United States Patent [19]
Land et al.

[11] **3,821,000**
[45] **June 28, 1974**

[54] SILVER IMAGE STABILIZATION WITH NOBLE METAL COMPOUNDS AND ENEDIOL DEVELOPERS

[75] Inventors: **Edwin H. Land,** Cambridge; **Stanley M. Bloom,** Waban; **Leonard C. Farney,** Melrose, all of Mass.

[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Nov. 7, 1972**

[21] Appl. No.: **304,489**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 145,044, May 19, 1971, Pat. No. 3,730,716.

[52] **U.S. Cl.** .... **96/76 R,** 96/48 PD, 96/50 R
[51] **Int. Cl.** **G03c 1/48**
[58] **Field of Search** .... 96/29, 76, 48 PD, 50 R

[56] **References Cited**

UNITED STATES PATENTS

3,615,440	10/1971	Bloom	96/29
3,704,126	11/1972	Land et al.	96/76 R
3,730,716	5/1973	Land	96/76 R

Primary Examiner—Ronald H. Smith
Assistant Examiner—John L. Goodrow
Attorney, Agent, or Firm—Robert M. Ford

[57] ABSTRACT

The present invention relates to a novel photographic film unit adapted to provide silver images of enhanced image stability which comprises photosensitive silver halide, a noble metal compound containing a noble metal ion below silver in the Electromotive Force Series of Elements, and a silver halide developing agent whose oxidation product is substantially nonoxidative to the thus-formed silver image for a time sufficient to enable the noble metal ion to contact said silver image to provide sustained and long-lasting stabilization effects.

26 Claims, No Drawings

SILVER IMAGE STABILIZATION WITH NOBLE METAL COMPOUNDS AND ENEDIOL DEVELOPERS

CROSS REFERENCE TO OTHER APPLICATIONS

This application is a continuation-in-part of application Ser. No. 145,044, filed May 19, 1971 now U.S. Pat. No. 3,730,716.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to providing new and improved silver and additive color diffusion transfer process photographic film units which preferably comprise a composite photosensitive element adapted to provide, as a function of the point-to-point degree of the element's photoexposure, integral negative and positive silver images which include a negative silver image in superposed relationship with a positive silver image.

2. Description of Prior Art

As disclosed in U.S. Pat. No. 2,861,885, desirable composite prints comprising both negative and positive images in superposition may be provided by a silver diffusion transfer reversal process employing a photosensitive silver halide emulsion which upon substantially full development of its exposed areas, as a function of exposure, provides a relatively low maximum density negative silver image with relation to the high maximum density positive silver image provided by a silver precipitating environment of the type detailed below. In a composite print produced in accordance with the disclosure of the cited patent, the covering power of a given mass of image silver in the print-receiving element is there stated to range from 14 to 15 times that of an equal mass of image silver in the silver halide element and, that for transparency employment, a maximum negative density of as high as 1.0 density units may be permissible where the maximum positive density is about four or more times as great.

The image-receiving element so employed is disclosed to be constituted as to provide an unusually effective silver precipitating environment which causes the silver deposited therein, in comparison with negative silver developed in the silver halide layer, to possess an extraordinarily high covering power, that is, opacity per given mass of reduced silver; see Edwin H. Land, One Step Photography, Photographic Journal, Section A., pp. 7–15, January, 1950.

Specifically, to provide such envirnoment, silver precipitation nuclei are disclosed to be disposed within the silver receptive stratum in clusters possessing a diameter directly proportional to the mass of image silver to be deposited in situ by reduction. Such conformation is employed to cause image silver to precipitate, in association with the silver precipitation nuclei clusters, with the required density and of a size directly related to the physical parameters of the clusters and the image silver thus precipitated, in situ, in galaxies of chosen physical parameters to provide image conformation in which the elemental silver of the image-receiving element may possess a very high order of covering power, for example, five to fifteen or more times that of the negative image silver in the silver halide layer.

In accordance with the disclosures of U.S. Pat. Nos. 2,726,154 and 2,944,894 additive multicolor reproduction may be accomplished by a diffusion transfer reversal process which specifically includes exposure of an integral multilayer film assemblage through an optical screen comprising a plurality of minute optical elements and carrying photosensitive and image-receptive layers. As disclosed, diffusion transfer processing may be accomplished by permeation of the photoexposed integral film unit with a fluid processing composition and the image-receptive layer retained in permanent fixed relationship to the screen during, and subsequent to, formation of the requisite transfer image, with the operator's option of separating the photosensitive layer from the remainder of the film unit, subsequent to transfer image formation, in film unit structures possessing the image-receiving layer intermediate the screen and emulsion components.

Integral additive color diffusion transfer film assemblages, essentially comprising photoresponsive material directly providing positive image formation and possessing the sensitivity to incident electromagnetic radiation and acuity of image formation necessary to effectively provide color photographic image reproduction, are disclosed and claimed in the following United States Patents which are directed, in general, to film unit assemblages which comprise a permanently fixed laminate including a support carrying on one surface an additive color screen, photosensitive silver halide and silver precipitating nuclei:

U.S. Patents Nos.	Issue Date
3,536,488	October 27, 1970
3,615,427	October 26, 1971
3,615,428	October 26, 1971
3,615,429	October 26, 1971
3,615,426	October 26, 1971

The aforementioned patents are incorporated by reference herein in their entirety.

In the above-indicated film assemblages the silver precipitating nuclei are present in a concentration effective to provide a silver image to the film unit possessing optical density inversely proportional to exposure of the photosensitive silver halide layer, and specifically, in a concentration adapted to provide a silver image derived from unexposed silver halide crystals possessing greater covering power than that of corresponding silver image derived from identical quantum of exposed silver halide crystals.

As set forth in the above-indicated patents improved image reproduction may be obtained by means of the improved silver image characteristics provided therein. Specifically, the above-indicated applications state that composite negative/positive silver image formation possessing an optical density inversely proportional to photoexposure of a photosensitive silver halide layer, characterized by improved silver image minimum and maximum optical densities and image acuity may be achieved by a process which includes exposing a photographic film unit, which comprises a permanent laminate containing a support carrying on one surface silver precipitating nuclei and photosensitive silver halide, and processing the film unit by contact, simultaneous with, or subsequent to, exposure, with an aqueous processing composition, containing a silver halide developing agent and a silver halide solvent, to provide to he film unit the direct formation of a silver image possessing particularly desired low minimum silver image optical density, in terms of exposed areas of the film unit, and high maximum silver image optical density, in terms of unexposed areas of the film unit, as a function of exposure and development of the film unit.

The above-mentioned film units are disclosed to be particularly desirable for employment as a cine film for motion picture projection by reason of the inherent ability to simply and effectively process such a film, employing relatively simple and stable processing compositions, without the necessity of providing a process and apparatus specifically adapted to effect stripping of a separate emulsion stratum from the remainder of the film unit to provide information recordation possessing the image integrity in reproduction characteristics required for effective employment of the film.

Such film assemblages are suitably employed in a cine film system such as that described in U.S. Pat. No. 3,615,127, which includes a compact cine film cassette or container adapted to allow exposure of a film assemblage as retained therein, subsequent processing of the film to provide the desired image record and projection of the resultant image record of other presentation for viewing purposes. Thus, th film assemblage may be exposed, processed, dried if necessary, and projected without transferring the film from its original container to any other container or even in effect removing the film from the original container. The cine film system of U.S. Pat. No. 3,615,127 includes a film processing station whereupon the exposed film strip is transported from a first storage reel, past an applicator where a moist processing composition to develop to a visible condition images recorded on the film is applied and thence to a second storage reel.

The processing composition may be applied to the film assemblage by a variety of methods such as, for example, doctor blades, extrusion heads, capillary applicators, wicks, and the like. The amount of processing composition applied to the assemblage should be controlled within relatively narrow limits, however, sufficient processing composition must be applied to adequately and completely permeate the assemblage to the depth necessary and in the quantity necessary to provide and desired image conformation.

The processing composition employed will generally include an alkaline material, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, or the like, and most preferably, in a concentration providing a pH to the processing composition in excess of about 12. The processing composition may, if desired, contain the sole silver halide developing agent or agents and/or solvent or solvents employed or silver halide developing agent and/or solvent in addition to that disposed as in the film unit. The relative proportions of the agents comprising the developing composition may be altered to suit the requirements of the operator. Thus, the developing composition may be modified by the employment of preservatives, alkalis, silver halide solvents, etc., other than those specifically mentioned herein. When desirable it is also contemplated to include in the developing composition components such as restrainers, accelerators, and the like, and the concentration of such agents may be varied over relatively wide range commensurate with the art.

In the film units and processes set forth in the above-indicated U.S. Pat. Nos. 2,726,154 and 2,944,894, and the above-indicated copending applications, a quantity of processing composition and reactants will inevitably be retained within the film unit, particularly if the image-receiving layer is maintained in permanent relationship with the emulsion as well as the screen, and this residuum may possess the capacity to deleteriously effect image quality over an extended period of time, in addition to conventional environmental degradation of image silver.

