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PERMANENT LAMINATE PHOTOGRAPHIC FILM

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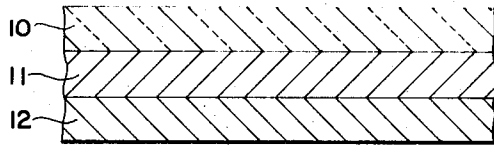


FIG. 1

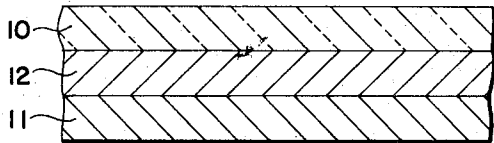


FIG. 2

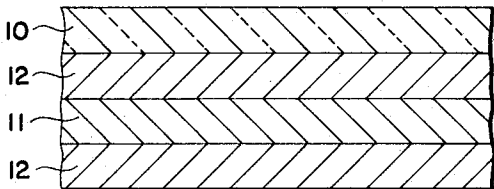


FIG. 3

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3,681,072

**PERMANENT LAMINATE PHOTOGRAPHIC FILM**  
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**Polaroid Corporation, Cambridge, Mass.**  
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**Int. Cl. G03c 5/54**

U.S. Cl. 96—29

20 Claims

## ABSTRACT OF THE DISCLOSURE

The present invention is directed to a photographic film unit which comprises a permanent laminate including a support carrying on one surface photosensitive silver halide crystals and silver precipitating nuclei and a layer comprising silver precipitating nuclei; and processes employing said film unit.

The present invention relates to photography and, more particularly, to photographic products and processes specifically adapted for direct positive image reproduction.

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 developing 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, N.Y. and Chapters VI, VII, VIII and IX 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.

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 XI of *Photographic Chemistry*, volume I, supra, and Chapter 17

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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 XXX 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 trans-

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fer 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 preferable to that of the second embodiment by reason of the higher photographic speeds practicably obtainable.

As disclosed in U.S. Pat. No. 2,712,995, direct production of a positive silver image may also be provided by employment of a spontaneously developable silver salt dispersion, that is, a silver salt dispersion such as silver oxalate, silver stearate, silver ferrocyanide, or certain silver chloride dispersions, which is directly reduced to elemental silver in the absence of exposure to bromide ions and to actinic radiation, and thus not as a function of the point-to-point incidence of actinic radiation. In the disclosed structure, the image-providing, spontaneously developable silver salt dispersion contains the minimal concentration of photosensitive silver bromide required to effect release of bromide ions, from the silver bromide crystals upon development in the absence of bromide and as a function of exposure, in the concentration required to inhibit, imagewise, spontaneous development of the silver salt dispersion. As further stated in the cited patent, the spontaneous development reaction of the silver salt dispersion may be enhanced by the addition of substances which act as nuclei for the reaction and the employment of a processing composition containing a silver halide solvent such as sodium sulfite. However, as disclosed in the patentee's subsequent U.S. Pat. No. 2,937,945, the silver images obtained by the process of the preceding patent show the drawback that the whites are impaired by the negative image formed from the photosensitive material, that is, the silver bromide dispersion. It is there stated that it is necessary to be especially careful to keep the amount of the silver bromide as small as possible so that the visible silver image originating from development of such material does not exceed the critical threshold required for effective employment of the resultant image. The last-identified patent denotes the improvement which consists of improving the quality of resultant image by disposition of the respective spontaneously developable silver salt dispersion and photosensitive silver bromide dispersion in separate layers, maintained in contact during development, but separated from one another subsequent to formation of the positive silver image.

As disclosed in French Pat. No. 53,513, third addition to French Pat. No. 873,507, it was also known pre-existing the last two mentioned patents that a primary negative image and a secondary positive image may be provided by exposing a silver halogenide emulsion containing silver precipitating agents and processing the thus exposed emulsion, for example, first with a silver halide developing formulation which does not contain a silver halide solvent and then with a developer formulation which does contain a silver halide solvent and, for the production of colored positive images, specifically a chromogenic developer formulation containing a silver halide solvent to provide, upon the subsequent elimination of the metallic silver images, the production of a colored positive image.

