye images are of a neutral density. Neutral density images can be formed from one or a mixture of couplers which react to form a neutral density dye or a combination of dyes which appear to be of neutral density. As with color image formation, subsequent to neutral density image formation, the silver of the picture record is removed by bleaching and fixing. The silver sound record can be retained in this type of film by the use of an auxiliary layer containing a bleach-inhibitor-releasing compound or coupler to yield a neutral density film having a picture record comprised of a dye or a mixture of dyes and a sound record comprised of silver.

The term "nondiffusible" used herein as applied to couplers and products derived from couplers has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through photographic hydrophilic colloid layers such as gelatin, particularly

during processing in aqueous alkaline solutions. The same meaning is attached to the term "immobile." The terms "diffusible" and "mobile" have a converse meaning. The terms "moderately diffusible" and "moderately mobile" are used to indicate compounds which do migrate or wander through photographic hydrophilic colloid layers, but the rate of diffusion of which is markedly slower than those compounds which can be labeled as diffusible or mobile, but whose rate of diffusion is significantly greater than those compounds which can be labeled non-diffusible or immobile.

A further understanding of the invention can be gained by reference to the drawings. FIG. 2 shows a diagrammatic plane view of typical motion picture film with a sound track. The sound track depicted in sound track area 11 is the variable area type. The frames depicted in picture area 12 represent the individual frames containing the picture record. Sprocket perforations 13 are used to transport film through the apparatus associated with motion picture preparation and viewing.

FIG. 1 depicts diagrammatically and sequentially the processing of one embodiment of my novel photographic element shown in cross-sectional view to produce a color picture record and a silver sound record. Processing is according to my novel method of processing. With reference to the embodiment shown in FIG. 1, transparent film support 22 has coated thereon gelatino silver halide, blue sensitive, yellow-forming layer 23, gelatino silver halide, red sensitive, cyan-forming layer 24, gelatino silver halide, green sensitive, magenta-forming layer 25 and gelatino silver halide, blue-green sensitive, cyan-forming bleach-inhibitor-releasing auxiliary layer 26. The sensitivity of layer 26 is such that the sensitivity peak falls at about 480 nm. The photographic speed of layer 26 is such that it is about 0.4 Log E slower than the slower of the blue (23) and green (25) sensitive layer when exposed at 480 nm. For simplicity in illustrating the invention, conventional subbing layers, interlayers and the overcoat have been omitted from the drawing. In stage 1, the element is exposed through the negative original depicted for simplification of the figure as a single layer 21 coated on transparent support 20. Exposure for the picture record is made with white light and for the sound record with blue-green light having a maximum intensity at about 480 nm. and a bandspread of about 20 nm. at half height. In practice, this original can be a multilayer, multicolor element or a scene as viewed through a camera lens. Also, in practice, the picture record and the sound track record would generally be on separate originals and separate exposures made from each of these originals a short interval of time apart.

In carrying out the process of the invention as illustrated in the drawing, subsequent to exposure, the latent image is developed in a color developer. The element then appears as in stage 2. Layers 23a, 24a and 25a in picture area 210 are comprised of silver and dye images. In picture area 29 these layers do not receive exposure and a latent image was not formed. Area 29 of these layers is thus comprised of silver halide. Auxiliary layer 26a because of its photographic speed and spectral sensitivity does not become exposed and is thus comprised of silver halide in both picture areas 29 and 210. Layers 23a, 25a and 26a because of their photographic speed and spectral sensitivity receive sound track exposure and are comprised of silver and dye images in sound track area 27 and silver halide in sound track area 28. Layer 26a contains a bleach-inhibitor-releasing coupler which reacts with oxidized color developing agent produced during the development of the latent sound track image in this layer and releases a bleach inhibitor forming moiety. In the embodiment depicted in the drawing the bleach inhibitor moiety formed is a moderately diffusing moiety which not only became adsorbed to the developed silver in area 27 of layer 26a but also diffused part of the way into layer 25a in area

27 and became adsorbed to developed silver present there. Layer 24a did not receive sound track exposure and is comprised of silver halide in both sound track areas 27 and 28. Subsequent to initial development, the element is contacted with a bleach-fix composition and is then washed. Stage 3 depicts the element subsequent to bleach-fixing and washing of the element. Layers 23b, 24b and 25b in picture area 29 are clear, the residual silver halide having been fixed out. Picture area 210 of these layers is comprised of dyes, the developed silver having been bleached and fixed out. Auxiliary layer 26b in picture areas 29 and 210 is now clear, the residual silver halide having been fixed out. All four layers in sound track area 28 and layer 24b in area 27 are now clear, the residual silver halide having been fixed out. Layer 23b and a lower part of layer 25b in sound track area 27 are comprised of dye, the developed silver in these layers having been bleached and fixed out since it was not protected with the bleach inhibitor formed during color development. Layer 26b and the upper part of layer 25b are comprised of silver and dye in sound track area 27 since these areas were protected with the bleach inhibitor formed during color development. The processed element is thus comprised of a dye picture record and a silver sound record. It can thus be seen that the silver sound record of this processed element is obtained by simple processing techniques and without any separate treatment bath for the production of the sound track.