SUMMARY OF THE INVENTION

The present invention is specifically directed to novel photographic film units uniquely adapted to provide silver images possessing image stability substantially in excess of that provided by prior art film units, which film units comprise, in essence, photosensitive silver halide, a novel metal compound containing a noble metal ion below silver in the Electromotive Force Series of Elements, and a silver halide developer whose oxidation product is substantially nonoxidative ot the thus-formed silver image for a time sufficient to enable noble metal ion provided by said noble metal compound to contact and interact with said silver image to provide sustained and long-lasting stabilization effects.

The formation of silver images, either negative or positive silver images, in the photosensitive element per se, or in an adjacent receiving layer, generally results in the almost immediate attack of the silver from a variety of sources, most importantly from any residual processing reagents which may be retained in contact with silver image, and also ambient environmental conditions. Thus, to achieve any significant level of stability, it has been generally preferred as far as possible to exclude air during the application of the processing composition, that is, during the formation of the silver image, and to remove as thoroughly and promptly as possible any residual processing reagents and reaction products thereof. As stated above, however, many film units and processes do not permit such stabilizing precautions to be taken.

Copending applications Ser. Nos. 95,443, filed Dec. 7, 1970, now abandoned, and 95,424 filed Dec. 7, 1970 now U.S. Pat. No. 3,704,126, issued Nov. 28, 1972 describe and claim the employment of certain noble metal compounds in the stabilization of silver images. By means of the present invention, still further enhancement of the stability of silver images can be achieved by substantially eliminating the almost immediate degradative attack on the silver image, thus preventing substantially any deterioration of the silver image to occur prior to the interaction of the aforementioned noble metal compounds with the silver image and the resulting stabilization produced thereby.

The present invention is particularly suitable for use in the formation of silver images provided by photographic silver diffusion transfer processes. Thus, the present invention is uniquely adapted to provide silver transfer images possessing image stability in excess of that provided by the prior art process and which process comprises, in essence, exposing to incident actinic radiation a silver diffusion transfer film unit which includes photosensitive silver halide and preferably silver precipitating nuclei; contacting the exposed film unit with a processing composition comprising a silver halide developing agent which provides an oxidation product which is substantially non-oxidative with respect to a silver image, thereby providing a visible silver image to the unit as a function of the point-to-point degree of exposure thereof; and contacting the silver image with a noble metal ion below silver in the Electromotive Force Series of Elements, at a concentration effective to enhance the stability of the silver image. If a transfer image is to be formed, a silver solvent is preferably employed. A preferred silver halide developing agent is an α, β-enediol silver halide developing agent.

The film units of the present invention are specifically adapted to improve silver image stability, particularly silver diffusion transfer image stability with respect to degradative attack by film unit retained residual processing reagents and environmental image contaminants, particularly when processing is carried out under conditions which do not exclude air, which conditions generally accelerate degradation of image silver.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, development of a latent image is carried out by contacting an exposed film unit, comprising photosensitive silver halide, with a silver halide developing agent, thereby providing a silver image as a function of the point-to-point degree of exposure thereof; and contacting said silver image with a noble metal ion below silver in the Electromotive Force Series of Elements, the oxidation products of said developing agent being substantially nonoxidative with respect to said silver image for a time sufficient to permit said metal ion to contact said silver image.

Thus, in the present invention, initial degradation of the silver image is obviated by employing a silver halide developing agent of the aforementioned character, i.e., one whose oxidation product is substantially nonoxidative to the silver of the image. Contrary to prior art systems, the silver image is not subject to immediate attack by the oxidation products of the developer, and, in addition, is protected from the degradative effects of residual processing reagents and reaction products and the environment. The above-described initial and immediate protection obtains for a time sufficient to permit the noble metal ion to contact the silver image to provide the long term stability enhancement.

Thus, in the present invention, the silver halide developer forms, upon reduction of silver halide, oxidation products which are chemically incapable of interaction with image silver to regenerate, by a further redox reaction, silver ion.

The present invention is directed to the long term stabilization of silver images. The silver images may be formed on a receiving layer spatially separated from the photosensitive element i.e., formed by diffusion transfer processing, by precipitation in said receiving layer, preferably by employing silver precipitating nuclei in said layer.

The novel system of the present invention can also be employed to provide enchanced stabilization of the silver image formed in the photosensitive element, i.e., a negative silver image or a direct positive image.

As examples of suitable silver halide developing agents, mention may be made of the hydroxylamines, such as N,N-diethylhydroxylamine, N,N-diethoxyethylhydroxylamine, and the α, β-enediols.

It should also be understood that an auxiliary developer, such as diaminoorthocresol or tolylhydroquinone may also be employed in the present invention.

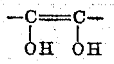
In a particularly preferred embodiment, the silver image is formed by diffusion transfer processing, and the silver halide developing agent is an α, β-enediol.

As previously characterized, a silver diffusion transfer process may be employed to provide a silver transfer image, which may comprise an integral negative silver image in superposed relationship to a positive silver image adapted to exhibit greater covering power than the negative image, by development of the latent image provided a photosensitive silver halide element by exposure and, substantially contemporaneous with such development, formation of a soluble silver complex by reaction of a silver halide solvent with unexposed and undeveloped silver halide of the element. The silver of the resultant soluble silver complex is, at least in part, precipitated in the presence of silver precipitating nuclei to provide the requisite positive silver image formation, which may optionally be retained in contiguous relationship to a negative silver image resultant from development of the latent image carried by exposed silver halide and the concomitant reduction of exposed silver halide to negative image silver, or separated therefrom subsequent to substantial transfer image formation.

In accordance with a preferred embodiment of the present invention, development of the latent image is carried out by contacting the exposed film unit with an α, β-enediol silver halide developing agent and contacting the thus-formed transfer silver image with a noble metal ion below silver in the Electromotive Force Series of Elements. Enhanced stability, of a degree heretofore unobtainable, is thereby provided to the image silver by employing the novel system of the present invention, i.e., the α, β-enediol silver halide developing agent and the noble metal ion, even under processing conditions generally considered to be most detrimental to film unit stability, particularly image silver stability, namely under conditions where air is not excluded as when the processing composition is flowed, sprayed or doctored onto the exposed film unit.

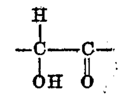
The α, β-enediol silver halide developing agent may be disposed initially in the film unit, i.e., prior to exposure of the film unit, or applied subsequent to exposure, for example, with the processing composition. The enediol developing agent may be disposed in any suitable layer in the film unit. For example, the enediol developer may be disposed in the layer containing the silver precipitating nuclei, the layer containing the photosensitive layer or in a separate layer, for example, disposed in a suitable polymeric layer such as gelatin or cellulose acetate hydrogen phthalate coated on one or more of the other layers in the film unit.

The α, β-enediol developing agents are compounds which contain, in their molecular structure, a segment having the following formula:



$$-\underset{OH}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}-$$

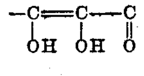
and wherein said segment does not form part of an aromatic ring. Thus, catechol, for example, is specifically excluded from the class of developing agents defined herein. It should be understood that the term, α, β-enediol, as used herein, is intended to refer to the above-indicated segment as well as the tautomer of said segment.



$$-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{O}{\|}}{C}-$$

The enediol developing agents suitable for use in the present invention preferably contain the above-indicated segment as a portion of a heterocyclic or carbocyclic ring.

In a particularly preferred embodiment, the α, β-enediols contain a segment of the formula:

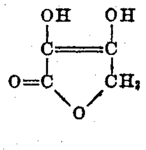


$$-\underset{\underset{OH}{|}}{C}=\underset{\underset{OH}{|}}{C}-\underset{\underset{O}{\|}}{C}$$

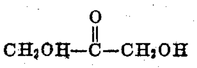
As examples of suitable α, β-enediols, mention may be made of the following:

ascorbic acid

isoascorbic acid

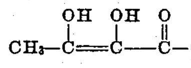


hydroxytetronic acid



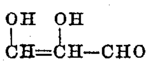
$$CH_2OH-\overset{\overset{O}{\|}}{C}-CH_2OH$$

dihydroxy acetone



$$CH_3-\overset{\overset{OH}{|}}{C}=\overset{\overset{OH}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

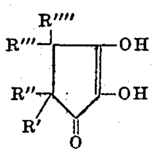
dimethyl reductone



$$\overset{\overset{OH}{|}}{C}H=\overset{\overset{OH}{|}}{C}H-CHO$$

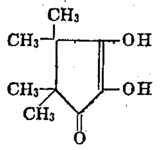
triose reductone

In a particularly preferred embodiment, the enediol silver halide developing agent comprises substituted reductic acid compounds of the formula:



wherein R', R'', R''' and R'''' each are selected from the group consisting of hydrogen and the radical -CH_2R'''' wherein R'''' is hydrogen or a monovalent organic radical selected from the group consisting of amino, cyano, halo, hydroxyl, carboxyl, sulfonyl, alkyl, cycloalkyl, aryl of the benzene or naphthalene series and alkaryl of the benzene or naphthalene series, at least one of said R', R'', R''' and R'''' being -CH_2R''''.