As disclosed in Belgian Pat. No. 545,678, direct production of a positive silver image may also be provided

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by employment of a silver halogenide emulsion containing silver precipitating nuclei and a sufficient concentration of a masking pigment, possessing a degree of light absorptivity at least similar to the light absorptivity of the negative image, that, subsequent to processing, the resultant negative image is invisible and only the positive image comprises a visible image.

In British Pat. No. 874,046, it is disclosed that three separate silver diffusion transfer positive images may be provided by exposure of a film unit comprising a photosensitive silver halide emulsion layer containing a silver precipitating agent located intermediate two separate image-receiving layers, one layer located on each side of the emulsion, and, subsequent to processing, separating the two image-receiving layers from their contiguous relationship with the emulsion and then mounting the silver halide emulsion layer on a support member.

However, for a plurality of reasons set forth in detail hereinafter, it would be particularly desirable to possess the wherewithal to fabricate an integral film assemblage essentially comprising a photoresponsive material directly providing positive image formation and possessing the sensitivity to incident electromagnetic radiation and acuity of image formation necessary to effectively provide photographic image reproduction.

Accordingly, it is a principle object of the present invention to provide new and improved photographic products, compositions and processes particularly adapted for the photographic reproduction of subject matter.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process of the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a diagrammatic enlarged cross-sectional view illustrating the association of element constituting one embodiment of the present invention, the thickness of the various materials being exaggerated;

FIG. 2 is a diagrammatic enlarged cross-sectional view, analogous to FIG. 1, illustrating the association of elements constituting another embodiment of the present invention; and

FIG. 3 is also a diagrammatic enlarged cross-sectional view, analogous to FIGS. 1 and 2, illustrating the association of elements constituting still another embodiment of the present invention.

As previously stated, a silver diffusion transfer reversal process may provide a positive silver transfer image by development of the latent image provided a photosensitive silver halide emulsion 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 emulsion. The resultant soluble silver complex is, at least in part, transported in the direction of a suitable print-receiving element and the silver of the complex there precipitated to provide the requisite positive silver image formation.

The silver receptive stratum employed may be so 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 emulsion, 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 environment, silver precipitation nuclei may 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 can be 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. The image silver thus precipitated in situ in galaxies of chosen physical parameters provides image conformation in which the elemental silver of the print-receiving element may possess a very high order of covering power, for example, five to fifteen or more times that of the negative elemental image silver in the silver halide element.

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 simplified silver diffusion transfer reversal processes employing a photosensitive silver halide emulsion which upon 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 its exposed areas, as a function of exposure, 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, accordingly, 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.

As disclosed in copending U.S. application Ser. No. 736,796, filed Apr. 1, 1968 in the name of Edwin H. Land, it has been unexpectedly discovered that a photosensitive material, specifically a photosensitive silver halide emulsion, may be employed to provide a direct positive visible silver image possessing the acuity necessary for effective image reproduction. For such employment, the emulsion is specifically formulated to contain silver precipitating nuclei dispersed throughout in a concentration effective to provide, subsequent to exposure and development with a processing composition containing a silver halide developing agent and a silver halide solvent, a positive silver image derived from unexposed silver halide crystals possessing greater covering power than the negative silver image derived from exposed silver halide crystals.

In general, in accordance with the teaching of the photographic art, "physically" developed silver is directly reduced from a fluid phase during development and essentially comprises relatively compact grains. In contradistinction, "chemically" developed silver, in all known conventional processes, is directly furnished from exposed silver halide crystals and essentially includes image silver in the general form of "fibers" or "filaments." The covering power, that is, the optical density per gram of silver per square meter, of the resultant silver image, in each instance, is a function of the aggregation and conformation of developed silver and, in general, may be considered to be inversely proportional to the diameter of the particles, or grains as aggregated, in the absence of considerations with respect to aggregate conformation.

