NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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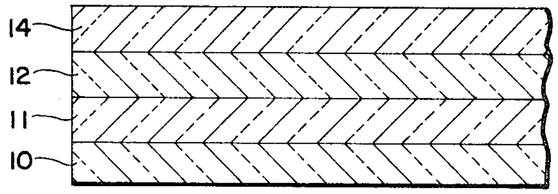

FIG. 1

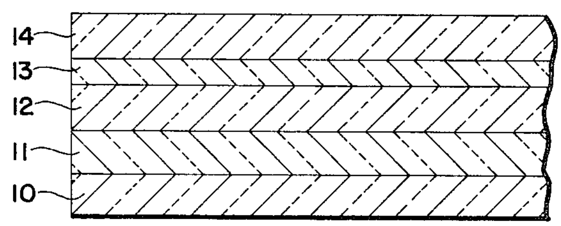

FIG. 2

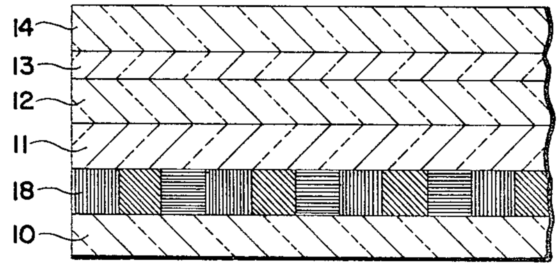

FIG. 3

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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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U.S. Cl. 96—29 13 Claims

ABSTRACT OF THE DISCLOSURE

A composite film structure comprising a laminate including a common support carrying on one surface, in order, a layer containing silver precipitating nuclei, an inert non-nucleated polymeric layer and a layer containing photosensitive silver halide crystals. Subsequent to exposure and processing, the layer containing photosensitive silver halide crystals may be removed thereby providing a film unit wherein a protective layer is located over the layer in which the image is formed, i.e., the layer containing the silver precipitating nuclei. In a particularly preferred embodiment, an additive color screen is employed between the support and the layer containing silver precipitating nuclei. The disclosed film structure is particularly suitable for use as motion picture film.

In general, photographic silver image reproduction may be provided by selective exposure of, for example, the preferred photoresponsive material, that is, photosensitive silver halide, and the resultant exposed material may be processed in the conventional manner. Specifically, the photoexposed emulsion thus may be developed by any of the conventional developing procedures known in the art to be adapted to effect reduction of photoexposed silver halide crystals. In general, such development will be effected by contact of the photoexposed emulsion with a solution containing a conventional development agent such as one or more of the conventional developing agents and compositions of same set forth in Chapter 14 of The Theory of the Photographic Process (Revised edition—1954), C. E. K. Mees, the MacMillan Co., New York, New York and Chapters 6, 7, 8 and 9 of Photographic Chemistry, volume I, P. Glafkides, Foundation Press, London, England. The preferred 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, p-phenylene diamines, and their various known functional homologues and analogues. The developing composition containing the specific silver halide developing agents selected will generally comprise an aqueous solution additionally containing at least an alkaline material such as sodium hydroxide or sodium carbonate or the like and may be contacted with the photoexposed silver halide material according to any of the conventional tray, tank, or the like, procedures. The composition may additionally and optionally contain one or more specific silver halide developing agents, preservatives, alkalis, restrainers, accelerators, etc., other than those specifically denoted in the cited reference material. The concentration of the various components employed may be varied over a wide range and, where desirable, any one or more of such components may be disposed in the photosensitive element, prior to exposure, and in a separate permeable layer of such element and/or in the emulsion comprising the photosensitive silver halide material itself.

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For the purpose of stabilizing the developed image, the emulsion may be fixed in any of the conventional fixing, washing, and/or drying procedures known in the art as, for example, those described in Chapter 11 of Photographic Chemistry, volumn I, supra, and Chapter 17 of The Theory of the Photographic Process, supra. For example, the photosensitive material retaining the developed image may be initially contacted with a stop bath adapted to terminate action of the developing agent on the photosensitive emulsion by converting the pH of the emulsion to that at which the selected silver halide developing agent or agents exhibit substantially no developing potential. Specifically, where the silver halide developing agent is organic compound exhibiting its developing action at an alkaline pH, for example, a hydroquinone, or the like, the emulsion may be subjected to an acid stop bath for a sufficient time interval as to effectively neutralize the silver halide developing potential of the selected developing agent.