Of the above-indicated class of substituted reductic acids, the preferred is tetramethyl reductic acid



It should be understood that the enediol silver halide developing agent may also be employed in an inactive condition, particularly if such developers are to be disposed in the film unit to avoid fogging or staining on storage. Such inactive species may be provided by acylating the hydroxyl groups, i.e., blocking said hydroxyl groups which groups which would be removed to regenerate the hydroxyl groups by the action of an alkaline processing composition.

It is beilieved that the α, β-enediol developing agents contribute to the enhanced stability of the image silver in combination with the noble metal ion by virtue of the formation of oxidation products which are relatively inert or innocuous with respect to the image silver. Thus, while prior art silver halide developers would form oxidation products deleterious to the image silver and which would result in attack on the image silver substantially immediately upon processing, particularly in the presence of air and retained residual processing reagents, the inert oxidation products of the enediol developers with the noble metal ion imparts a degree of stability heretofore unobtainable, particularly under a normally adverse environment for image silver stability.

The noble metal may be provided to the silver transfer image by the employment of a noble metal ion donor compound which is preferably soluble in the processing composition selected to effect the diffusion transfer process, but which when predisposed in the film unit for solubilization by the composition is substantially insoluble in the film unit medium within which it is disposed during storage and most preferably is solubilized at a rate particularly adapted to avoid deleterious interaction during the initial stage in the development of latent image impressed upon the film unit's silver halide by photoexposure. Commensurate with the employment of conventional alkaline processing compositions and the substantially neutral pH environment of silver diffusion transfer film unit sheet elements in general employment, the preferred noble metal ion donors for distribution within such sheet elements will comprise substantially water-insoluble, alkaline processing composition soluble noble metal donors.

In the practice of the present invention, the noble metal donor may comprise inorganic and organic noble metal compounds and in the preferred embodiments of the invention will comprise an organometal compound which is substantially water-insoluble, alkaline solution soluble and may specifically comprise a compound of the formula: M - X wherein M is a noble metal less reactive than silver, i.e., below silver in the Electromotive, Force Series of Elements and X is a complexing ligand, preferably an organic ligand, which in the preferred embodiments of the invention provides a substantially water-insoluble complex.

The noble metal ions required are those from metals less reactive than silver, that is, those below silver in the Electromotive Force Series of Elements, preferably, palladium, platinum and gold and most preferably Au^{+1} and Au^{+3}.

The particular organic ligand preferably selected will be one which will strongly bond to both the noble metal ion with which it is initially associated and also silver ion displaced from the positive image, should impart a relatively low degree of water solubility to the complex and must not deleteriously interfere with the photographic utility of the film unit.

As will be further described in specific detail below, and subject to the criteria set forth herein, the selected noble metal compound may be disposed in various locations in the film unit such as, for example, in the photosensitive layer, in the image-receiving layer, in a separate layer, or in the processing composition, recognizing that the compound must be selected to avoid any deleterious sensitometric effect to the film unit or interference with positive silver image formation, and must be stable in the particular environment in which it is disposed, e.g,. in an alkaline processing composition medium.

In a particularly preferred embodiment of the present invention, an organic ligand is selected which is a sulfur containing moiety since such ligands possess a specifically desired affinity for noble metal ions. Particularly preferred for such ligands are sulfur atom containing heterocyclic moities which form stable, substantially water-insoluble organometal compounds with noble metals, and particularly those ligands which possess a preferential affinity for silver ions.

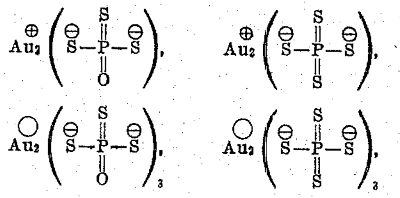
As examples of ligands contemplated for employment in the practice of the present invention, mention may be made of:

2-mercaptobenzimidazole, 2-mercaptoacetamidothiadiazole, 2-mercapto-N-methylimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 1-(3′, 5′-dicarboxyphenyl)-5-mercaptotetrazole, 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzselenazole, phenanthroline, 2,2′-dipyridyl, 8-aminoquinoline, and the like.

In general, it has been found that the substantially water-insoluble noble metal compounds employed in accordance with the present invention may be added to the film unit at any stage during its manufacture. The addition, therefor, may be made before, during or subsequent to fabrication of the film unit although, as stated herein, the compound will preferably be added as a coating final to, for example, the photosensitive silver halide coating solution prior to its application to a supporting member. It will be recognized that the noble metal compound employed in accordance with the invention may also be utilized in combination with additional known image modifying adjuvants such as toning agents, and the like, where desired.

In the preferred embodiment of the present invention, the moble metal compound must be substantially water-insoluble, that is, sufficiently insoluble in the aqueous media constituting the film unit as to prevent deleterious sensiometric interaction between photosensitive silver halide and the noble metal compound during storage, exposure and initial critical stages in the processing of the unit. In general, the compound selected will preferably possess a solubility in water of less than about 10^{-5} moles/liter and will most preferably be adapted to be solubilized by processing composition, for example, alkaline processing composition, at a rate ineffective to interfere with the constitution of and for the development of latent image carried by photoexposed silver halide.

As examples of suitable noble metal compounds, contemplated for employment in the practice of the present invention, mention may be made of organometal compounds such as, for example, gold mercaptobenzimidazole, gold mercaptoacetimidothiazole, gold mercapto-N-methylimidazole, gold phenylmercaptotetrazole, etc., and inorganic noble metal compounds such as, for example,



$$\overset{\oplus}{Au_2}\left(\overset{\ominus}{S}-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{P}}-\overset{\ominus}{S}\right),\quad \overset{\oplus}{Au_2}\left(\overset{\ominus}{S}-\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{P}}-\overset{\ominus}{S}\right),$$

$$\overset{\bigcirc}{Au_2}\left(\overset{\ominus}{S}-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{P}}-\overset{\ominus}{S}\right)_3,\quad \overset{\bigcirc}{Au_2}\left(\overset{\ominus}{S}-\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{P}}-\overset{\ominus}{S}\right)_3,$$

gold thiourea, gold thiocyanate, gold chloride, sodium chloroaurate, etc., and corresponding platinum, palladium, and the like, noble metal analogues.

In general, the optimum concentration of compound to be employed should be determined empirically for each specific photographic film unit system. However, it has been determined that, in general, the preferred concentration to be utilized based upon noble metal will fall within the range of about 1 percent to 20 percent of the silver present in the photosensitive silver halide layer.

Although concentrations in excess of the stated range may be employed, increasing the concentration beyond the designated limits generally provides no commensurate beneficial results. Conversely, concentrations below that of the designated range, however, merely decrease stabilization of the resultant silver transfer image below the beneficial level generally sought, but does not obliterate obtaining beneficial stabilization results.

In point of fact, advantageous results are obtained employing minimal concentrations of compound adapted to provide a metal ion interchange with minimal quantities of elemental image silver.

While not intending to be bound by theory, it is believed that partial replacement of elemental image silver by the selected noble metal ion donated by the compound provides a decrease in the reactivity of the image silver with respect to interaction with degradative materials provided by residual processing reagent present in the film unit or the environment. Specifically, in the preferred embodiments of the present invention, silver ions derived from image silver may be displaced by noble metal ions derived from the compound by a redox reaction resulting in the generation of noble metal and complexed silver ions thus providing to at least a portion of the silver image a less reactive component.

As stated above, the noble metal ion donor may be disposed in a variety of locations in the film unit. Suitable film units include, but are not limited to those set forth in, the aforementioned U.S. Pat. Nos. 3,536,488; 3,615,427; 3,615,428; 3,615,429; and 3,615,426. Thus, the present invention includes film units comprising a photosensitive silver halide layer and a silver precipitating nuclei containing imagereceiving layer adapted to provide positive silver image formation in the reception layer by diffusion transfer processing, which the image-receiving layer may be maintained in superposed relationship with the negative image or separated therefrom, and film units which comprise structures adapted to provide direct positive silver image formation such as, for example, film units possessing silver precipitating nuclei directly associated with photosensitive silver halide.

As will be readily recognized, additional layers may be optionally included in the film unit such as, for example, a separate layer retaining the noble metal donor of the present invention as well as spacer layers, barrier layers, protective layers, stripping layers, and support layers.