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

EXAMPLE 1

Strips of photographic elements having coated on a transparent cellulose acetate film support a single gelatino silver chlorobromide (80/20) emulsion layer having an average grain size of 0.1 micron and containing about 200 mg./ft.² gelatin and silver halide BIR coupler and competing coupler coverages as shown in Table I-B below are exposed to a step exposure object and processed according to the procedure specified in Table I-A. The processing procedures are as shown below:

TABLE I-A

Procedure Number.....	1	2	3
Processing temperature.....	38° C.....	24° C.....	26.5° C.....
1. Color develop.....	38 sec.....	9 min.....	5 min., 20 sec.
2. Stop-fix.....	40 sec.....	2 min.....	2 min.
3. Wash.....	60 sec.....	2 min.....	2 min.
4. Bleach-fix.....	40 sec.....	2 min.....	1 min., 30 sec.
5. Wash.....	80 sec.....	6 min.....	6 min.
6. Stabilize.....	10 sec.....	10 sec.....	10 sec.

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

(1) COLOR DEVELOPER

Sodium hexametaphosphate	g--	2
Sodium sulfite, desiccated	g--	4
2 - amino - 5 - diethylaminotoluene monohydrochloride	g--	3
Sodium carbonate, monohydrated	g--	20
Potassium bromide	g--	2
Water to make 1 liter (pH 10.65).		

(2) STOP-FIX BATH

Sodium thiosulfate	g--	240
Sodium sulfite, desiccated	g--	15
Acetic acid, 28%	ml..	48
Boric acid, crystals	g--	7.5
Potassium alum	g--	15
Water to make 1 liter.		

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(4) BLEACH-FIX BATH

Ethylenediamine tetraacetic acid, sodium-iron salt -----g--	60
Sodium sulfite -----g--	12
Ammonium thiosulfate, 60% solution -----ml--	200
Ethylenediamine tetraacetic acid, tetrasodium salt -----g--	6.7
Ammonium thiocyanate -----g--	12
Water to make 1 liter (pH 6.8).	

(6) STABILIZER

Formaldehyde (37% solution) -----	20
Octylphenoxy polyethoxy ethanol (Triton X-100) --	2
Water to make 1 liter.	

Control runs are made to determine percent silver retained by omitting processing steps 4 (bleach-fix) and 5 (wash). These control strips then contain only developed silver, the residual silver halide having been fixed out. Silver density measurements are made on a densitometer at 900 nm. and the silver density of the control strip is divided into the silver density of the strip which was bleach-fixed to determine the percent retained silver. These values are shown in Table I-B.

TABLE I-B

Element No.	BIR Coupler		Competing Coupler		Silver as silver halide, mg./sq. ft.	Process procedure (° C.)	Percent silver retained
	Name ¹	Mg./sq. ft.	Name ¹	Mg./sq. ft.			
1-----	A	13	G	75	62	1 (38)	100
2-----	B	12	G	75	75	2 (24)	100
3-----	B	12	G	75	75	3 (26.5)	100
4-----	B	12	G	75	75	1	100
5-----	B	12	H	107	73	1	100
6-----	C	12	G	75	73	1	100
7-----	C	12	J	75	70	1	100
8-----	C	12	K	97	67	1	100
9-----	C	12	H	107	67	1	100
10-----	C	12	L	75	69	1	100
11-----	D	12	K	97	67	1	100
12-----	D	12	L	75	73	1	100
13-----	E	13	G	75	67	1	100
14-----	E	13	H	107	67	1	100
15-----	F	30	G	75	73	1	100

¹ BIR Couplers:

- A. 1-hydroxy-4-[1-(3-undecanamidophenyl)-tetrazol-5-ylthio]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide.
 B. 1-hydroxy-4-(5-nonanamido-1,3,4-thiadiazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide.
 C. 1-hydroxy-4-(5-nonanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide.
 D. 1-hydroxy-4-(5-nonanamido-1,3,4-thiadiazol-2-ylthio)-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide.
 E. 1-hydroxy-4-[5-(3,5,5-trimethylhexanamido)-1,3,4-thiadiazol-2-ylthio]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide.
 F. α-(pivalyl)-α-(5-nonanamido-1,3,4-thiadiazol-2-ylthio)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)-butyramido]-acetanilide.
 Competing Couplers:
 G. 1-hydroxy-N-(2-n-tetradecyloxyphenyl)-2-naphthamide.
 H. 1-(2,4,6-trichlorophenyl)-3-[3-γ-(2,4-di-tert-amylphenoxy)-acetamido]-benzamidol-5-pyrazolone.
 J. 1-hydroxy-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide.
 K. 1-(6-chloro-2,4-dimethylphenyl)-3-[α-(m-pentadecylphenoxy)-butyramido]-5-pyrazolone.
 L. 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone.

The above results demonstrate that sufficient bleach inhibitor is released imagewise during development to retain all the developed silver during bleach-fixing of the element. When the above described gelatino silver halide emulsion layers are coated as the auxiliary layer over a multilayer color photographic element having three faster speed picture recording gelatino silver halide emulsion color-forming units and the element is exposed to a color picture record without exposing the auxiliary layer and a sound record and processed as above, color picture records comprised of dye and substantially free of silver and an excellent sound record comprised of silver are obtained.

EXAMPLE 2

Strips of a single layer photographic element identical to element 2 of Example 1 are exposed to a step exposure

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object and processed at 38° C. according to the procedures shown in Table II.