The emulsion may then be subjected to a fixing bath in order to effect removal of unexposed photoresponsive silver halide from the emulsion in accordance with the conventional procedures known to the art as adapted to effect same and as further detailed in the last cited references.

In general, the fixing agent employed may comprise a bath of a silver halide solvent such as sodium thiosulfate which is effective to remove substantially all types of silver halides from disposition in the emulsion strata originally containing the photosensitive silver halide without deleterious attack upon the conformation of the developed silver image. Subsequent to fixation, all residual traces of the fixing agent may be removed by aqueous wash contact, in order to insure the permanency of the developed image.

Where positive silver image formation is desired, that is, an image provided in terms of unexposed portions of the emulsion, reversal processing may be employed in its conventional manner, or a direct positive emulsion may be employed, or the positive image may be provided by diffusion transfer processing.

In the first alternative denoted above, the reversal processing may be accomplished in the conventional manner by developing the photoexposed emulsion by any of the conventional procedures known in the art as adapted to effect development of the latent image resultant from photoexposure such as, for example, the procedures identified above. Subsequent to development of the latent image to a visible silver image, the resultant developed image may be effectively removed in the conventional manner by contact of the image with any of the conventional agents known in the art as adapted to effect removal of a photographic silver image without deleterious effect upon unexposed photosensitive silver halide such as, for example, the bleaching agents and bleaching baths set forth in Chapter 30 of Photographic Chemistry, volume II, supra. Subsequent to the removal of the developed image by, for example, bleaching, the photosensitive silver halide remaining in the emulsion structure may be converted to a developable state by physical fogging resultant from, for example, exposure of actinic radiation, and/or chemical fogging, for example, by contact with a conventional fogging agent or the like, and in turn, the resultant fogged silver halide may be developed and, where desired, stabilized, in the manner set forth above, to provide the requisite positive silver image formation.

In the second alternative denoted above, the requisite positive silver image formation may be provided by employment of a conventional direct positive silver halide emulsion which may be directly developed, in the presence of a fogging agent, according to the procedure described above, to provide the requisite positive silver image formation.

In the third alternative denoted above, the positive silver image formation may be provided by diffusion transfer processing wherein the latent image provided to the photosensitive silver halide emulsion by exposure is developed and, substantially contemporaneous with such development, a soluble complex is obtained, for example, by reaction of a silver halide solvent with unexposed and undeveloped silver halide of the emulsion. The resultant soluble silver complex may be, at least in part, transported in the direction of a suitable print-receiving element, and the silver of the complex precipitated in such element to provide the requisite positive silver image formation. The resultant positive silver image in this embodiment, a silver transfer image, may be viewed as a reflection print or a transparency.

Of the three alternatives denoted above, production of the positive image by diffusion transfer processing is clearly preferable to that denoted by the first alternative in view of the effective simplicity of the processing involved and is clearly preferably to that of the second embodiment by reason of the higher photographic speeds practicably obtainable.

In general, color photographic reproduction may be provided by exposing a photoresponsive material such as, for example, a photosensitive silver halide emulsion, 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 in the photoresponsive material through the same or a similar screen element in appropriate registration with the image. For the reproduction of subject matter in color and in accordance with the principles of additive color photography, 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 is 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 by the photoresponsive material 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.

Additive color photographic reproduction thus may be provided by exposing a photoresponsive material, preferably a photosensitive silver halide emulsion, through an additive color screen having a plurality of filter media or screen element sets each of an individual additive color such as red, blue, or green, and by viewing the resultant photographic image, preferably a silver image, subsequent to development of such image, through the same or a substantially identical screen element suitably registered.

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, where required, 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.

Subsequent to selective exposure of, for example, the preferred photoresponsive material, that is, photosensitive silver halide, the resultant exposed material may be processed in the same manner as black-and-white photographic film is conventionally processed, as described above.

Although, as disclosed in U.S. Pat. No. 2,614,926, the positive silver transfer image formation may be provided by an additive multicolor diffusion transfer reversal process which includes exposure of a silver halide emulsion layer through an additive color screen and separation of the emulsion layer, from contact with the remainder of the film unit, subsequent to processing, while retaining filter media and reception layer in fixed relationship, an alternative process will comprise that disclosed in U.S. Pats. Nos. 2,726,154 and 2,944,894, which are directed to a diffusion transfer reversal process which specifically includes exposure of an integral multilayer film assemblage through a screen possessing a plurality of minute optical elements and carrying photosensitive and image-receiving layers. As disclosed in the cited patents, transfer processing of the exposed film may be accomplished by permeation of the exposed integral film unit with a liquid processing composition and the image-receiving 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.