In the preferred embodiment of the present invention the film unit comprises a support preferably transparent to actinic radiation and carrying on a first surface a photosensitive silver halide layer and a layer containing silver precipitating nuclei dispersed therein and, for color image reproduction, an additive color screen is interposed between the transparent support and the photosensitive silver halide layer.

Employment of the preferred organometal complexes or compounds wherein the ligand is an organic sulfur-containing heterocyclic ligand of the type which acts as a silver halide photographic stabilizing agent may effectively enhance storage stability of the film unit in which the complex is disposed. Thus, rather than inducing deleterious effects to the film in which it is disposed, the noble metal complex may additionally provide resistance to the normal storage fog degradation generally encountered in silver halide emulsions.

As will be readily recognized, the metal ion donor may also be located in whole or in part in a separate layer in the film unit, preferably adjacent to the layer in which the image silver is to be located; directly in the image-receiving layer and associated with the silver precipitating nuclei, or in the liquid processing composition, and a plurality of donors may be optionally employed, which donors may be disposed, individually or in combination, at one or more of such locations. As stated above, in the instance that the donor is disposed in the processing composition, the specific ligand should be selected to avoid any degradative effects which may occur during storage in the specific media of the processing composition, generally a highly alkaline medium. In instances where is is desired is distribute a noble metal ion donor to the silver image by means of a processing composition in which it fails to exhibit required storage stability, the donor may be initially disposed in association with a selected processing composition applicator such that it is solubilized by and incorporated in the composition immediately preceding, or during, application of the composition to the film unit as, for example, initially disposed in a processing composition applicator wick which provides the transport conduit between the storage chamber for the composition and the film unit during processing.

In addition to the above-mentioned stabilization properties, that is, stabilization of silver image quality and resistance to degradation of the silver image from resistance to degradation of the silver image from residual reagent and atmospheric contact, it has also been discovered that visual image quality with respect to toning may be achieved such as to provide a "blacker" or more neutral silver image.

In a plurality of the above-described film units, the negative silver is also available for interaction with the noble metal, particularly where an integral unit is employed or where the metal donor is initially disposed in the photosensitive silver halide layer. In such units, although the entire amount of silver initially in the unit remains present, in composite film unit structures the negative silver is not visually present to the observer by reason of the difference in covering power and physical state between the respective positive image silver and the negative image silver. It is believed that by reason of, for example, covering power and physical state, including surface area of individual image silver particles, the present invention is preferentially effective with respect to effecting stabilization of the desired positive transfer silver image possessing the physical character described above, without appreciable deleterious effect with respect to the covering power of either the negative or the positive silver image. In addition, it is understood that negative image may act as a deposition matrix to effect removal, from the active photographic system, of noble metal ion in excess of that required to effect stabilization of the positive silver image.

Although as previously stated, a specifically preferred noble metal ion comprises gold ions, it has been found that the employment of the stated metal does not result in the deposition of "red" gold contaminating image integrity. Thus, the photographic quality of the image is not impaired by extraneous reactions of the preferred metal ion and the gold component has not been found to deposit on, or to interfere with, the operation of conventional silver transfer image nucleating sites.

In the practice of the present invention, the silver precipitating nuclei may be disposed within the photosensitive silver halide stratum of the film unit assemblages, in a separate layer or layers or element contiguous one or both surfaces of the silver halide stratum and the silver halide stratum may comprise two or more silver halide strata, each optionally retaining silver precipitating nuclei, and may include a separate silver precipitating nuclei layer positioned intermediate separate silver halide strata.

For the purpose of insuring the production of a positive image possessing a high covering power, the silver precipitating nuclei will be disposed within the film unit in a concentration per unit area effective to cause image silver derived from unexposed silver halide crystals to possess the desired opacity per given mass of in situ reduced silver.

In general, silver precipitating nuclei comprise a specific class of adjuncts well known in the art as adapted to effect catalytic reduction of solubilized silver halide specifically including heavy metals and heavy metal compounds such as the metals of Groups IB, IIB, IVA, VIA, and VIII and the reaction products of Groups IB, IIB, IVA, and VIII metals with elements of Group VIA, and may be effectively employed in the conventional concentrations traditionally employed in the art, preferably in a relatively low concentration in the order of about $1 - 25 \times 10^{-6}$ moles/ft.^{2}.

Especially suitable as silver precipitating agents are those disclosed in U.S. Pat. No. 2,698,237 and specifically the metallic sulfides and selenides, there detailed, these terms being understood to include the selenosulfides, the polysulfides, and the polyselenides. Preferred in this group are the so-called "heavy metal sulfides." For best results it is preferred to employ sulfides whose solubility products in an aqueous medium at approximately 20° C. vary between 10^{-23} and 10^{-30}, and especifally the salts of zinc, copper, cadium and lead. Also particularly suitable as precipitating agents are heavy metals such as silver, gold, platinum, palladium, etc., and in this category the noble metals illustrated are preferred and are generally provided in the matrix as colloidal particles.

In particular, it has been discovered that improved color reproduction in accordance with the principles of additive color photography may be obtained by means of the improved image characteristics provided by reason of the present invention. Specifically, it has been found that composite negative/positive silver image formation, particularly adapted for additive color reproduction and characterized by improved silver image minimum and maximum optical densities and image acuity may be achieved by a process which includes exposing a photographic film unit, which comprises a color screen in association with a photosensitive silver halide layer fabricated to conform to the parameters previously set forth and having associated therewith silver precipitating nuclei, wherein the exposure of the emulsion is effected by radiation traversing through the color screen and the processing of the film is accomplished by contact, simultaneous with, or subsequent to, exposure, with an aqueous processing composition, containing a silver halide developing agent and a silver halide solvent, to provide to the film unit the direct formation of a silver image possessing required low silver image optical density, in terms of exposed areas of the film unit, and required high silver image optical density, in terms of unexposed areas of the film unit, as a function of exposure and development of the film unit.

Color photographic reproduction may thus be provided by exposing the above described photoresponsive silver halide stratum, to selected subject matter, through an optical screen element possessing filter media or screen elements of selected radiation modulating characteristics such as filter media selectively transmitting predetermined portions of the electromagnetic radiation spectrum's visible segment. The color information thus recorded is read out by viewing resultant image conformation through the same or a similar screen element in appropriate registration with the image. The individual filter media or screen elements constituting the optical screen will be constructed to effect selective filtration of predetermined portions of the visible electromagnetic spectrum substantially corresponding to its red, blue and green regions and color information recordation will be accomplished by point-to-point incidence of radiation actinic to the selected photoresponsive material as modulated by such screen element. Visual reproduction of the information content recorded is accomplished by read out of the impressed image as modulated by the original or a substantially identical screen element in accurate registration with the image record.

Although for color information recordation purposes, the photoresponsive material and optical screen may comprise separate and distinct elements appropriately registered during periods of exposure and viewing and the optical screen element may be temporarily or permanently positioned on the surface of a transparent carrier opposite that retaining the photoresponsive material, for practical purposes, it is preferred to permanently position the photoresponsive material in direct contiguous relationship to the color screen during exposure, in order to maximize the acuity of the resultant image record.

Subsequent to exposure of the photoresponsive material to actinic radiation transmitted through and filtered by the optical screen, the resultant photoexposed element may be further processed in accordance with the materials selected and generally without regard to the filter screen when the latter element is stable with respect to and/or protected from contact with the processing compositions and components selected. Such protection and stability will ordinarily be enhanced and facilitated by disposition of the filter screen between a transparent, processing composition impermeable carrier and the photoresponsive material, and, in particular, where such configuration additionally includes the presence of a processing composition barrier element or layer intermediate the screen and the photoresponsive material.

The preferred film assemblages will comprise a panchromatically sensitized silver halide stratum possessing the parameters previously set forth positioned contiguous a surface of the multicolor additive color screen which, in the preferred assemblage denoted above, may also possess the image-receiving component intermediate a silver halide stratum and the color screen, to allow exposure of the emulsion to be accomplished through a color screen, including through a transparent supporting member, if present, and formation of the requisite positive silver image in immediate, contiguous relationship to the color screen employed during exposure. Such embodiment obviates the necessity of registering the color screen with the resultant positive silver image, for viewing purposes, in that the screen employed for exposing may also be employed for viewing and is in automatic registration with the positive silver image.

Thus a preferred embodiment of the present invention for the reproduction of color information in accordance with the principles of additive color photography may comprise a film unit assemblage which contains an additive multicolor screen comprising a geometrically repeditive plurality of actinic radiation-filtering colored elements including a set of primary blue-colored filtered elements, a set of primary green-colored filter elements and a set of primary red-colored filter elements arranged in a repeditive distribution in side-by-side relationship in a substantially single plane positioned intermediate a transparent support member and a photosensitive silver halide stratum conforming to the parameters set forth above and having silver precipitating nuclei associated therewith in any of the manners previously detailed.