TABLE II

Procedure Number	1	2	3	4	5
1. Prebath.....	10	10	10	10	10
2. Wash.....	10	10	10	10	10
3. Color develop.....	90	90	90	90	90
4. Wash.....	10	10	10	10	10
5. Stop.....				60	
6. Stop-fix.....	60	60	60		
7. Wash.....		30	30	30	
8. Bleach-fix.....		60	90	60	60
9. Wash.....	120	120	120	120	120
10. Stabilize.....	10	10	10	10	10
Retained silver density.....	100%	100%	88%	71%	

The chemical composition of the processing baths for steps 3, 6 and 9 are the same as processing baths 1, 2 and 6, respectively, of Example 1. The chemical composition of the other baths is shown below:

(1) PREBATH

Borax -----g--	20
Sodium sulfate, desiccated -----g--	100
Sodium hydroxide, 10% solution -----ml--	10
Water to make 1 liter (pH 9.3).	

(5) STOP BATH

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

(8) BLEACH-FIX (ALL PROCEDURES EXCEPT NO. 3)

Hydrochloric acid, conc. -----ml--	9.2
Sodium sulfite -----g--	12
Ammonium iron ethylenediamine tetraacetic acid (1.56 molar sol.) -----ml--	92
Ammonium thiosulfate (60% sol.) -----ml--	200
Water to make 1 liter (pH 6.5).	

(8) BLEACH-FIX (PROCEDURE NO. 3)

Ethylenediamine tetraacetic acid, sodium-iron salt -----g--	60
Ethylenediamine tetraacetic acid, tetrasodium salt -----g--	7
Sodium sulfite -----g--	20
Ammonium thiosulfate (60% sol.) -----ml--	200
Potassium iodide -----g--	4
Water to make 1 liter (pH 6.8).	

The figures in Table II represent the time in seconds for each step processing sequence. The element processed according to procedure No. 1 is fixed but not bleach-fixed. Since the element is not bleached, it contains 100% of the developed silver and serves as a control to measure the effectiveness of the bleach inhibitor to retain silver during the bleach-fix step. The percent retained silver is determined in the same manner as in Example 1. The retained silver density in all cases represents sufficient density for a high quality silver sound track. When the above described gelatino silver halide emulsion layer is coated as the auxiliary layer over a multilayer color photographic element having three faster speed picture recording gelatino silver halide emulsion color-forming units and the element is exposed to a color picture record without exposing the auxiliary layer and a sound record and processed according to any of procedures 2 to 5 described above, color picture records comprised of dye and substantially free of silver and an excellent sound record comprised of silver are obtained.

EXAMPLE 3

Three multilayer color photographic elements having picture recording and sound recording areas and each having three picture recording color-forming units each sensitive to a different primary color region of the visible spectrum and an auxiliary sound recording layer of the composition indicated below and sensitive to the blue

region of the visible spectrum and having the element structures described below are exposed to color picture negatives with white light and to a sound record negative through a filter pack which transmits a narrow band of light having a peak at 470 nm. and a 20 nm. band-spread at one-half transmittance and processed according to procedure No. 2 of Example 2. In the following element structure descriptions, the approximate coverages of all components are expressed parenthetically as milligrams per square foot.

Element structure 1

A transparent cellulose acetate film support is coated, on one surface in order from the support, with (1) a blue sensitive picture recording photographic color-forming unit comprised of gelatin (340), silver (60) as silver bromiodide, 1% iodide, a nondiffusible open-chain ketomethylene yellow forming photographic coupler (130) and dibutyl phthalate as coupler solvent (130), (2) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (3) a red sensitive picture recording photographic color-forming unit comprised of gelatin (280), silver (40) as silver chlorobromide, 20% bromide, a nondiffusible phenolic cyan forming photographic coupler (75) and dibutyl phthalate as coupler solvent (225), (4) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (5) a green sensitive picture recording photographic color-forming unit comprised of gelatin (220), silver (80) as silver chlorobromide, 20% bromide, a nondiffusible 5-pyrazolone magenta forming photographic coupler (135) and tricresyl phosphate (65) as coupler solvent, (6) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (7) an auxiliary sound recording layer sensitive to the blue region of the visible spectrum comprised of gelatin (150), silver (70) as silver chlorobromide, 20% bromide, of about 0.1 micron average grain size, BIR coupler A of Example 1 (13), coupler G of Example 1 (75), 2,5-dioctyl hydroquinone (7.5) and tricresyl phosphate (45) as coupler solvent, and (8) an overcoat comprised of gelatin (90).

Element structure 2

A transparent cellulose acetate film support is coated, on one surface in order from the support, with (1) a blue sensitive picture recording photographic color-forming unit comprising gelatin (340), silver (60) as silver bromiodide, 1% iodide, a nondiffusible open-chain ketomethylene yellow forming photographic coupler (130) and dibutyl phthalate (130) as coupler solvent, (2) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (3) a red sensitive picture recording photographic color-forming unit comprised of gelatin (280), silver (40) as silver chlorobromide, 20% bromide, a nondiffusible phenolic cyan forming photographic coupler (75) and dibutyl phthalate (225) as coupler solvent, (4) an auxiliary sound recording layer sensitive to the blue region of the visible spectrum comprised of gelatin (150), silver (70) as silver chlorobromide, 20% bromide, of about 0.1 micron average grain size, BIR coupler A of Example 1 (13), coupler G of Example 1 (75), 2,5-dioctyl hydroquinone (7.5) and tricresyl phosphate (45) as coupler solvent, (5) a green sensitive picture recording photographic color-forming unit comprised of gelatin (220), silver (80) as silver chlorobromide, 20% bromide, a nondiffusible 5-pyrazolone magenta forming photographic coupler (135) and tricresyl phosphate (65) as coupler solvent, and (6) an overcoat comprised of gelatin (90).