Improved integral silver diffusion transfer film assemblages essentially comprising photoresponsive material directly providing positive image formation and possessing the sensitivity to incident magnetic radiation and acuity of image formation necessary to effectively provide photographic image reproduction, both black and white and assemblages including optical screen elements to provide color photographic image reproductions, are disclosed and claimed in the following copending applications which are directed in general to film unit assemblages which comprise a permanently fixed laminate which includes a support carrying on one surface of said support photosensitive silver halide crystals and silver precipitating nuclei:

Applications Ser. Nos.:	Filing date
736,796	June 13, 1969
889,656	Dec. 31, 1969
889,657	Dec. 31, 1969
889,660	Dec. 31, 1969
889,636	Dec. 31, 1969

The aforementioned applications 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 applications, improved image reproduction may be obtained by means of the improved silver image characteristics provided by reason of the invention. 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 at least two separate and discrete layers containing silver precipitating nuclei and a photosensitive silver halide layer positioned intermediate two silver precipitating nuclei containing layers 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 the 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 immediately subsequent to exposure.

The processing comoposition employed will 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 employed or a silver halide developing agent 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. When desirable it is also contemplated to include in the developing composition components such as restrainers, accelerators, and the like. The concentration of such agents may be varied over relatively wide range commensurate with the art.

A novel film unit has now been found which is not susceptible to the deficiencies of the prior art.

SUMMARY OF THE INVENTION

The present invention is directed to a photographic film unit which comprises a laminate including a support carrying on one surface, in order, a layer containing silver precipitating nuclei, an inert non-nucleated protective layer, and a layer containing a photosensitive silver halide emulsion. The purpose of the non-nucleated protective layer is to provide a barrier between the layer carrying the transferred silver image after the emulsion layer has been removed subsequent to processing. The material for said protective layer is selected from one which is readily permeable to the processing composition and which will not provide sites for the nucleation of the silver forming the transferred image. Thus, the term "inert" refers to the inactivity of the layer with respect to the photographic process. In a particularly preferred embodiment, particularly when the film unit is employed as motion picture film, the protective layer contains dispersed therein a friction reducing agent or lubricating composition which, during processing, will bloom to the outer surface of the protective layer thereby imparting the necessary slip properties to the film unit subsequent to the removal of the emulsion layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic enlarged cross-sectional view illustrating a photographic film unit of the present invention; and

FIGS. 2 and 3 inclusive are diagrammatic enlarged

cross-sectional views analogous to FIG. 1 illustrating preferred film units of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been discovered that distinctly advantageous results may be achieved with respect to the protection, stability and quality of the silver image formed by diffusion transfer in an initially integral film unit wherein the emulsion layer is removed subsequent to processing. The above-mentioned advantageous results are achieved by providing a layer adjacent to the layer in which the silver image is formed, i.e. adjacent to the layer containing silver precipitating nuclei, whereby said image layer is intermediate said support and said adjacent layer. It is particularly preferred that the outermost layer in the film unit after removal of the emulsion layer is the above-indicated protective layer.

In other words, a protective layer is provided to the film unit distal to the common support layer.

In an alternative embodiment, a diffusible stabilizer to impart a greater degree of permanence and stability to the silver image may be employed.

Specifically, it has been discovered that improved image reproduction and protection of the processed film may be obtained by means of the film unit of the present invention. The novel film unit of the present invention is composed of a common support carrying on one surface a photosensitive layer containing silver precipitating nuclei, a photoinsensitive, inert, processing composition permeable, non-nucleated protective layer and a photosensitive layer containing silver halide crystals.

The film unit of the present invention is exposed to actinic radiation wherein the image is recorded in the photosensitive layer. An alkaline processing composition is applied to the film unit and a positive silver image is formed in the photoinsensitive layer containing the silver precipitating nuclei by a diffusion transfer mechanism. It is noted that the non-nucleated photoinsensitive layer will not trap or retain any of the silver by virtue of its lack of nucleating sites. Thus, the transfer mechanism proceeds through the non-nucleated photoinsentive layer substantially unaffected. Subsequent to image formation in the nucleated photoinsensitive layer, the emulsion is removed by various methods, for example, tank washing, squeegeeing, tape stripping, roller stripping, and the like. A film unit is then provided wherein the layers enclosing the photoinsensitive image layer are represented by an impermeable support layer on one side and a protective polymeric layer on the opposite side.