In conventional development practice, employing either so-called "physical" or "chemical" development, both types of development occur to an extent, however, "chemical" development is characterized by the fact that the major portion of the developed elemental silver is derived from direct chemical reduction of exposed silver halide crystals and only a substantially inconsequential proportion of the image silver is derived from solution physical development. Conversely, "physical" development is characterized by the fact that a predominant proportion of the

developed silver is derived from direction solution physical development and only a minimal proportion of the resultant image silver is derived from chemical development.

In accordance with aforementioned copending U.S. application Ser. No. 736,796, a photosensitive silver halide emulsion may be fabricated to provide as a function of exposure, upon development in the presence of a silver halide solvent, elemental silver image formation of a character previously unknown to the photographic art. Specifically it there disclosed that image silver derived from direct development, in the presence of a silver halide solvent, of photoexposed silver halide crystals comprising an emulsion formulation fabricated as there detailed, that is, photoexposed silver halide crystals having directly associated therewith an effective concentration of silver precipitating nuclei, is characterized by the substantial absence of "fiber" or "filamentary" conformation. The image silver conformation so provided is substantially restricted to elemental silver grains or particles possessing a diameter substantially equal to the original diameter of the unexposed photosensitive crystals constituting the emulsion. Amplification of the thus produced negative silver image to provide an optical density beyond that provided by elemental silver image particles or grains of a diameter directly comparable to the emulsion's original crystal diameters, generally ranging, according to the prior art, in size from about 1 to 3.5 microns in "high speed" photographic materials, resultant from increased image grain diameter pursuant to crystal surface area growth, directly or by reason of elemental silver fiber or filament production, has been discovered to be effectively prevented by development of the emulsion's exposed silver halide crystals in direct contiguous relationship with silver precipitating nuclei, present in an effectively inhibiting concentration, with a processing composition containing a silver halide solvent.

Photosensitive silver halide emulsion of the "high speed" type generally employed for photographic reproduction are characterized by the presence of photoreponsive silver halide crystals possessing active sensitivity centers or sites which are believed to comprise minute aggregates of silver sulfide, the sulfide of which is derived from active sulfur naturally present initially in the polymeric matrix, for example, a gelatin matrix, or added to the formulation during fabrication. For optimum sensitivity there should be a limited but effective number of sensitivity sites in each crystal, particularly at the surface of the crystals. Upon exposure to incident electromagnetic radiation actinic to the crystals, it is understood that photons absorbed by the crystals provide photoelectrons within the crystals which are capable of diffusion to the sensitivity sites which possess a lower conductivity bond level and, in effect, provide such sites with a negative charge which precipitates, at the sites, as elemental silver, free silver ions originally disposed within the crystal lattice. During development of the exposed silver halide crystals, the silver halide developing agent, a reducing agent, provides additional electrons which serve to effect precipitation of additional silver ion of the crystals resulting in the extrusion of fibrous or filamentary elemental silver at surface sensitivity sites and which continues until reduction of the crystals is complete.

As disclosed in aforementioned U.S. application Ser. No. 736,796, the presence of the silver precipitating nuclei contiguous the silver halide crystals during the development process effectively acts to substantially prevent the microscopic elemental silver filament or fiber extrusion beyond the crystal surface with the concomitant result of restricting image grain size to that of the crystal. Accordingly, the covering power of the resultant negative image in each instance is limited to that provided by elemental silver grains or particles possessing a diameter substantially equal to that of the original crystals dispersed in the photosensitive matrix and absent amplification due

to the diameter increase of conventional negative image elements resultant from filamentary image silver.

For the purpose of insuring the production of a positive image possessing a high covering power, the silver precipitation nuclei will be disposed within the photosensitive silver halide emulsion 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.

Reference to the photomicrographs comprising FIGS. 2 to 6, inclusive, of the drawings set forth in aforementioned U.S. application Ser. No. 736,796 further illustrates in factual detail the preceding discussion.

