

United States Patent

[11] 3,615,520

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[73]	Assignee	Polaroid Corporation Cambridge, Mass.

[56]		References Cited	
		UNITED STATES PATENTS	
2,861,885	11/1958	Land	96/29
2,712,995	7/1955	Weyde	96/29 X
		FOREIGN PATENTS	
545,678	3/1956	Belgium	

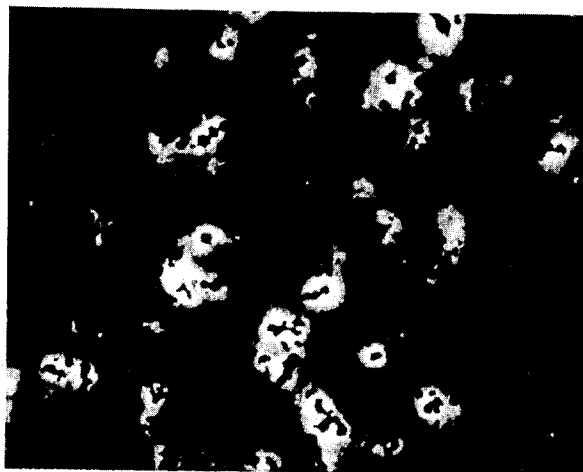
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[54] NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

15 Claims, 6 Drawing Figs.

[52]	U.S. Cl.....	96/64, 96/48, 96/76
[51]	Int. Cl.....	G03c 5/24, G03c 1/06
[50]	Field of Search.....	96/29, 87, 64, 76, 48

ABSTRACT: The present invention relates to a photographic film unit which comprises a support carrying on one surface a photosensitive silver halide emulsion comprising silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride, such as, for example, silver iodobromide, silver chloriodobromide, and silver precipitating nuclei; and to specified photographic processes employing such film units.



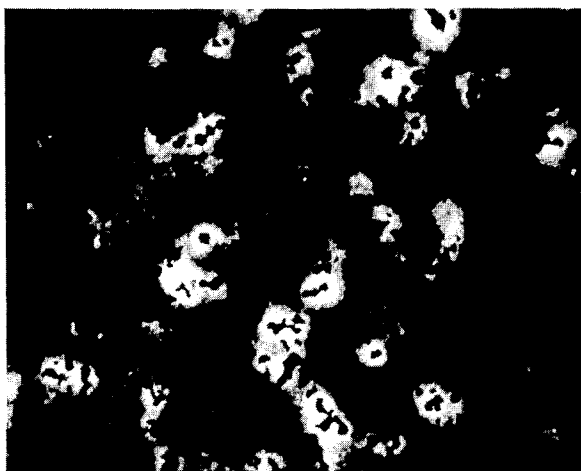


FIG. 2

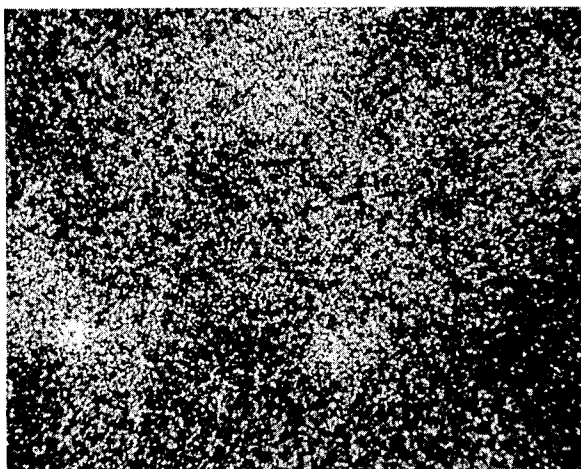


FIG. 3



FIG. 1

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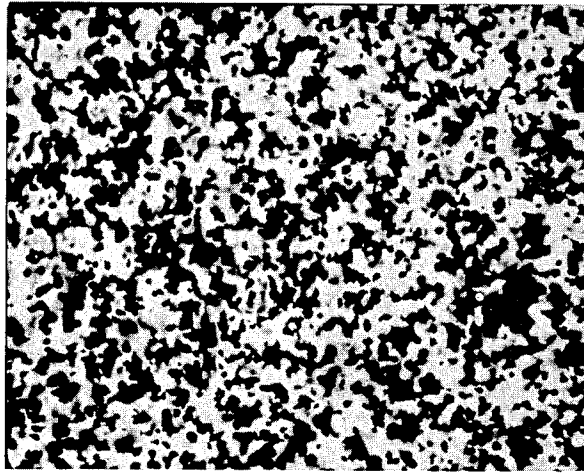