The protective layer is a photoinsensitive layer which does not contain any nucleation sites for the silver so that such layer will provide no interference with the transfer and formation of the silver image in the nucleated adjacent layer. As examples of suitable materials which may be employed as the photoinsensitive non-nucleated protective layer, mention may be made of natural polymeric materials such as gelatin, casein, and the like; alginates, chitin, and synthetic polymeric materials such as polyvinyl alcohol, polyvinyl acetate, nylon and the like. The particular polymeric material is selected by the operator with regard to the degree and type of protection desired in a particular film unit, e.g., abrasion resistance. A particularly preferred class of materials are those which form a hard, horny, and yet flexible layer. Most preferred is deacetylated chitin. The term deacetylated chitin as employed herein is intended to refer to the product prepared by removing in whole, or in part, the acetyl groups in the polymeric acetamide derivative of a carbohydrate, technically designated as chitin. It is also intended to include any other products substantially identical therewith as, for example, where such product is produced synthetically.

The employment of deacetylated chitin as the protective layer is particularly advantageous because of the property of said chitin to form a substantially water-insoluble, abrasion resistant matrix which can retain flexibility subsequent to contact with alkali, for example, the alkaline medium provided by the photographic processing composition. Thus, the employment of deacetylated chitin as a protective layer provides an initial material which offers substantially no resistance to the passage of image silver and processing composition therethrough but which will, subsequent to the image formation, provide a highly effective, protective abrasion resistant layer.

As stated above, the novel film unit of the present invention is particularly suitable for employment as cine film. It has been conventional with the processing of such film to provide a lubricant or friction reducing agent to the film during processing. It has now been found that by employing the novel film unit of the present invention, the additional treatment to provide the necessary lubrication or slip characteristics to the film unit does not require any external application or additional processing step. The aforementioned slip characteristics may be applied to the film unit of the present invention by incorporating in the non-nucleated protective polymeric layer a friction reducing agent prior to the casting of the layer in the formation of the film unit. Preferably the friction reducing agent employed is less dense than the protective layer in which it is incorporated and thus will bloom to the outer surface of the protective layer, i.e., that surface of the protective layer nearest to the emulsion layer. Alternatively, the friction reducing agent employed may become more incompatible as the pH increases, so that contact with the alkaline processing composition will result in the agent blooming to the surface of the layer. Upon removal of the emulsion layer and any other layers associated therewith, the outermost surface of the protective layer will have associated therewith friction reducing material which will impart the necessary slip characteristics to the film unit. Since motion picture film is rolled up upon itself, it is obvious that certain quantity of friction reducing agent will become dislodged from the surface of the protective layer and will adhere to the support layer superposed thereon by virtue of the winding, thereby imparting slip characteristics to both sides of the film unit. It should be noted that while a friction reducing material which will bloom to the surface a substantially uniform distribution of friction reducing agent within the protective layer is still suitable since even the uniform distribution will provide a certain amount of friction reducing agent available at the interface between the protective layer and adjacent outer layers and will further provide for the ready removal of said outer layers.

As examples of suitable friction reducing agents, mention may be made of waxes, preferably paraffin wax, and microcrystalline waxes. A preferred wax is carnauba wax. Fatty acids are also suitably employed. Particulate polymeric materials are also advantageously employed, preferably particles of polyfluorocarbons, such as polytetrafluoroethylene, approximately 0.3–1 micron in diameter.

The formation of the film unit should provide for the ready detachment of the emulsion layer subsequent to processing. Thus, care should be taken that adhesion of the photosensitive silver halide emulsion layer to the adjacent layers should not be so great that uneven removal of the emulsion is accomplished. It is preferred, therefore, that the silver halide emulsion layer be treated with conventional hardeners known in the art, for example, alginates in the case of gelatin silver halide emulsion layers, in order to provide sufficient integrity to the layer itself to insure the ready removal of the layer completely without leaving portions thereof adhered to the adjacent layers of the film unit. In a particularly preferred embodiment, a stripping layer is employed adjacent the photosensitive silver halide emulsion layer. Said stripping layer provides for the ready detachment of the emulsion layer from the remainder of the film unit, and preferably the material which is at least softened by the processing composition which is employed in forming the photographic image. Materials useful as stripping layers in photosensitive elements are well known to the art, and they include, for example, materials which are attacked or softened by alkaline solutions employed in the photographic processsing compositions. As examples, mention may be made of cellulose acetate hydrogen phthalate and acid functional waxes such as methyl acrylate/acrylic acid copolymers.