It will be specifically recognized, however, that in embodiments of the invention which employ a separate photoinsensitive silver precipitating nuclei containing layer, intermediate a color screen and a photosensitive silver halide layer, such nuclei containing layer should most preferably possess a thickness of less than about a wavelength of light so that for all practical optical purposes the photosensitive silver halide emulsion layer will be effectively located next adjacent the color screen whereby minimizing to a maximum extent any possible optical parallex problems during radiation transmission, as well as any substantial lateral diffusion of silver image-forming components during processing of the film unit.

The photoresponsive silver halide materials employed in the practice of the present invention will, as previously described, comprise a crystal of a compound of silver, for example, one or more of the silver halides, such as photosensitive silver chloride, silver iodide, silver bromide, and preferably, mixed silver halides, such as silver chlorobromide, silver iodochloride, silver iodobromide or silver iodochlorobromide, of varying halides ratios and the silver concentrations despersed in a processing composition permeable binder material such as gelatin and the like, most preferably silver iodobromide and iodochlorobromide, particularly that comprising ~ 1 to 9 percent iodide by weight of silver.

The preferred silver halide type photosensitive layers employed for the fabrication of the photographic film unit, may be prepared by reacting a water-soluble silver halide, such as ammonium, potassium or sodium chloride, preferably together with corresponding iodide and bromide, in an aqueous solution of a peptizing agent such as colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts, for example, employing the preferred gelatin matrix material, by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or, alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,624,929; 2,728,662, and the like; after ripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for example, chemical sensitizing agents and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., Photography — Its Materials and Processes, 6th Ed., 1962.

Optical sensitization and preferably panchromatic sensitization of the emulsion's silver halide crystals may then be accomplished by contact with optical sensitizing dye or dyes; all according to the traditional procedures of the art, or described in Hamer, F. M. The Cyanine Dyes and Related Compounds.

Subsequent to optical sensitization, any further desired additives, such as coating aids and the like, may be incorporated in the emulsion and the mixture coated according to the conventional photographic emulsion coating procedures known in the art.

As the binder for the photoresponsive material, the aforementioned gelatin may be, in whole or in part, replaced with some other natural and/or synthetic processing composition permeable polymeric material such as albumin; casein; or zein or resins such as cellulose derivative, as described in U.S. Pat. Nos. 2,322,085 and 2,541,474; vinyl polymeric such as described in an extensive multiplicity of readily available U.S. and foreign patents or the photoresponsive material may be present substantially free of interstitial binding agent as described in U.S. Pat. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, Comment on Non-Gelatin Film, B. J. O. P., 434, Sept. 15, 1961; and Belgian Pat. Nos. 642,577 and 642,558.

One procedure particularly useful for the production of one preferred gelatino silver halide emulsion comprises the formulation, in the manner previously detailed, of a silver iodochlorobromide emulsion containing in order of ~ 1 percent iodide by initially forming a silver chloride emulsion, adding to the emulsion the requisite bromide and iodide, separating from the formulation undesired reaction products, and afterripening the resultant silver iodochlorobromide emulsion in combination with the selected auxiliary sensitizing, speed increasing, etc., adjuncts elected.

Specifically, the specified emulsion may be formulated by a conventional double jet addition, over a period of 3 minutes and 25 seconds, at a rate of 1,800 cc. per minute of 1,026 gms. of potassium chloride in 5,336 gms. of distilled water at 60° C. and 2,000 gms. of silver nitrate in 5,336 gms. of distilled water to a solution at 80° C. comprising 205 gms. of potassium chloride, 5,750 gms. of distilled water and 2,560 gms. of a solution formed by dissolving 800 gms. of gelatin in 8,800 mls. of distilled water, adjusting the pH to 10±0.1 with 50 percent sodium hydroxide, adding over a 30 minute period and at 40° C. with stirring 88 gms. of phthalic anhydride in 616 mls. of acetone, and after 30 minutes at 40° C. adjusting the pH to 6 with 50 percent sulfuric acid. After a digestion period of 5 minutes at 80° C., 60 gms. of potassium iodide and 1,337 gms. of potassium bromide in 5,336 gms. of water is added to the formulation, over a period of 3 minutes and 25 seconds, at a rate of 1,800 cc. per minute and at 60° C. and the resultant emulsion digested for a further period of 35 minutes at 80° C. The resultant silver iodochlorobromide emulsion is precipitated at 20° C. by reduction of the pH to about 2.7 with sulfuric acid, the precipitate separated from the supernatant liquid and washed with chilled distilled water until the wash water exhibits a conductivity of ~ 50 to 100 μ mhos/cm, the volume adjusted with distilled water for the addition of 950 gms. of gelatin, and the emulsion then afterripening for 210 minutes at a temperature of 54° C. and a pH of 5.7.

The silver precipitating nuclei and/or discrete nuclei layer or layers may be realized by the application of, location of, and/or in situ generation of, the nuclei, which may be similar or dissimilar, directly or indirectly in or as the respective layer and in the presence or absence of binder or matrix material and, in the latter instance, may comprise one or more adjacent or separate strata of a permeable material containing one or more nuclei types disposed in one or more such layers. Matrix materials adapted for such employment may comprise both inorganic and organic materials, the latter type preferably comprising natural or synthetic, processing composition permeable, polymeric materials such as protein materials, for example, glues, gelatins, caseins, etc.,; carbohydrate materials, for example, chitins, gums, starches, alginates, etc.; synthetic polymeric materials, for example, of the vinyl or cellulosic types such as vinyl alcohols, amides and acrylamides, regenerated celluloses and cellulose ether and esters, polyamides and esters, etc., and the like; and the former type preferably comprising submacroscopic agglomerates of minute particles of a water-insoluble, inorganic, preferably siliceous material such, for example, as silica aerogel as disclosed in U.S. Pat. No. 2,698,237.

Where the silver precipitating agent is one or more of the heavy metal sulfides or selenides, it may be preferable to prevent the diffusion and wandering of the sulfide or selenide ions, as the case may be, by also including, in the silver precipitating layers or in separate layers closely adjacent thereto, at least one metallic salt which is substantially more soluble in the processing agent than the heavy metal sulfide or selenide used as the silver precipitating agent and which is irreducible in the processing agent. This more soluble salt has, as its cation, a metal whose ion forms sulfides or selenides which are difficultly soluble in the processing agent and which give up their sulfide or selenide ions to silver by displacement. Accordingly, in the presence of sulfide or selenide ions the metal ions of the more soluble salts have the effect of immediately precipitating the sulfide or selenide ions from solution. These more soluble or ion-capturing salts may be soluble salts of any of the following metals: cadmium, cerium (ous), cobalt (ous), iron, lead, nickel, manganese, thorium and tin. Satisfactory soluble and stable salts of the above metals may be found, for example, among the following groups of salts: the acetates, the nitrates, the borates, the chlorides, the sulfates, the hydroxides, the formates, the citrates and the dithionates. The acetates and nitrates of zinc, cadmium, nickel, and lead are preferred. In general, it is also preferable to use the white or lightly colored salts although for certain special purposes the more darkly colored salts may be employed.

The previously mentioned ion-capturing salts may also serve a function of improving the stability of the positive image provided they possess, in addition to the aforementioned characteristics, the requisites specified in U.S. Pat. No. 2,584,030. For example, if the ioncapturing salt is a salt of a metal which slowly forms insoluble or slightly soluble metallic hydroxides with the hydroxyl ions in the alkaline processing liquid, it will suitably control the alkalinity of the film unit to substantially, if not totally, prevent the formation of undesirable developer stains.

In accordance with a particularly preferred embodiment of the present invention, photosensitive and image-receiving strata carrying the image silver are fabricated to substantially prevent microscopic distortion of the image conformation by preventing microscopic migration or diffusion of image elements within the polymeric matrix. In general, conventional photographic image elements may ordinarily comprise a microscopically dynamic system without seriously noticeable disadvantages to the conventional employment of the image. However, for particularly accurate color reproduction in accordance with the principles of additive color photography, microscopic distortion of image elements is preferably obviated to insure maximization of the accuracy of image registration with the appropriate individual optical filter elements of the additive color screen associated with the image-carrying element. Specifically, it has been found that a photosensitive film unit comprising photosensitive emulsion containing silver halide crystals and silver precipitating nuclei dispersed in a polymeric binder and where employed photoinsensitive image-receiving layers containing silver precipitating nuclei dispersed in a polymeric binder, the binders of which possess a lattic effective to substantially prevent microscopic migration or diffusion of image silver, provide color reproduction acuity particularly desired for effective color reproduction in the manner previously described.