There is thus provided by means of the presence of photosensitive silver halide crystals or grains dispersed in an environment containing silver precipitating nuclei or agents which in the presence of a solvent developer composition cause exposed grains to be reduced to opaque structures smaller in presented area than the area of the same grains developed in an identical developer composition absent such precipitating nuclei. Silver image masses derived from exposed silver halide grains developed in accordance with the present invention, accordingly, possess low optical covering power as compared with the covering power provided by identical grains developed in the same solvent developer absent the presence of the precipitating environment. Specifically, the disclosed system provides for the production of a direct positive silver image in which the mass distribution of silver is substantially uniform macroscopically and nonuniform microscopically, and in which the transmissivity of silver image mass is a function of the quantity of actinic radiation which exposed the photosensitive silver halide. The exposed silver halide grains are reduced, in situ, as compact masses possessing low covering power simultaneously with reduction, in situ, of unexposed silver halide grains as colloidal dispersions possessing high covering power. The direct positive silver image thus produced in situ possesses extraordinary high sharpness when compared with transfer processes in which unexposed silver halide grains are dissolved and transferred to the ultimate image-carrying site.

In accordance with the present invention, however, it has now been quite unexpectedly discovered that distinctly advantageous results are achieved in the production of direct positive silver image formation by the employment of a film unit comprising a photosensitive silver halide stratum retaining silver precipitating nuclei in functionally contiguous relationship to at least one strata comprising silver precipitating nuclei.

Specifically, it has been unexpectedly discovered that silver image formation, in accordance with the disclosure of that application, possessing optical density inversely proportional to exposure of the emulsion, characterized by improved silver image minimum and maximum optical densities may be achieved by the presence of last-identified stratum or strata comprising silver precipitating nuclei. There is thus provided and the present invention is specifically directed to a film unit assemblage structure which is a permanent laminate and comprises a photosensitive silver halide layer containing photosensitive silver halide layer containing photosensitive silver halide crystals and silver precipitating nuclei and at least one separate, substantially discrete layer containing silver precipitating nuclei, which structure provides for 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 a high maximum silver image optical density in terms of unexposed areas of the film unit, as a function of exposure and development of the unit in the presence of a silver halide developing agent and a silver halide solvent.

As stated, the concentration of silver precipitating nuclei present in the film unit are disposed in a concentration effective to provide a silver image possessing an optical

density inversely proportional to exposure of the emulsion and in effect provides a silver image derived from unexposed silver halide crystals possessing greater covering power than a silver image derived from exposed silver halide crystals, by reason of the fact that the image silver derived from unexposed silver halide crystals comprises silver of a first physical character and image silver derived from exposed silver halide crystals comprises silver of a second physical character and that the first physical character silver possesses higher optical density than the second physical character silver per unit mass.

It has been specifically found that in the preferred embodiments of the present invention, the film unit is adapted as specifically detailed herein to provide a differential

$$\Rightarrow \sim 1.0 \text{ and specifically } \Rightarrow \sim 1.5$$

density units between the predetermined maximum image density of the developed negative silver image, i.e.,  $D_{\min.}$ , and the predetermined minimum image density of developed positive silver, i.e.,  $D_{\max.}$ . In a particularly preferred embodiment, the film unit is fabricated to provide a maximum silver image density

$$\Leftarrow \sim 0.5 \text{ and, more particularly, } \Leftarrow \sim 0.3$$

density units upon development of completely exposed areas of the silver halide stratum and will possess silver precipitating nuclei in a concentration effective to provide a minimum image density

$$\Rightarrow \sim 1.0 \text{ and specifically } \Rightarrow \sim 1.8$$

preferably, in excess of  $\sim 2.0$  and, most preferably,  $\sim 3.0$  density units derived from processing of unexposed silver halide grains. In such preferred embodiment, the silver halide stratum will ordinarily comprise panchromatically sensitized silver iodochlorobromide or silver iodobromide, particularly that containing 1 to 9 percent iodide by weight of silver, dispersed in a permeable colloidal binder which, in a preferred embodiment comprises gelatin sufficiently hardened to provide a hydration factor, upon contact of aqueous processing composition preferably possessing a pH in excess of  $\sim 12$ , effective to prevent swelling in excess of a magnitude equal to its ambient size within a period of  $\angle \sim 15$  seconds.