Element structure 3

A transparent cellulose acetate film support is coated, on one surface in order from the support, with (1) a blue sensitive picture recording photographic color-forming unit comprised of gelatin (340), silver (60) as silver bromiodide, 1% iodide, a nondiffusible open-chain

ketomethylene yellow forming photographic coupler (130) and dibutyl phthalate (130) as coupler solvent, (2) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (3) an auxiliary sound recording layer sensitive to the blue region of the spectrum comprised of gelatin (150) silver (70) as silver chlorobromide, 20% bromide, of about 0.1 micron average grain size, BIR coupler A of Example 1 (13), coupler G of Example 1 (75), 2,5-dioctyl hydroquinone (7.5) and tricresyl phosphate (45) as coupler solvent, (4) a red sensitive picture recording photographic color-forming unit comprised of gelatin (280), silver (40) as silver chlorobromide, 20% bromide, a nondiffusible phenolic cyan forming photographic coupler (75) and dibutyl phthalate (225) as coupler solvent, (5) an interlayer comprised of gelatin (60) and 2,5-dioctyl hydroquinone (7.5), (6) a green sensitive picture recording photographic color-forming unit comprised of gelatin (220), silver (80) as silver chlorobromide, 20% bromide, a nondiffusible 5-pyrazolone magenta forming photographic coupler (135) and tricresyl phosphate (65) as coupler solvent, and (7) an overcoat comprised of gelatin (90). The processed films contain yellow, magenta and cyan dye picture records substantially free of silver and excellent silver sound records. The processed films when projected with an optical sound projector give an excellent picture record and sound record.

EXAMPLE 4

Strips of photographic elements having coated on a transparent cellulose acetate film support a single gelatino fogged direct-positive silver halide emulsion layer of the type described in French Pat. No. 1,520,821, containing silver as silver halide, BIR coupler and competing coupler as shown in Table IV-B below are exposed to a step exposure object and processed according to the procedure specified in Table IV-A.

TABLE IV-A

(1) Black and white develop	sec.	30
(2) Stop bath	sec.	30
(3) Wash	min.	1
(4) Reversal flash expose.		
(5) Color develop	min.	4
(6) Wash	min.	1
(7) Bleach-fix	min.	1
(8) Wash	min.	1
(9) Stabilize	sec.	10
Process temperature	° C.	52

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

(1) BLACK AND WHITE DEVELOPER

H ₂ SO ₄	ml.	1.8
Sodium sulfite	g.	25
4-hydro dimezone	g.	0.6
K ₂ CO ₃	g.	16.0
Hydroquinone	g.	8.0
NaBr	g.	1.5
NaHCO ₃	g.	12.0
KI	mg.	7
Diethylene glycol	cc.	12.0
Water to 1 liter (pH 9.9).		

(2) STOP BATH

Water	ml.	800
Acetic acid (glacial)	ml.	27
NaHSO ₃	g.	9.7
Water to 1 liter.		

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(5) COLOR DEVELOPER

Sodium sulfite -----g--	2.5
4 - amino - 3 - methyl-(N-ethyl-N-methoxyethyl) aniline-1,5-naphthalene disulfonic acid (color dev. agent) -----g--	14.0
K ₂ CO ₃ -----g--	36.0
NaBr -----g--	.3
KI -----g--	.028
CZA (citrazinic acid) -----g--	1.0
KOH (45% solution) -----ml--	3.0
DTOD (3,6-dithiaoctane-1,8-thiol) -----g--	1.0
Water to 1 liter (pH 10.7).	

(7) BLEACH-FIX SOLUTION

Sodium iron EDTA -----g--	60.0
Sodium sulfite -----g--	12.0
Ammonium thiocyanate -----g--	12.0
Ammonium thiosulfate (60% solution) -----ml--	200
Tetrasodium EDTA -----g--	6.7
Water to 1 liter (pH 6.68).	

(9) STABILIZER

Formaldehyde (37% w. solution) -----	20
Octylphenoxy polyethoxy ethanol (Triton X-100) --	2
Water to make 1 l.	

TABLE IV-B
[Element composition]

Element number	Gelatin (mg./ft. ²)	Coupler *		Silver as halide (mg./ft. ²)
		BIR (mg./ft. ²)	Competing (mg./ft. ²)	
1-----	200	0	G (75)	71
2-----	200	A (30)	G (75)	71
3-----	200	C (25)	G (75)	79

* Couplers No. A, C and G are listed in the footnotes to Table I-B.

The silver density measurements are made on a densitometer at 900 nm. and the results are shown in Table IV-C below:

TABLE IV-C
[Processed element silver density]

Element number	Silver density			
	Developed		Retained	
	Min. E	Max. E	Min. E	Max. E
1-----	1.40	0.96	0.05	0.06
2-----	1.42	0.96	0.05	0.86
3-----	1.58	1.02	0.04	0.84

NOTE.—min. E=minimum exposure; Max. E=maximum exposure.

The above results demonstrate that sufficient bleach inhibitor is released imagewise during development to retain a substantial portion of the developed silver during the bleach-fixing of the element. The silver retained during the bleach-fixing represents a negative image rather than the normal positive that would be obtained had the auxiliary layer been comprised of negative developing out silver halide and the element had been reversal processed in the same manner as the above photographic elements. When the above described gelatino silver halide emulsion layers are coated as the auxiliary layer over a multilayer reversal color photographic element having three faster speed conventional picture recording gelatino silver halide emulsion color-forming units, which units are so disposed and sensitized that each is essentially sensitive to a different primary color region of the visible spectrum and which auxiliary layer does not form an image upon image-forming exposure of the picture recording units and the element is exposed to a color picture record without exposing the auxiliary layer and to a sound record and processed as outlined in Table IV-A, color picture records comprised of dye and substantially free of silver and excellent negative sound records comprised of silver are obtained.