The desired polymeric binder lattice property may be readily achieved by selection of a polymeric material possessing the property of sufficiently fixing spacially image components, or a polymeric material, otherwise desired, may be modified, for example, by crosslinking and/or hardening, to the extent necessary to provide the desired spacial maintenance of image components, that is, a rigidity effective to maintain positive image components in registration with the individual optical filter elements of the color screen through which the photosensitive emulsion was exposed. For example, a preferred polymeric binder material, that is, gelatin, may be hardened by contact with conventional hardening agents to the extent necessary to provide the desired rigidification of the photographic image. Where desired discrete particulate materials facilitating increased processing composition penetration of the photosensitive element, without deleterious effect on the polymeric matrix's lattice, may be advantageously incorporated in the photosensitive element for the purpose of expediting processing of the element.

Production of color screen, in accordance with the art may be prepared by totally mechanical means, as for example, by printing or ruling a dyeable substrate, for example, with a greasy ink formulation, in accordance with the desired filter pattern, subjecting the substrate to suitable coloration, in areas which do not possess the repellant ink mask, effecting removal of the mask, and repeating this procedure, in accordance with the geometrical pattern of filter elements desired, a sufficient number of times to provide the desired multiplicity of diversely colored filter element; directly printing a carrier substrate with the desired dye formulations in accordance with the predetermined filter pattern and repeating this printing procedure a sufficient number of times to provide the multiplicity of colored filter elements desired, or depositing, as an irregular filter screen pattern, a thin layer comprising a random distribution of small grains, such as starch grains, which have been independently colored with the colors desired for optical filtering effects. Alternatively, color screen may be prepared by photomechanical methods of the type initially proposed by, for example, Ducos Du Hauron in the nineteenth century, which comprise, in general, coating a suitable support or film base with an adhesive composition having coated thereon a photosensitive colloid composition, as for example, dichromated gelatin, effecting exposure of the sensitive gelatin layer by incident actinic radiation, through a suitable mask which provides an exposure pattern devised in accordance with the desired optical filter element arrangement, effecting differential hardening of the sensitized material as a function of the point-to-point degree of exposure, removing unexposed unhardened material by solvent contact, subjecting the remaining hardened material to a suitable dyeing procedure in order to provide a first-colored optical filter element series, and repeating this procedure, employing appropriate masks, as often as necessary to provide the number of optical filter element types desired in the final color screen element.

Although color screen may be produced by traditional contact printing or projection type photomechanical processes, a particularly preferred process for the production of color screen comprises the process set forth in U.S. Pat. No. 3,284,208 which includes, in essence, successively coating the smooth surface of a lenticular film with a plurality of photoresponsive layers and sequentially subjecting the coatings to selectively displaced radiation incident on, and focused by, the lenticules receiving same, in order to provide selective exposure of the coating. Subsequent to each exposure, unexposed coating is removed and the resultant resist dyed in order to provide a series of chromatic filter elements, prior to the deposition of the next succeeding photoresponsive layer. Each such exposure is derived from electromagnetic radiation incident on the lenticular film at an angular displacement specifically adapted to provide the desired plurality of chromatic filter element series in substantial side-by-side or screen relationship and adapted to filter predetermined wavelengths of light.

For the preparation of the preferred trichromatic additive screens, the exposed area of each photoresponsive area will generally comprise about one-third of the layer contiguous each lenticule receiving exposing radiation. Although all three exposures may be accomplished by radiation incident on the lenticules of the lenticular film at three separate angles each adapted to provide exposure about one-third of the area contiguous each lenticule receiving radiaiton, it will be recognized that the terminal chromatic filter formation may also be provided by exposing the terminal photoresponsive layer to diffuse radiation traversing through the lenticular film and masked by the previously formed chromatic filter elements.

At a stage subsequent to formation of the first and second series of filter elements, the lenticular configuration will be constituted as a continuous smooth surface. In the instances where the lenticules comprise a separate stratum temporarily affixed to the surface of a support on which the color screen is formed, such separate stratum may be stripped from the support. Alternatively, where the lenticules comprise an integral component of the film base or support and have been provided to the base by pressure and/or solvent deformation of the base, a continuous smooth surface may be reconstituted by application of suitable solvent and the deformation pressures produced during the manufacturing of lenticular film base released to provide reconsitution of the base's original configuration. Where desired, for example, for optical transmission purposes, the reconstituted surface may be polished, for example, by surface contact with an appropriate rotating polishing cylinder or drum, for the time interval necessary to provide the desired optical characteristics to the film base surface.

Optionally the external surface of the color screen may be overcoated with a protective polymeric composition, such as nitrocellulose, cellulose acetate, and the like, for the purpose of protecting the screen from processing composition deformation during employment of the resultant film unit. The external surface of the color screen may then have applied thereto the remaining layers constituting the film assemblage as detailed hereinbefore.

Apparatus particularly adapted to facilitate effecting exposure of the lenticular film in accordance with the aforementioned U.S. Pat. No. 3,284,208 is disclosed and claimed in U.S. Pat. No. 3,318,220.

The support or film base employed may comprise any of the various types of transparent ridged of flexible supports, for example, glass, polymeric films of both the synthetic type and those derived from naturally occurring products, etc. Especially suitable materials, however, comprise flexible transparent synthetic polymers such as polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycol terephthalic acid; polymeric cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetatebutyrate, or acetate propionate; polycarbonates; polystyrenes; and the like.

The present invention will be illustrated in greater detailed in conjunction with the following illustrative constructions which set forth representive embodiments and photographic utilizations of the film units of the present invention, which however, are not limited to the details there set forth but are intended to be illustrative only.

The smooth surface of a lenticular film comprising a polyester film base may have bonded to one surface a cellulose acetate butyrate layer comprising 550 lenticules per inch, each of which may possess a plano-convex configuration for condensing the incident radiation into converging rays and a focal length generally in the order of about 100 microns in air and, as a result of this short focal length, imaging objects over about one inch from the lens surface at infinity, may be coated on the opposite surface with an adhesive composition comprising 70 cc. of methanol, 1.25 grams of nitrocellulose, and 30 cc. of butyl alcohol. A first layer of gelatin sensitized by the addition of 15 weight percent potassium dichromate (based on dry gelatin), may then be coated on the external surface of the first adhesive layer. The first gelatin layer may then be exposed to ultraviolet radiation, in accordance with the previously detailed explanation, and the resultant photoexposed carrier subjected to a water wash in order to provide removal of unexposed sensitized gelatin, in accordance with the exposure pattern contained in the first gelatin layer. The web may then be treated with an acid dyeing bath comprising 1.17 percent Direct Red C.I. 81; 0.32 percent Direct Yellow C.I. 4; and 2.95 percent glacial acetic acid, rinsed to effect removal of excess dye, dried and a second adhesive composition containing 70 cc. of methanol, 30 cc. of butyl alcohol, and 1.25 grams of nitrocellulose overcoated thereon. A second layer of gelatin sensitized by the addition of 15 weight percent potassium dichromate may be coated on the second adhesive layer. The second photosensitized gelatin layer may also be exposed to ultraviolet radiation in accordance with the previously detailed description. The second gelatin layer may then be washed with water to effect removal of unexposed photosensitive gelatin, in the manner previously detailed, and the remaining gelatin resist dyed by contact with an acid dyeing bath containing 0.83 percent Acid Green C.I. 7; 0.32 percent Direct Yellow C.I. 4; and 2.86 percent glacial acetic acid. The web may then be rinsed to effect removal of any residual excess dye, dried and coated with a third adhesive composition comprising 30 cc. butanol, 1.25 grams of nitrocellulose, and 70 cc. of methanol. A third layer of gelatin sensitized with 15 weight percent potassium dichromate may then be coated on the external surface of the third adhesive layer and the third photosensitive gelatin layer subjected to exposure by ultraviolet radiation, in accordance with the description detailed previously. The third layer of photosensitive gelatin may then be washed in order to provide the desired resist formation and the resultant resist dyed by contact with a solution containing 1.0 percent Blue T Pina and 1 percent glacial acetic acid, washed to effect removal of residual dye and dried. A protective overcoat layer may be provided by coating the external surface of the multicolor screen element with a composition comprising 70 cc. methanol, 30 cc. butanol, and 5 grams of nitrocellulose.

Subsequent to formation of the color screen, the lenticulated cellulose acetate butyrate may be removed from the polyester base and the external surface of the polymeric protective coating may be coated with a composition comprising deacetylated chitin and copper sulfide at a coverage of about 4.4 mgs./ft.^{2} deacetylated chitin and 0.25 mgs./ft.^{2} copper sulfide. On the external surface of the silver precipitating agent containing layer may then be coated a hardened gelatino silver iodobromide emulsion coated at a coverage of 150 mgs./ft.^{2} gelatin and 100 mgs./ft.^{2} silver and containing 7.4 mgs./ft.^{2} propylene glycol alginate, 2.9 mgs./ft.^{2} sodium dioctylsulfosuccinate and, overcoating the emulsion layer, a layer of gelatin containing gold complex of the species and at the concentration identified below.