It will be specifically recognized, however, that in a preferred embodiment of the invention the photoinsensitive silver precipitating nuclei containing layer should most preferably possess a thickness of less than about a wavelength of light, whereby minimizing to a maximum extent substantial lateral diffusion of silver image-forming components during processing of the film unit.

Referring to FIG. 1, there is shown a diagrammatic enlarged cross-sectional view of a film unit constructed in accordance with a preferred embodiment of the present invention. The film unit is shown to specifically comprise a flexible transparent film base or support member 10 carrying on one surface, in order, a photosensitive silver halide stratum 11 containing dispersed therethroughout silver precipitating nuclei and a substantially photoinsensitive layer 12 comprising silver precipitating nuclei.

In the preferred embodiment of the invention illustratively detailed in FIG. 2, photoinsensitive layer 12 is shown positioned intermediate support 10 and photosensitive stratum 11 and in the preferred embodiment denoted in FIG. 3, two separate and distinct photoinsensitive layers 12 are shown individually located adjacent the opposite major surfaces of photosensitive layer 11.

The photoresponsive material of photographic stratum 11 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, silver chloroiodobromide or silver iodobromide, of varying halides ratios and the silver concentrations previously identified most preferably dispersed in a processing composition permeable binder material which additionally contains

silver precipitating agents dispersed throughout the emulsion in a concentration effective to provide a vigorous elemental silver deposited therein in terms of the unexposed areas of the emulsion, as a function of its point-to-point degree of exposure, in comparison with exposed areas of the emulsion, to possess with high covering power, that is, opacity per given mass of 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 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  $1-25 \times 10^{-6}$  moles/ft.<sup>2</sup>.

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 11, 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. Pat. No. 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 on support 10 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. 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.

The discrete silver precipitating nuclei layer or layers 12 may be realized by the application of, location of, and/or in situ generation of, the nuclei directly or indirectly contiguous one or both surfaces of the photosensitive layer in the presence or absence of binder or matrix material and, in the latter instance, may comprise one or more adjacent or separated strata of a permeable material contiguous either or both surfaces 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 ethers and esters, polyamides and esters, etc., and the like; and the former type preferably comprising submicroscopic 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 preferably 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 and silver precipitating nuclei 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 spacial 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 process of the element.

Support or film base 10 may comprise any of the various types of transparent ridged 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, acetatebutyrate, or acetate propionate; polycarbonates; 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 gelatin, deacetylated chitin and 4,6-diamino-ortho cresol at a coverage of 3.75 mgs./ft.<sup>2</sup> gelatin, 3.75 mgs./ft.<sup>2</sup> deacetylated chitin and 0.7 mgs./ft.<sup>2</sup> diamino-ortho cresol. On the external surface of the gelatin layer a hardened gelatino silver iodobromide emulsion containing cadmium sulfide and silica may then be coated at a coverage of 200 mgs./ft.<sup>2</sup> gelatin, 100 mgs./ft.<sup>2</sup> silver, 0.97 mgs./ft.<sup>2</sup> cadmium sulfide, 0.026 mgs./ft.<sup>2</sup> chrome alum, 0.78 mgs./ft.<sup>2</sup> algin, and 200 mgs./ft.<sup>2</sup> silica. The resultant film unit may then be overcoated with a layer comprising deacetylated chitin and copper sulfide at a coverage of 3 mgs./ft.<sup>2</sup> deacetylated chitin and 1 mg./ft.<sup>2</sup> copper sulfide.

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 - thiocarbocyanine hydroxide in optionally effective concentrations. To the resultant panchromatically sensitized silver iodobromide emulsion, there may then be provided, prior to coating, the cadmium sulfide silver precipitating agent, formed in situ by the addition of substantially equimolar quantities of cadmium nitrate and sodium sulfide solutions, and the siliceous porosity providing and antishrinkage agent.

The film unit, fabricated as detailed above, may be subjected to exposing electromagnetic radiation incident on the transparent base and developed by contacting the film unit 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.