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EXAMPLE 5

A control photographic element is provided comprising a cellulose triacetate support having thereon a gelatin silver chlorobromide (80 mole percent of the halide being chloride) emulsion layer coated at a silver coverage of about 200 mg. per square foot and gelatin at about 400 mg. per square foot, and containing 80 mg. per square foot of the photographic competing coupler 1-hydroxy-2-[Δ - (2,4-di-tert-amylphenoxy)-n-butyl]naphthamide dissolved in about 120 mg. per square foot of the coupler solvent di-n-butylphthalate. A test photographic element is prepared in the same way, except that it also contains 40 mg. per square foot of the BIR hydroquinone compound 2,3-dimethyl - 5 - [1 - (3 - nonanamidophenyl)-tetrazolyl - 5 - ylthio]hydroquinone. The photographic elements are processed as described in Example 1. The results show that the test coating retained sufficient silver after bleach-fixing to provide a useful sound track, whereas the control coating failed to retain any significant quantity of silver. Similar results are obtained when the above process is repeated, but replacing the color developer with a black-and-white developer, e.g., the one described in Example 4. Results generally similar to those in Example 3 are obtained when that example is repeated but the BIR hydroquinone compound of the present example is substituted for BIR coupler A in element structures 1, 2, and 3.

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 multilayer color photographic element comprising a support having coated thereon, on one surface, (1) three picture recording photographic color-forming units, each unit comprising at least one silver halide emulsion layer which is so disposed and sensitized that each color-forming unit is essentially sensitive to a different primary color region of the visible spectrum and contains a nondiffusing color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing dye essentially complementary in color to the sensitivity of the unit in which it is incorporated and (2) an auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing a nondiffusing bleach-inhibitor-releasing compound which forms a ballasted silver bleach inhibitor upon reaction with oxidized developing agent.

2. A multilayer color photographic element comprising a support having coated thereon: (1) a picture recording color-forming unit comprising at least one photographic silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing yellow dye; (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing cyan dye; (3) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing magenta dye; and, (4) an auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing at least one nondiffusing bleach-inhibitor-releasing compound which forms a ballasted silver bleach inhibitor upon reac-

tion with oxidized aromatic primary amine color developing agent.

3. A multilayer color photographic element of claim 2 wherein said nondiffusing compound in said auxiliary layer is a bleach-inhibitor-releasing hydroquinone.

4. A multilayer color photographic element of claim 3 wherein said bleach-inhibitor-releasing hydroquinone is 2,3-dimethyl - 5 - [1-(3-nonanamidophenyl)-tetrazolyl-5-ylthio]-hydroquinone.

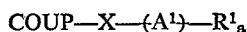
5. A multilayer color photographic element of claim 1 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

6. A multilayer color photographic element of claim 2 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

7. A multilayer color photographic element of claim 3 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

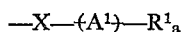
8. A multilayer color photographic element comprising a support having coated thereon (1) a picture recording color-forming unit comprising at least one photographic silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing yellow dye, (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing cyan dye, (3) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing magenta dye and (4) a sound recording auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing at least one nondiffusing bleach-inhibitor-releasing coupler which forms a ballasted silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent.

9. A multilayer color photographic element comprising a transparent support having coated thereon, on one surface, (1) three picture recording photographic color-forming units, each unit comprising at least one silver halide emulsion layer which is so disposed and sensitized that each color-forming unit is essentially sensitive to a different primary color region of the visible spectrum and contains a non-diffusing color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing dye essentially complementary in color to the sensitivity of the unit in which it is incorporated and (2) an auxiliary sound recording silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing a silver bleach-inhibitor-releasing coupler which forms a ballasted silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent, said bleach-inhibitor-releasing coupler having the following formula:



wherein:

COUP is a photographic color coupler radical substituted in its coupling position with the group



X represents sulfur or selenium;

the group $-(\text{A}^1)-\text{R}^1_a$ represents an organic radical that forms a ballasted silver bleach inhibitor with the X radical when said coupler is reacted with oxidized aromatic primary amine color developing agent;

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

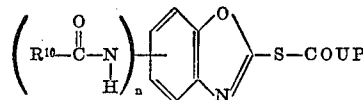
R^1 represents nitro, halo, an alkyl group, an aryl group, a thio group containing from 3 to 22 carbon atoms, an amido group containing from 4 to 22 carbon atoms, a carbonyl group, a carbamoyl group, an alkoxy group or an aryloxy group;

A^1 represents a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring or a 3 to 10 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 does not represent a carbonyl group, a carbamoyl group or an amido group when A^1 represents a carbonyl group or a thiocarbonyl group and such that the grouping $\text{R}^1_a-(\text{A}^1)-$ represents a moiety having a molecular weight of from 125 to 1,000 and such that when A^1 represents a carbocyclic ring or a heterocyclic ring, said carbocyclic or heterocyclic ring is substituted with a hydrophobic moiety.

10. A multilayer color photographic element of claim 9 wherein A represents a radical containing a 5 to 6 membered heterocyclic ring containing at least one nitrogen atom.

11. A multilayer color photographic element of claim 10 wherein $\text{R}^1_a-(\text{A})-$ represents a benzoxazole radical, a benzothiazole radical, a benzimidazole radical, a thiazole radical, a triazole radical or a 1-phenyltetrazole radical.