The thickness of the non-nucleated protective material is not critical provided the transfer of silver is not impeded. However, the thickness of the film is preferably maintained at a minimum. In the case of deacetylated chitin, for example, the film thickness may range from 0.1 to 0.5 micron; however, 0.3 micron is preferred.

Such a film assemblage is suitably employed in a motion picture system such as that described in application Ser. No. 776,481, filed Nov. 18, 1968, which comprises a compact motion picture cassette capable of performing the functions of exposing a photosensitive film contained therein and subsequently processing the film to develop images recorded thereon, removing the emulsion layer and also projecting the images or otherwise presenting them for viewing purposes. Thus, the film assemblages may be exposed, chemically processed, dried if necessary, and projected without transferring the film from its original container to any other container or even removing the film from the original cassette. The motion picture system of the above-indicated applications include a film processing station wherein the exposed film strip is passed from the take-up reel past an applicator where a moist film developing composition to develop the visible condition images recorded on said film is applied. The emulsion layer is removed and the film then passed to a second reel. An alternative method of processing the film unit of the present invention is found in application Ser. No. 54,488 filed concurrently herewith.

The processing composition may be applied to the films by a variety of methods, such as, for example, doctor blades, extrusion heads, capillary applicators, wicks, tanks, and the like.

Referring to FIG. 1, there is shown a diagrammatic enlarged cross-sectional view of a film unit of the present invention. The film unit as shown specifically comprises a flexible transparent film base or support member **10** carrying on one surface thereof, in order, a photoinsensitive layer **11** having associated therewith a silver precipitating nuclei, an inert, processing composition permeable, non-nucleated, polymeric photoinsensitive layer **12**, and a photosensitive silver halide stratum **14**. FIG. 2 is an alternative structure for a film unit similar in construction to that shown in FIG. 1 except that a preferred layer **13** is included which is a stripping layer, which is softenable or soluble in the alkali processing composition to facilitate the removal of a layer **14** leaving intact a film unit **20** with the diffusion transfer image recorded in layer **11** and protected by the photoinsensitive layer **12**. FIG. 3 contains a particularly preferred film unit for use in the present invention wherein support member **10** carries on one surface, in order, additive multicolor screen **14** positioned intermediate support **10**, and photoinsensitive layer **11** which contains silver precipitating nuclei and in which the transfer image is formed. As in FIGS. 1 and 2 the film unit of FIG. 3 also shows the photoinsensitive protective layer **12**, stripping layer **13** and photosensitive layer **14**.

The photoresponsive material of photographic emulsion **12** will, as previously described, preferably 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, or most preferably, mixed silver halides, such as silver chlorobromide or silver iodobromide, of varying halide ratios and the silver concentrations previously identified most preferably dispersed in a processing composition permeable binder material.

In general, silver precipitating nuclei comprise a specific class of adjuncts well known in the art adapted to effect catalytic reduction of solubilized silver halide specifically including heavy metals and heavy metal compounds such as the metals of Groups I–B, II–B, IV–A, VI–A, and VIII and the reaction products of Groups I–B, II–B, IV–A, and VIII metals with elements of Group VI–A, 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 $1\text{–}25\times10^{-6}$ 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 especially the salts of zinc, copper, cadmium and lead. Also particularly suitable as precipitating agents are heavy metals such as silver, gold, platinum and palladium and in this category the noble metals illustrated are preferred and are generally provided in the matrix as colloidal particles.

The preferred silver halide type photographic emulsion **12**, 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 bromide, preferably together with a corresponding iodide, 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. Pats. Nos. 2,614,928; 2,614,929; 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 derivatives, as described in U.S. Pats. Nos. 2,322,085 and 2,541,474; vinyl polymers 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. Pats. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, Comment On Non-Gelatin Film, B. J. O. P., 534, Sept. 15, 1961; and Belgian Pats. Nos. 642,557 and 642,558.