A film unit fabricated and processed in the general manner detailed above exhibited a  $D_{\max}$  silver coverage of 89.8 mgs./ft.<sup>2</sup> and a  $D_{\min}$  silver coverage of 89.8 mgs./ft.<sup>2</sup> and an optical density of 1.80 and 0.35, respectively.

Comparison of a film unit fabricated and processed in the general manner detailed above, verses a film unit fabricated and processed in substantially the same manner with the significant exception that the stated discrete silver precipitating nuclei containing layer was absent clearly illustrated the unexpectedly improved results provided by means of the present invention. Specifically, a film unit fabricated to be directly comparative with the film unit detailed above and possessing no separate layer containing silver precipitating nuclei contiguous the photosensitive silver halide emulsion layer, exhibited a  $D_{\max}$  silver coverage of 89.5 mgs./ft.<sup>2</sup> and a  $D_{\min}$  silver coverage of 89.5 mgs./ft.<sup>2</sup> and an optical density of 1.30 and 0.33, respectively.

Additional film units may be fabricated and processed in the manner detailed above and optimized to exhibit a  $D_{\max}$  of 3.3 and a  $D_{\min}$  of 0.3 and to thus provide a differential of 3.0 density units and, in effect, a percent transmission ratio of about 1,000:1, and, where desired, for example, by reason of selected color screen parameters, a  $D_{\max}$  of 4.0 and a  $D_{\min}$  of 0.3 to provide a

differential of 3.7 density units and thus a percent transmission ratio of about 5,000:1.

In contradistinction to developed negative image silver in conventional processes, including the silver diffusion transfer reversal process identified above, film units fabricated and processed in accordance with the present invention clearly exhibit substantially no negative image "fiber" or "filament" formation and, accordingly, substantially no negative image amplification resultant from such conformation.

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

As denoted by the illustrative example, 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 antishrinkage 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 layer. In addition, the emulsion or silver precipitating nuclei containing stratum distal the color screen 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 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 photo-

graphic 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 a 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, 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, 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 effects 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 shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic film unit which is a permanent laminate comprising a support carrying a photosensitive silver halide layer comprising photosensitive silver halide crystals and silver precipitating nuclei and a layer comprising silver precipitating nuclei.

2. A photographic film unit as defined in claim 1 wherein said silver precipitating nuclei are present in a concentration effective to provide a silver image possessing optical density inversely proportional to exposure of the emulsion.

3. A photographic film unit as defined in claim 2 wherein said silver precipitating nuclei are 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.

4. A photographic film unit as defined in claim 1 which is a permanent laminate and comprises a transparent support carrying, in contiguous relationship, a first substantially discrete photosensitive silver halide emulsion layer comprising, dispersed in a processing composition permeable polymeric binder, photosensitive silver halide crystals and silver precipitating nuclei and a second substantially discrete photoinsensitive layer comprising silver precipitating nuclei present in a concentration effective to provide upon development in the presence of a silver halide solvent, as a function of exposure, a silver image comprising said first and said second physical character silver.

5. A photographic film unit as defined in claim 3 which is a permanent laminate and comprises a transparent support carrying on one surface a photosensitive silver halide emulsion comprising photosensitive silver halide crystals and silver precipitating nuclei in superposed relationship with a substantially photoinsensitive layer comprising silver precipitating nuclei, said silver precipitating nuclei present in a concentration effective to provide upon processing in the presence of a silver halide solvent, as a function of exposure, a silver image derived from development of exposed silver halide crystals possessing a maximum image density at least 1.0 density unit less than the maximum density of a silver image derived from development of unexposed silver halide crystals.

6. A photographic film unit as defined in claim 5 which is a permanent laminate and comprises a transparent support carrying on one surface a photosensitive silver halide emulsion first layer comprising photosensitive silver halide crystals and silver precipitating nuclei dispersed in a processing composition permeable binder and a substantially photoinsensitive second layer comprising silver precipitating nuclei dispersed in a processing composition permeable binder, said silver precipitating nuclei present in a concentration effective to provide upon processing in the presence of a silver halide solvent, as a function of exposure of the unit to actinic radiation, a minimum image density not in excess of about 0.5 and a maximum image density of not less than about 1.5.