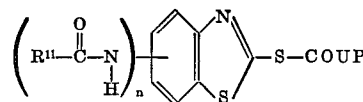
12. A multilayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 4, R^{10} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

13. A multilayer color photographic element of claim 12 wherein n represents 1 and R^{10} represents an alkyl group having from 8 to 12 carbon atoms.

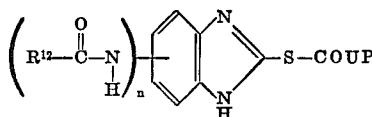
14. A multilayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 4, R^{11} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

15. A multilayer color photographic element of claim 14 wherein n represents 1 and R^{11} represents an alkyl group having from 8 to 12 carbon atoms.

16. A multilayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:

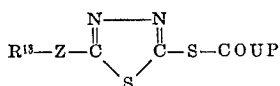


wherein n represents a positive integer of from 1 to 4, R^{12} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

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17. A multilayer color photographic element of claim 16 wherein n represents 1 and R^2 represents an alkyl group having from 8 to 12 carbon atoms.

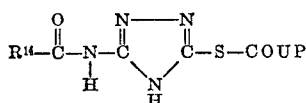
18. A multiayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein Z represents a member selected from the group consisting of sulfur and the group $-\text{NHCO}-$, R^{13} represents an alkyl group having from 5 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

19. A multilayer color photographic element of claim 18 wherein R^{13} represents an alkyl group having from 8 to 12 carbon atoms.

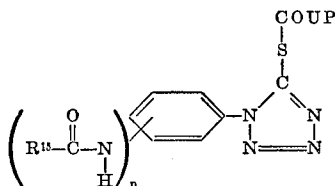
20. A multilayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein R^{14} represents an alkyl group having from 5 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

21. A multilayer color photographic element of claim 20 wherein R^{14} is an alkyl group having from 8 to 12 carbon atoms.

22. A multilayer color photographic element of claim 9 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 5, R^{15} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

23. A multilayer color photographic element of claim 22 wherein n represents 1 and R^{15} represents an alkyl group having from 8 to 12 carbon atoms.

24. A multilayer color photographic element of claim 9 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

25. A multilayer color photographic element of claim 16 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

26. A multilayer color photographic element of claim 22 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 micron to 0.5 micron.

27. A multilayer color photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum containing a non-diffusing yellow dye forming photographic color coupler, (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing cyan dye forming photo-

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graphic color coupler, (3) an auxiliary sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording color-forming units and containing the bleach-inhibitor-releasing coupler 1-hydroxy-4-(5-nonanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide, said bleach-inhibitor-releasing coupler being capable of forming 5-nonanamido-1,3-benzimidazol-2-ylthiol upon reaction with oxidized aromatic primary amine color developing agent and (4) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing magenta forming photographic color coupler.

28. A multilayer color photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a non-diffusing yellow dye forming photographic color coupler, (2) a picture recording photographic silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing cyan dye forming photographic color coupler, (3) an auxiliary sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording layers and containing the bleach-inhibitor-releasing coupler 1-hydroxy-4-[1-(3-nonanamidophenyl)-5-tetrazolylthio]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide, said bleach-inhibitor-releasing coupler being capable of forming 1-(3-nonanamido-phenyl)-5-tetrazolylthiol upon reaction with oxidized aromatic primary amine color developing agent and (4) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing magenta forming photographic color coupler.

29. A multilayer color photographic element comprising a support having coated thereon (1) a picture recording photographic unit comprising at least one silver halide emulsion layer and (2) an image recording auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of said picture recording unit, said auxiliary layer containing (1) at least one nondiffusing bleach-inhibitor-releasing compound which forms a ballasted silver bleach inhibitor upon reaction with oxidized color developing agent and a scavenger for oxidized developing agent, the bleach-inhibitor-releasing compound and the scavenger having about the same rate of reactivity with the oxidized developing agent.

30. A multilayer color photographic element of claim 29 wherein said nondiffusing bleach-inhibitor-releasing compound in said auxiliary layer is a photographic coupler; said scavenger is a photographic color coupler; and, said couplers in said auxiliary layers are present in a concentration sufficient to react with essentially all of the oxidized developer formed as a result of the development of the exposed silver halide in said auxiliary layer.

31. A multilayer color photographic element as defined in claim 30 wherein said scavenger is a photographic color coupler which reacts with oxidized color developing agent to form a cyan dye which absorbs radiation having a wavelength longer than about 700 nm.

32. A multilayer color photographic element as defined in claim 1 wherein said auxiliary layer contains a competing coupler which reacts with oxidized developing agent to form a nondiffusible cyan dye which adsorbs radiation longer than about 700 nm.

33. A multilayer color photographic element as defined in claim 9 wherein said auxiliary layer contains a competing coupler which reacts with oxidized developing

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agent to form a nondiffusible cyan dye which adsorbs radiation longer than about 700 nm.

34. In a process of forming separate silver and dye image records in an exposed photographic element comprising a support having coated thereon a picture recording photographic unit comprising at least one silver halide emulsion layer, and an auxiliary silver image-producing silver halide emulsion layer, which method includes (1) forming dye and a first silver image in said picture recording unit; (2) reacting the silver halide in said auxiliary layer with a photographic developing agent to form a second silver image and oxidized photographic developing agent; and (3) bleaching and fixing said photographic element to remove said first silver image while retaining said second silver image: the improvement wherein said auxiliary layer contains at least one non-diffusing bleach-inhibitor-releasing compound which forms a ballasted silver bleach inhibitor upon reaction with said oxidized developing agent.