The gelatino silver iodochlorobromide emulsion employed may be prepared as previously detailed and chemically sensitized, at about 56°C., by the addition of a sensitizing amount of a solution containing 0.1 gram of ammonium thiocyanate in 9.9 cc. of water and 1.2 cc. of a solution containing 0.097 gram of gold chloride in 9.9 cc. of water. The resultant emulsion may then be panchromatically sensitized by the sequential addition of 0.1 percent, by weight, methanol solutions of anhydro 5,5′-diphenyl-3,3′-bis-(4-sulfobutyl)-9-ethyloxacarbocyanine hydroxide and anhydro 5,5-dimethyl-3,3′-bis-(3-sulfopropyl)-9-ethylthiacarbocyanine hydroxide in optionally effective concentrations.

The copper sulfide silver precipitating agent may be provided in situ by the addition of substantially equimolar quantities of copper nitrate and sodium sulfide solutions to the deacetylated chitin coating solution prior to application of the composition to the color base support.

The film unit, fabricated either substantially as detailed above or in accordance with any one or more of the structural embodiment denoted above, may be subjected to exposing electromagnetic radiation incident on the transparent base and developed by temporary contact of the film unit, for about 60 seconds, with one of the processing compositions identified below to provide a positive silver image possessing the optical characteristics described hereinbefore and the acuity required for additive color reproduction.

Processing Composition A		
1624	cc.	water
15	g.	carboxymethyl cellulose
64.3	g.	sodium hydroxide
89.1	g.	sodium sulfite
52.8	g.	sodium thiosulfate
50	cc.	of a surfactant (reaction product of nonyl phenol and glycidyl)
40	g.	cystine
—		silver halide developer
Processing Composition B		
11,125	cc.	water
600	g.	carboxymethyl cellulose
625	g.	sodium hydroxide
648	g.	sodium sulfite
1600	g.	sodium thiosulfate
720	cc.	of a surfactant (reaction product of nonyl phenol and glycidyl)
42	g.	nitrobenzimidazole
—		silver halide developer

For purposes of illustrating the advantageous results achieved by reason of the present invention, film units, fabricated and processed in the general manner detailed above, were subjected to an accelerated aging test which comprised the exposure of processed units to an environmental temperature of 100°F. at a relative humidity of 100 percent, for 72 hours.

The following tables set forth the density of the indicated component of transmitted light as measured on a densitometer.

TABLE 1

The film units were processed with Processing Composition A plus the indicated developers and 0.02 g./10 cc. of processing composition of diamino orthocresol as an auxiliary developer.

	92 mg. silver/No gold compound			86.1 mg. silver/9.6 mg. gold Mercaptobenzimidazole		
	Red	Green	Blue	Red	Green	Blue
Toluhydroquinone (0.423 g./10 cc. of processing composition)						
before test	2.17	2.81	3.07	2.25	2.65	3.05
after	.49	1.06	.90	2.05	1.86	2.66
% of original D_{max} retained	23	38	29	91	70	87
Dimethylhydroquinone (0.47 g./10 cc. of processing composition)						
before test	1.03	1.54	1.80	1.54	2.06	2.70
after	.24	.33	.34	1.43	1.43	1.89
% of original D_{max} retained	23	21	19	93	69	70

TABLE 1 – Continued

The film units were processed with Processing Composition A plus the indicated developers and 0.02 g./10 cc. of processing composition of diamino orthocresol as an auxiliary developer.

	92 mg. silver/No gold compound			86.1 mg. silver/9.6 mg. gold Mercaptobenzimidazole		
	Red	Green	Blue	Red	Green	Blue
Tetramethyl reductic acid (0.58 g./10 cc. of processing composition)						
before test	1.46	1.97	2.60	1.64	2.03	2.76
after	.95	1.41	1.86	1.64	1.93	2.26
% of original D_{max} retained	65	72	72	99	100	82
Ascorbic acid (0.6 g./10 cc. of processing composition)						
before test	1.55	2.06	2.64	1.64	1.92	2.77
after	.59	.93	1.16	2.26	2.23	3.06
% of original D_{max} retained	38	45	44	137	116	110

TABLE 2

The film units were processed with Processing Composition B plus the indicated developers and 0.02 g./10 cc. of processing composition of diamine orthocresol as an auxiliary developer.

	92 mg. silver/No gold compound			86.1 mg. silver/9.6 mg. gold Mercaptobenzimidazole		
	Red	Green	Blue	Red	Green	Blue
Toluhydroquinone (0.423 g./10 cc. of processing composition)						
before test	2.63	3.17	3.52	2.41	2.75	3.23
after	1.10	1.69	1.97	2.20	2.50	2.70
% of original D_{max} retained	42	53	56	91	91	84
Dimethylhydroquinone (0.47 g./10 cc. of processing composition)						
before test	2.42	3.03	3.42	2.01	2.48	3.10
after	.42	1.01	1.23	1.29	1.81	2.28
% of original D_{max} retained	21	33	36	64	73	74
Tetramethyl reductic acid (0.589 g./10 cc. of processing composition)						
before test	2.11	2.49	2.62	2.11	2.34	2.82
after	1.59	1.98	2.22	2.09	2.33	2.54
% of original D_{max} retained	75	80	85	101	100	90
Ascorbic acid (0.6 g./10 cc. of processing composition)						
before test	2.19	2.61	3.14	1.95	2.35	2.90
after	1.15	1.73	2.33	2.11	2.32	2.51
% of original D_{max} retained	53	66	74	108	101	87

From the foregoing data it will be readily noted that the previously described significant improval in silver transfer image stability is directly achieved by means of the present invention when the exposed film unit is contacted with the described silver halide developing agent and noble metal ions.

In one embodiment of the present invention, the film unit employs ascorbic acid as the developing agent, gold mercaptobenzimidazole as the noble metal ion-providing compound and colloidal gold as the silver precipitating nuclei.

As denoted above, the photosensitive silver halide stratum and/or the silver precipitating nuclei containing stratum may have advantageously incorporated therein discrete particulate materials providing increased porosity to the film unit, without deleterious effect on the dimensional stability of the binder lattice, in particular, those materials which additionally act as an anti-swelling agent for the binder material and, accordingly, act to facilitate the prevention of the carried image's microscopic distortion, particularly, with respect to an associated color screen, such as discrete silica particles dispersed, for example, in a concentration of about 0.3 to 1.5 silica per part binder, for the purpose of facilitating processing composition permeation of the film unit's silver halide crystal and silver precipitating nuclei containing layer or layers. In addition, the silver halide or silver precipitating nuclei containing stratum may be advantageously overcoated with a processing composition permeable polymeric material such as a hardened gelatin pad or the like to advantageously promote uniformity in processing composition permeation of such stratum, by modulating any wave front resultant from initial surface contact with the liquid employed and to thereby promote uniform maintenance of the polymeric binder's physical characteristics.

Although chrome alum and particularly algin have been advantageously employed as hardening agents for the polymeric gelatin emulsion binder, it will be recognized that substantially any hardening or crosslinking agent may be employed, where necessary and with respect to any one or more layers of the film unit, which does not provide deleterious photographic effects, to the extent required to provide a binder lattice which effectively inhibits to a substantial effect, migration of image silver. An extensive collection of hardening agents are disclosed in the art as specifically adapted to effect handling or crosslinking of photographic polymeric binder material compositions and by reason of their inocuous photographic effects are to be preferred in the practice of the present invention. The sole requirement for effective operation of the film unit is that the emulsion's polymeric lattice be constructed to provide the optical image parameters denoted hereinbefore. Thus, substantially any conventional hardening and crosslinking agent may be selected from those set forth throughout, for example, the pertinent patent literature regarding such agents, and the concentration employed, as known in the art, will be dependent upon the relative activity of the selected agent, or agents, and the relative amount of hardening or crosslinking to be effected. The specific concentration of a selective hardening or crosslinking agent, to be contacted with a selected polymeric binder, may be readily determined empirically, within the specific context of ultimate photographic employment, by screening. It will be further recognized that any of the various processing composition permeable, synthetic or natural polymeric materials, possessing the physical characteristics required to provide the results denoted above, may be substituted in replacement of the specifically illustrated polymeric materials provided with such selected polymer provides a matrix which is not deleterious to photosensitive silver halide crystals and possesses a lattice allowing processing in the manner previously described.

Suitable silver halide solvents for employment in the practice of the present invention include conventional fixing agents such as the previously noted sodium thiosulfate, sodium thiocyanate, ammonium thiocyanate, the additional agents described in U.S. Pat. No. 2,543,181, and the associations of cyclic imides and nitrogenous bases such as associations of barbiturates or uracils and ammonia or amines and other associations described in U.S. Pat. No. 2,857,274.

Where desired conventional silver toning agent or agents may be disposed within the emulsion composition in a concentration effective to provide a positive image toned in accordance with the desires of the operator.