7. A photographic film unit as defined in claim 6 wherein said permeable binder of said second layer comprises deacetylated chitin.

8. A photographic film unit as defined in claim 1 including a separate processing composition permeable polymeric layer containing a silver halide developing agent positioned intermediate said support and said photosensitive silver halide emulsion.

9. A photographic film unit as defined in claim 1 wherein said layer comprising silver precipitating nuclei layer is located intermediate said support and said photosensitive emulsion.

10. A photographic film unit as defined in claim 9 including a second layer comprising silver precipitating nuclei located contiguous the surface of said photosensi-

tive emulsion opposite said first-mentioned layer comprising silver precipitating nuclei.

11. A photographic film unit as defined in claim 1 wherein said silver precipitating nuclei comprise metallic sulfides, metallic selenides or colloidal noble metals and said nuclei are present in a concentration of about 1 to  $25 \times 10^{-6}$  moles/ft.<sup>2</sup>.

12. A photographic film unit as defined in claim 1 wherein said photosensitive emulsion is located intermediate said support and said layer comprising silver precipitating nuclei.

13. A photographic film unit as defined in claim 11 which is a permanent laminate and comprises a transparent support carrying on one surface a photosensitive silver iodobromide emulsion layer comprising panchromatically sensitized silver iodobromide crystals and silver precipitating nuclei dispersed in a processing composition permeable binder matrix, said silver precipitating nuclei comprising metallic sulfide, metallic selenide or colloidal noble metal silver precipitating nuclei present in a concentration effective to provide upon development of exposed silver iodobromide crystals in the presence of a silver halide solvent, as a function of the point-to-point degree of exposure to actinic radiation, a maximum silver image density not in excess of about 0.3 and a maximum silver image density of developed silver derived from unexposed silver halide crystals of not less than about 1.8.

14. A photographic process which comprises, in combination, the steps of exposing a photographic film unit comprising a permanent laminate containing a photosensitive silver halide layer comprising photosensitive silver halide crystals and silver precipitating nuclei and a layer comprising silver precipitating nuclei, contacting said exposed silver halide layer with an aqueous processing composition containing a silver halide developing agent and a silver halide solvent thereby providing a visible silver image to said film unit in terms of the unexposed areas of said silver halide layer as the function of the point-to-point degree of exposure thereof, and maintaining said laminate intact subsequent to processing.

15. A photographic process as defined in claim 14 which comprises, in combination, the steps of exposing a photographic film unit comprising a permanent laminate containing a transparent support carrying on one surface a photosensitive silver halide emulsion layer comprising photosensitive silver halide crystals and silver precipitating nuclei dispersed in a processing composition permeable polymeric binder in superposed relationship to a substantially photoinsensitive layer comprising silver precipitating nuclei, said 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 maintaining said laminate intact subsequent to processing.

16. A photographic process as defined in claim 15 wherein said silver precipitating nuclei comprises metallic sulfides, metallic selenides or colloidal noble metals.

17. A photographic product which comprises a permanent composite film unit including a transparent flexible support having associated therewith a developed, photoexposed preformed silver halide stratum possessing silver precipitating nuclei and a preformed stratum possessing silver precipitating nuclei, said strata taken together containing a silver image possessing optical density inversely proportional to photo-exposure of said stratum.

18. A photographic product as defined in claim 17 wherein said positive silver image possesses maximum

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density at least 1.0 density units greater than the maximum density of said negative silver image in exposed areas of said silver halide stratum.

19. A photographic product as defined in claim 18 wherein said negative silver image possesses a maximum density in exposed areas of said silver halide stratum not in excess of about 0.5 and a maximum density of said positive silver image in terms of unexposed areas of said silver halide stratum of not less than about 1.5.

20. A photographic film unit as defined in claim 4 wherein said polymeric binder comprises gelatin having dispersed therein silica in a concentration of about 0.3 to 1.5 parts silica per part gelatin.

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