35. The process defined in claim 34 wherein the non-diffusing compound in said auxiliary layer is a bleach-inhibitor-releasing hydroquinone.

36. The process defined in claim 35 wherein said bleach-inhibitor-releasing hydroquinone is 2,3-dimethyl-5-[1-(3-nonanamidophenyl)-tetrazol-5-ylthio]hydroquinone.

37. The process of claim 34 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 to 0.5 micron.

38. The process of claim 35 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 to 0.5 micron.

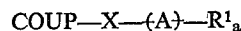
39. The process of claim 36 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 to 0.5 micron.

40. The process of producing a picture record and a silver sound record in an exposed photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing yellow dye, (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primary sensitive to the red region of the visible spectrum and containing a nondiffusing photographic coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing cyan dye, (3) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing cyan dye and (4) a sound recording auxiliary photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing at least one nondiffusing bleach-inhibitor-releasing coupler which forms a ballasted silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent which process comprises (A) developing silver halide in said element with aromatic primary amine color developing agent to form a picture record comprising silver and a nondiffusible dye in said picture recording units and a sound record comprising silver in said auxiliary layer, oxidized aromatic primary amine color developing agent reacting with said bleach-inhibitor-releasing coupler in said auxiliary layer to imagewise release ballasted silver bleach inhibitor and (B) removing the residual silver halide and bleachable

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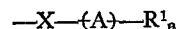
silver remaining after step (A) by bleaching and fixing while retaining silver in said auxiliary layer to form said silver sound record.

41. The process of producing a picture record and a silver sound record in an exposed photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) three picture recording photographic color-forming units, each unit comprising at least one silver halide emulsion layer which are so disposed and sensitized that each said unit is essentially sensitive to a different primary color region of the visible spectrum and contains photographic color coupler which reacts with oxidized aromatic primary amine color developing agent to form a nondiffusing dye essentially complimentary in color to the sensitivity of the unit in which it is incorporated and (2) an auxiliary sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units, said auxiliary layer containing a silver bleach-inhibitor-releasing coupler which forms a ballasted silver bleach inhibitor upon reaction with oxidized aromatic primary amine color developing agent, said bleach-inhibitor-releasing coupler having the following formula:



wherein:

COUP is a photographic color coupler radical substituted in its coupling position with the group



X represents sulfur or selenium;

the group $-(\text{A})-\text{R}^1_a$ represents an organic radical that forms said silver bleach inhibitor with the X radical when said coupler is reacted with oxidized aromatic primary amine color developing agent;

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

R^1 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;

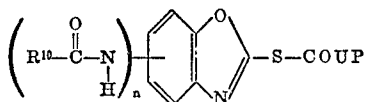
A^1 represents a carbonyl group, a thiocarbonyl group, a carboxymethylene group, a 3 to 6 membered carbocyclic ring or a 3 to 10 membered heterocyclic ring containing at least one carbon atom and at least one heteroatom selected from the group consisting of nitrogen, oxygen, sulfur and selenium such that R^1 does not represent a carbonyl group, a carbamoyl group or an amido group when A^1 represents a carbonyl group or a thiocarbonyl group and such that the grouping $\text{R}^1_a-(\text{A})-$ represents a moiety having a molecular weight of from 125 to 1,000 and such that when A^1 represents a carbocyclic ring or a heterocyclic ring, said carbocyclic or heterocyclic ring is substituted with a hydrophobic moiety which process comprises (A) developing a silver halide in said element with aromatic primary amine color developing agent to form a picture record comprising silver and a nondiffusing dye in said picture recording units and a sound record comprising silver in said auxiliary layer, oxidized aromatic primary amine color developing agent reacting with said bleach-inhibitor-releasing coupler and said auxiliary layer to imagewise release ballasted silver bleach inhibitor and (B) removing the residual silver halide in the element and the bleachable silver remaining after step (A) by bleaching and fixing while retaining silver in said auxiliary layer to form said silver sound record.

42. The process of claim 41 wherein A represents a radical containing a 5 to 6 membered heterocyclic ring, said ring containing at least one nitrogen atom.

43. The process of claim 42 wherein $\text{R}^1_a-(\text{A})-$ represents a benzoxazole radical, a benzothiazole radical, a benzimidazole radical, a thiadiazole radical, a triazole radical or a 1-phenyltetrazole radical.

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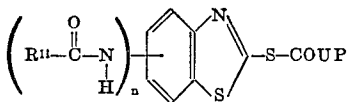
44. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 4, R^{10} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

45. The process of claim 44 wherein n represents 1 and R^{10} represents an alkyl group having from 8 to 12 carbon atoms.

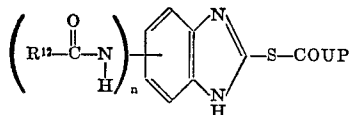
46. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 4, R^{11} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

47. The process of claim 46 wherein n represents 1 and R^{11} represents an alkyl group having from 8 to 12 carbon atoms.

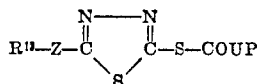
48. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 4, R^{12} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

49. The process of claim 48 wherein n represents 1 and R^{12} represents an alkyl group having from 8 to 12 carbon atoms.