In the preferred embodiment of the present invention, the processing composition will include an alkaline material, for example, sodium hydroxide, potassium hydroxide or sodium carbonate, or the like, and most preferably in a concentration providing a pH to the processing composition in excess of about 12. The processing composition may, where desired, contain the sole silver halide developing agent or agents employed, or a silver halide developing agent in addition to that disposed within the film unit; however, disposition of one or more developing agents in the emulsion and/or permeable layer directly associated therewith, intermediate the emulsion and a color screen, is a particularly preferred embodiment, for the purpose of providing enhanced image acuity, by more readily facilitating directly initiated development at radiation exposed areas of the emulsion without the necessity of diffusing such agents to such sites by means of the processing composition selected.

The preferred silver halide developing agents generally comprise organic compounds and, in particular, comprise organic compounds of the aromatic series containing at least two hydroxyl and/or amino groups wherein at least one of such groups is in one of ortho or para positions with respect to at least one other of such groups such as, for example, the various known hydroquinones, p-aminophenols, and their various known functional homologues and analogues.

It will be apparent that the relative proportions of the agents comprising the processing composition set forth herein may be altered to suit the requirements of the operator, however, the processing composition solvent employed will generally comprise water and will possess a solvent capacity which does not deleteriously hydrate the selected binder lattices beyond that required to provide the preferred image formation. Accordingly, no adjunct should be included within such composition which deleteriously effects the lattice parameters required for such image formation.

In the description herein, each color series of filter elements has been described as covering that part of the total area in proportion to the total number of colors used, i.e., in the tricolor system, each color occupies one-third of the total area. This may vary quite widely before having noticeable effect to the observer and, in fact, may be compensated by changing the intensity of the colors. In actual practice, if one dye is of greater intensity than the others, a deliberate compensation may be made by reducing the total relative area of the intense color. The aspect of relative areas is well known in the art so that when relative areas are used in this application, it is intended to include the variances which the art would recognize as being successful.

Various colors and numbers of colors may be used in this invention but the preferred system, as previously mentioned, is a tricolor arrangement of the three primary colors, red, green, and blue.

It will be recognized, however, that, in accordance with the instant disclosure, a plurality of chromatic filter element series may be provided, the number of series being solely determined by the optical parameters of the resultant color screen desired.

For example, a four-color system such as red, green, violet-blue and orange-yellow could also be effectively employed in accordance with the teachings of the instant disclosure.

In the practice of the present invention, additive trichromatic color screens possessing 550, 756, and 1125 triplets/inch may be readily employed and it has been found that image resolution obtained by means of the present invention exceeds that obtainable in prior art processes. Such increased resolution specifically facilitates the acuity of color reproduction to be achieved by the practice of the invention and the silver halide stratum will be panchromatically sensitized to provide equal image production, as a direct function of incident exposing radiation, throughout the response portion of the radiation spectrum to further enhance the acuity of color information recordation by the emulsion.

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of enhancing adhesion, and that one or more of the described layers may comprise a composite of two or more strata which may be contiguous or separated from each other.

Since certain changes may be made in the above product, process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic process which comprises, in combination, the steps of:

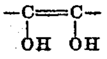
a. exposing a photographic film unit comprising photosensitive silver halide;

b. contacting said exposed film unit with a processing composition containing an α,β-enediol silver halide developing agent, thereby providing a visible silver image to said unit as a function of the point-to-point degree of exposure thereof; and

c. contacting said silver image with a noble metal ion below silver in the Electromotive Force Series of Elements.

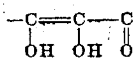
2. A process as defined in claim **1** wherein said processing composition includes a silver halide solvent and said visible silver image is formed by silver diffusion transfer and said film unit includes silver precipitating nuclei.

3. A process as defined in claim **2** wherein said enediol silver halide developing agent contains, in its molecular structure, a segment of the formula:



$$-\underset{OH}{C}=\underset{OH}{C}-$$

4. A process as defined in claim **3** wherein said enediol silver halide developing agent includes in its molecular structure, a segment of the formula:



$$-\underset{OH}{C}=\underset{OH}{C}-\underset{\overset{\|}{O}}{C}$$

5. A process as defined in claim **2** which comprises, in combination, the steps of:

a. exposing a photographic film unit comprising a transparent support carrying on a first surface a substantially photosensitive layer comprising silver precipitating nuclei and a photosensitive silver halide layer comprising photosensitive silver halide crystals, and a noble metal ion below silver in the Electromotive Force Series of Elements;

b. contacting said silver halide emulsion with an aqueous processing composition containing an α,β-enediol silver halide developing agent and a silver halide solvent for a period of time effective to provide a visible silver image to said film unit, as a function of exposure; and

c. coacting said silver image with a noble metal ion below silver in the Electromotive Force Series of Elements in a concentration effective to enhance the stability of said silver image.

6. A process as defined in claim **5** which comprises, in combination, the steps of:

a. exposing a photographic film unit which comprises a permanent fixed laminate containing a transparent support carrying a trichromatic additive color screen comprising red, green and blue optical filter elements, a substantially photoinsensitive layer comprising silver precipitating nuclei dispersed in a processing composition permeable matrix, a photosensitive silver halide emulsion comprising photosensitive silver halide crystals dispersed in a processing composition permeable polymeric binder and a nobel metal ion below silver in the Electromotive Force Series of Elements, said exposure accomplished by actinic radiation transmitted through said screen;

b. contacting said silver halide emulsion with an aqueous processing composition containing an α,β-enediol silver halide developing agent and a silver halide solvent for a period of time effective to provide a visible silver image to said film unit, in terms of the unexposed areas of said emulsion, as a function of the point-to-point degree of emulsion exposure, and coaction between said silver image and said noble metal ion effective to enhance the stability of said silver image; and

c. maintaining said laminate intact subsequent to processing.

7. A process as defined in claim **6** wherein said developing agent is tetramethyl reductive acid and said noble metal ion is gold ion.

8. A process as defined in claim **1** wherein said noble metal compound is an organometal compound of the formula:

$$M—X$$

wherein M is a noble metal ion below silver in the Electromotive Force Series of Elements and X is a ligand which provides a substantially water-isoluble, alkaline solution soluble complex.

9. A process as defined in claim **8** wherein M comprises gold, platinum or palladium.

10. A process as defined in claim **9** wherein said gold is Au^{+1}.

11. A process as defined in claim **9** wherein said gold is Au^{+3}.

12. A silver diffusion transfer photographic process as defined in claim **8** wherein X is selected from the group consisting of 2-mercaptobenzimidazole, 1-phenyl-5-mercaptotetrazole and N'-methyl-2-mercaptoimidazole.

13. A process as defined in claim **5** wherein said processing composition contains an auxiliary developing agent.

14. A process as defined in claim **13** wherein said auxiliary developing agent is diaminoorthocresol.

15. A photographic film unit comprising a permanent laminate adapted to be processed by diffusion transfer processing which comprises a common transparent support carrying on one surface a layer comprising silver precipitating nuclei and a layer comprising photosensitive silver halide crystals, and a noble metal below silver in the Electromotive Force Series of Elements, adapted to interact with a silver image provided by processing of the film unit, in a concentration effective to enhance the stability of said silver image and an α,β-enediol silver halide developing agent.

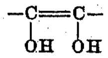
16. A film unit as defined in claim **15** wherein said noble metal is disposed in said layer containing said photosensitive silver halide crystals.

17. A film unit as defined in claim **15** wherein said noble metal is disposed in said layer containing said silver precipitating nuclei.

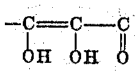
18. A film unit as defined in claim **15** which includes a processing composition permeable layer, said permeable layer having said noble metal disposed therein.

19. A film unit as defined in claim **15** which includes an additive color screen.

20. A film unit as defined in claim **15** wherein said α,β-enediol developing agent contains, in its molecular structure, a segment of the formula:



$$-\underset{OH}{C}=\underset{OH}{C}-$$



$$-\underset{OH}{C}=\underset{OH}{C}-\underset{\overset{\|}{O}}{C}$$

21. A film unit as defined in claim **20** wherein said segment is part of an heterocyclic structure.

22. A film unit as defined in claim **20** wherein said segment is part of a carbocyclic ring.

23. A film unit as defined in claim **15** wherein said noble metal compound is present in a concentration in terms of noble metal within the range of about 1% to 20% of the silver present as silver halide.

24. A film unit as defined in claim **15** wherein said noble metal compound possesses the formula:

$$M—X$$

wherein M is a noble metal below silver in the Electromotive Force Series of Elements and X is an organic ligand which provides a substantially water-insoluble complex.

25. A film unit as defined in claim **24** wherein X is 2-mercaptobenzimidazole, 1-phenyl-5-mercaptotetrazole or N'-methyl-2-mercaptoimidazole.

26. A film unit as defined in claim **24** wherein M comprises gold, platinum or palladium and said α,β-enediol silver halide developing agent is tetramethyl reductic acid.

* * * * *