Matrix materials adapted for employment as layer **11** or **12** 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 ethers 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 the 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 ion-capturing 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 is 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 disadvantage to the conventional employment of the image. However, for particularly accurate information recordation, microscopic distortion of image elements is preferably obviated to insure maximization of the accuracy of image reproduction. Specifically, it has been found that a photosensitive film unit comprising photosensitive emulsion containing silver halide crystals dispersed in a polymeric binder and a photoinsensitive image-receiving layer containing silver precipitating nuclei dispersed in a polymeric binder, the binders of which possess a lattice effective to substantially prevent microscopic migration or diffusion of image silver, provide image reproduction acuity particularly desired for effective information recordation 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 spacially maintain positive image components. 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.

Support or film base **10** may comprise any of the various types of transparent rigid or 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, acetate butyrate, or acetate propionate, polycarbonate; polystyrenes; and the like.

The present invention will be illustrated in greater detail in conjunction with the following specific example which sets forth a representative fabrication of the film units of the present invention, which however, is not limited to the detailed description herein set forth but is intended to be illustrative only.

A gelatin subbed cellulose triacetate film base may be coated with a composition comprising deacetylated chitin and copper sulfide at a coverage of 4.4 mgs./ft.^{2} deacetylated chitin and 0.25 mg./ft.^{2} copper sulfide. A second layer of deacetylated chitin having 10% of microcrystalline wax incorporated therein is coated thereon at a coverage of 25 mgs./ft.^{2}. On the external surface of the preceding layer a hardened gelatino silver iodobromide emulsion may then be coated at a coverage of 200 mgs./ft.^{2} gelatin, 100 mgs./ft.^{2} silver and 4.0 mgs./ft.^{2} algin.

The gelatino silver iodobromide emulsion employed may be prepared by heating a mixture comprising 80 grams of gelatin in 880 grams of water at a temperature of about 40° C. for the period required to dissolve the gelatin. The pH of the resultant solution may be adjusted to 10±0.1 and 8.8 grams of phthalic anhydride in 61.6 cc. of acetone added to the solution over a period of 30 minutes. Subsequent to addition of the phthalic anhydride, the reaction mixture may be maintained at the stated temperature and pH for a period of about 30 minutes and then adjusted to a final pH of about 6.0.

To a solution comprising 226 grams of the gelatin phthalic anhydride derivative, prepared as above, 161 grams of potassium bromide, 2 grams of potassium iodide, and 1200 grams of water may be added a solution comprising 200 grams of silver nitrate in 1600 grams of water, at a rate of about 140 cc. per minute, for a period of about 3 minutes, held 10 minutes and the addition continued for a period of about 9 minutes. The resulting emulsion may then be precipitated by reducing the pH to about 2.5–3.0 with sulfuric acid. The precipitate may then be separated from the supernatant liquid and washed until the wash water is essentially free of excess potassium bromide. Ninety-five grams of gelatin may then be added to the precipitate, the volume adjusted with water to 845 cc., and dissolved by heating to about 38° C., for about 20 minutes, at a pH of about 5–6, and about 1.0 cc. of 1,N-potassium bromide added to the emulsion. To the reaction mixture, at about 56° C., may be added about 5 cc. of a solution containing 0.1 gram of ammonium thiocyanate in 9.9 cc. of water and 0.4 cc. of a solution containing 0.097 gram of gold chloride in 9.9 cc. of water, and the mixture ripened at that temperature for about 37 hours. The resultant emulsion may then be panchromatically sensitized by the sequential addition of 0.1%, by weight, methanol solutions of anhydro-5,5'-diphenyl - 3,3' - bis - (4 - sulfobutyl) - 9 - ethyl - oxacarbocyanine hydroxide and anhydro - 5,5' - dimethyl-3,3' - bis - (3 - sulfopropyl) - 9 - ethyl - thiacarbocyanine hydroxide in optionally effective concentrations. The copper sulfide silver precipitating agent may be provided, prior to coating, by the in situ addition of substantially equimolar quantities of copper acetate and sodium sulfide solutions.

The film unit, fabricated as detailed above, and in the form of a motion picture film strip, may be subjected to exposing electromagnetic radiation and developed by contacting the film unit in a device similar to that disclosed in application Ser. No. 738,464 for about 2 seconds with a processing composition comprising 180 cc. of water, 8.33 grams of sodium hydroxide, 16 grams of sodium thiosulfate, 6.48 grams of sodium sulfite, 0.42 gram of 6-nitrobenzimidazole, and 5 grams of 2,6-dimethylhydroquinone, to provide production of a positive silver image possessing the optical characteristics described hereinbefore and the acuity required for effective image reproduction, to remove the emulsion layer and rewound upon itself.