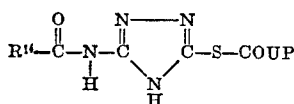
50. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein Z represents a member selected from the group consisting of sulfur and the group $-\text{NHCO}-$, R^{13} represents an alkyl group having from 5 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

51. The process of claim 50 wherein R^{13} represents an alkyl group having from 8 to 12 carbon atoms.

52. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:

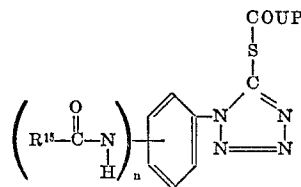


wherein R^{14} represents an alkyl group having from 5 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

53. The process of claim 52 wherein R^{14} is an alkyl group having from 8 to 12 carbon atoms.

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54. The process of claim 41 wherein said bleach-inhibitor-releasing coupler has the following formula:



wherein n represents a positive integer of from 1 to 5, R^{15} represents an alkyl group having from 1 to 17 carbon atoms and COUP represents a photographic coupler substituted in its coupling position with the thio radical.

55. The process of claim 54 wherein n represents 1 and R^{15} represents an alkyl group having from 8 to 12 carbon atoms.

56. The process of claim 41 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 to 0.5 micron.

57. The process of claim 48 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of from 0.05 to 0.5 micron.

58. The process of claim 54 wherein the silver halide of said auxiliary photographic silver halide emulsion layer has an average grain size of 0.05 to 0.5 micron.

59. The process of producing a picture record and a silver sound record in an exposed photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a nondiffusing yellow dye forming photographic color coupler, (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing cyan dye forming photographic color coupler, (3) an auxiliary sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units and containing the bleach-inhibitor-releasing coupler 1-hydroxy-4-(5-nonanamido-1,3-benzimidazol-2-ylthio)-N-(2-n-tetradecyloxyphenyl)-2-naphthamide and (4) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a nondiffusing magenta dye forming photographic color coupler which comprises (A) developing said exposed element with aromatic primary amine color developing agent to form a picture record comprising silver and a nondiffusing dye in said picture recording layers and a sound record comprising silver in said auxiliary layer, oxidized aromatic primary amine color developing agent reacting with said bleach-inhibitor-releasing coupler in said auxiliary layer to image-wise release 5-nonanamido-1,3-benzimidazol-2-ylthiol and (B) removing the residual silver halide and the bleachable silver remaining after step (A) by bleaching and fixing while retaining silver in said auxiliary layer to form said silver sound record.

60. The process of producing a picture record and a silver sound record in an exposed photographic element comprising a transparent support having coated thereon, on one surface in order from the support, (1) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the blue region of the visible spectrum and containing a nondiffusing yellow dye forming photographic color coupler, (2) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the red region of the visible spectrum and containing a nondiffusing cyan dye forming photographic color coupler, (3) an auxiliary

sound recording photographic silver halide emulsion layer which does not form an image upon image-forming exposure of the picture recording units and containing the bleach-inhibitor-releasing coupler 1-hydroxy-4-[1-(3-nonanamidophenyl) - 5-tetrazolylthio]-N-(2-n-tetradecyloxyphenyl)-2-naphthamide and (4) a picture recording photographic color-forming unit comprising at least one silver halide emulsion layer primarily sensitive to the green region of the visible spectrum and containing a non-diffusing magenta dye forming photographic color coupler which comprises (A) developing said exposed element with aromatic primary amine color developing agent to form a picture record comprising silver and a nondiffusing dye in said picture recording layers and a sound record comprising silver in said auxiliary layer, oxidized aromatic primary amine color developing agent reacting with said bleach-inhibitor-releasing coupler in said auxiliary layer to imagewise release 1-(3-nonanamidophenyl)-5-tetrazolylthiol and (B) removing the residual silver halide and the bleachable silver remaining after step (A) by bleaching and fixing while retaining silver in said auxiliary layer to form said silver sound record.

61. A process as defined in claim 34 wherein said auxiliary layer contains, in addition to said bleach-inhibitor-releasing compound, a scavenger for oxidized developing agent; the bleach-inhibitor-releasing compound and the scavenger having about the same rate of reactivity with oxidized developing agent.

62. A process as defined in claim 61 wherein said bleach-inhibitor-releasing compound is a photographic color coupler; said scavenger is a photographic color coupler; and, said couplers are present in a concentration sufficient to react with essentially all of the oxidized developer formed as a result of the development of the exposed silver halide in said oxidizing layer.

63. A process as defined in claim 62 wherein said scavenger is a photographic color coupler which reacts with oxidized color developing agent to form a cyan dye

which absorbs radiation having a wavelength longer than 700 nm.

64. In a multilayer color photographic element comprising a support having coated thereon:

(1) three picture-recording photographic color-forming units, each unit comprising at least one silver halide emulsion layer, each color-forming unit having an effective sensitivity to a different primary color region of the visible spectrum and containing a non-diffusing color coupler to react with oxidized aromatic primary amine color developing agent to form a nondiffusing dye essentially complementary in color to the sensitivity of the unit in which it is incorporated; and

(2) an auxiliary image-recording unit comprising a photographic silver halide emulsion layer;

said photographic element being capable of recording:

(1) an auxiliary record comprising silver, at least a portion of said silver record being in said auxiliary unit; and,

(2) a picture record comprising silver and dye, essentially all of said picture record silver being in said picture color-forming units;

the improvement wherein said silver halide emulsion layer of said auxiliary unit contains a nondiffusing bleach-inhibitor-releasing compound to form a ballasted silver bleach inhibitor by reaction with oxidized developing agent.

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U.S. Cl. X.R.

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