A film unit fabricated and processed in the general manner detailed above exhibited a $D_{max.}$ of 3.8 and a $D_{min.}$ of 0.5.

As previously stated, the photosensitive silver halide emulsion and/or the silver precipitating nuclei containing layer 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 antiswelling agent for the emulsion's 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 emulsion and silver precipitating nuclei containing layers. In addition, the silver precipitating nuclei containing stratum distal the 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 hardening or crosslinking of photographic polymeric binder material compositions and by reason of their innocuous 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 that 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 a permeable layer directly associated therewith, intermediate the emulsion and support, is a particularly preferred embodiment, for the purpose of providing unexposed image acuity, which more readily facilitates 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.

It will be apparent that the relative proportions of the agents comprising the developing composition set forth herein may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the situation of preservatives, alkalies, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. The concentration of such agents may be varied over a relatively wide range commensurate with the art.

The processing composition solvent employed, however, 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 affects the lattice parameters required for such image formation.

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 or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic film unit which comprises a transparent flexible polymeric support carrying on one surface, in order, an additive color screen, a first photoinsensitive layer comprising silver precipitating nuclei dispersed in a processing composition permeable binder, a substantially inert, non-nucleating photoinsensitive layer comprising a processing composition permeable binder, and at least a first photosensitive silver halide emulsion layer comprising photosensitive silver halide crystals dispersed in a processing composition permeable binder.

2. A product as defined in claim **1** wherein said non-nucleated photoinsensitive layer is deacetylated chitin.

3. A product as defined in claim **1** wherein said non-nucleated photoinsensitive layer has associated therewith a friction reducing agent.

4. A product as defined in claim **3** wherein said friction reducing agent is dispersed through said non-nucleated photoinsensitive layer.

5. A product as defined in claim **3** wherein said friction reducing agent is microcrystalline wax.

6. A product as defined in claiu **1** including a separate processing composition permeable polymeric layer containing a silver halide developing agent positioned intermediate said common support and photosensitive silver halide emulsion.

7. A photographic process which comprises, in combination, the steps of exposing a photographic film unit comprising a laminate which contains a common support carrying on one surface, in order, an additive color screen, a first photoinsensitive layer comprising silver precipitating nuclei dispersed in a processing composition permeable binder; an inert, photoinsensitive non-nucleated layer; and a layer comprising photosensitive silver halide; said silver precipitating nuclei present in a concentration effective to provide a silver image derived from unexposed silver halide crystals possessing greater covering power than a silver image derived from exposed silver halide crystals; contacting said silver halide emulsion with an aqueous processing composition containing a 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 emulsion exposure, derived from unexposed silver halide crystals possessing greater covering power than the silver image derived from exposed silver halide crystals and stripping said silver halide emulsion layer subsequent to processing.

8. A photographic process as defined in claim **7** which comprises, in combination, the steps of exposing a photographic film unit which comprises a laminate containing a transparent support carrying on one surface, in order, a first substantially photoinsensitive layer comprising silver precipitating nuclei dispersed in a processing composition permeable matrix; and substantially inert, photoinsensitive non-nucleated, processing composition permeable polymeric matrix, and a photosensitive silver halide emulsion comprising photosensitive silver halide crystals dispersed in a processing composition permeable polymeric binder, said silver precipitating nuclei present in a con- concentration effective to provide upon development, as a function of exposure, a silver image derived from development of unexposed silver halide crystals possessing a maximum image density at least 1.0 density units greater than the maximum density of the silver image derived from development of exposed silver halide crystals; contacting said silver halide emulsion with an aqueous processing composition containing a 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, said visible silver image derived from development of unexposed silver halide crystals and possessing a maximum image density at least 1.0 density units greater than the maximum density of developed silver derived from development of exposed silver halide crystals, and stripping said emulsion layer subsequent to said processing.

9. A photographic process as defined in claim **7** wherein said non-nucleated photoinsensitive layer is deacetylated chitin.

10. A photographic process as defined in claim **7** wherein said non-nucleated photoinsensitive layer has associated therewith a friction reducing agent.

11. A photographic process as defined in claim **10**

wherein said friction reducing agent is microcrystalline wax.

12. A photographic process as defined in claim **7** wherein said silver halide emulsion comprises a silver iodobromide emulsion.

13. A photographic process as defined in claim **12** wherein said silver iodobromide emulsion is panchromatically sensitized.

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