FIG. 4

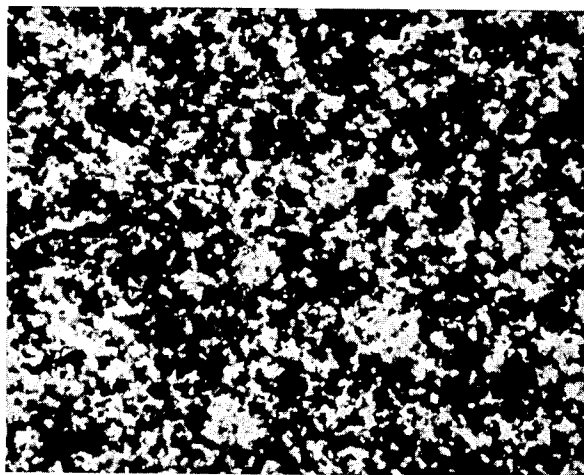


FIG. 5

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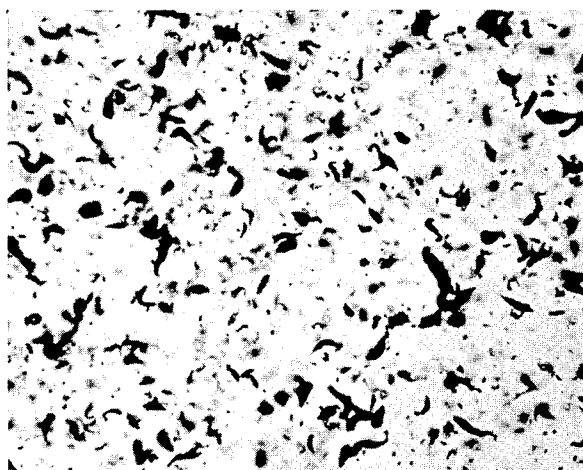


FIG. 6

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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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, New York 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 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 in 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. Sub-

sequent 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 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 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 preferably 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 preexisting 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 sequentially treating the thus exposed emulsion 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 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.

However, for a plurality of reasons set forth in detail hereinafter, it would be particularly desirable to possess the herewithal 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 in silver.

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 elements constituting one embodiment of the present invention, the thickness of the various materials being exaggerated;

FIG. 2 is a photomicrograph of integral positive and negative silver image formation in a maximum density area of a silver image provided, in accordance with the present invention, at a magnification of 1280 x;

FIG. 3 is a photomicrograph of positive diffusion transfer silver image formation in a corresponding maximum density area of a silver transfer image, provided in accordance with the teachings of U.S. Pat. No. 2,861,885, *infra*, at a magnification of 1280 x;

FIG. 4 is a photomicrograph of integral negative and positive silver image formation in a minimum density area of a silver image, provided in accordance with the present invention, at a magnification of 1280 x;

FIG. 5 is a photomicrograph of negative silver image formation in a corresponding maximum density area of the photosensitive silver halide emulsion stratum of a silver diffusion transfer film unit fabricated and processed in accordance with U.S. Pat. No. 2,861,885, *infra*, at a magnification of 1280 x; and

FIG. 6 is a photomicrograph of negative silver image formation in a minimum density area of the photosensitive silver halide emulsion stratum of a silver diffusion transfer film unit, fabricated and processed in accordance with U.S. Pat. No. 2,861,885, *infra*, at a magnification of 1280 x, which integrates with the maximum density area of the silver transfer image of FIG. 3 as an integral composite print to be viewed by reflection or transmission.

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, a soluble silver complex is obtained, 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, Jan. 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 the type detailed above. In a composite print produced in accordance with the disclosure of the cited patent, the covering power of a given mass of image silver in the print-receiving element is there stated to range from 14 to 15 times that of an equal mass of image silver in the silver halide element and, 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.

It has now been unexpectedly discovered that a photoresponsive 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 teachings 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", 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 developed elemental 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 direct solution physical development and only a minimal proportion of the resultant image silver is derived from chemical development.

In accordance with the unexpected discovery which constitutes the present invention, however, 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 has been now discovered 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 detailed herein, 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 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 emulsions of the "high speed" type generally employed for photographic reproduction are characterized by the presence of photoresponsive 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.

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 further illustrates in factual detail the preceding discussion. FIG. 2 is a photomicrograph, having a magnification factor of 1,280 : 1, of integral positive and negative image silver in a maximum density area, provided in accordance with the present invention, employing a film unit fabricated and processed as detailed hereafter. For the purposes of direct comparison with the results detailed in the photomicrograph of FIG. 2, FIG. 3 is a photomicrograph, having the same magnification, of positive diffusion transfer image silver in a corresponding maximum density area, provided in accordance with the disclosure of U.S. Pat. No. 2,861,885, discussed above, employing a film unit fabricated and processed as detailed hereafter. As can be readily observed from examination of the respective photomicrographs, the covering power of the image provided by the film unit fabricated and processed in accordance with the present invention clearly exceeds that of the comparative film unit by a grossly extensive margin. It would appear that the high covering power properties of FIG. 2's film unit may be due, in large part, to the unexpectedly efficient utilization of silver accorded by reason of the present invention; the specific mathematical percent gain of which is detailed hereafter.

FIG. 4 is a photomicrograph of integral negative and positive image silver, in a minimum density area, of the image provided by the film unit of FIG. 2 and at the same magnification. Again, for the purpose of direct comparison with the results detailed in the photomicrograph of FIG. 4, FIG. 5 details negative image silver formation in a corresponding maximum density area of the film unit of FIG. 3's silver halide emulsion stratum at the same magnification. Analogous to the comparative evaluation of FIGS. 2 and 3, FIGS. 4 and 5 clearly detail the undesirably high negative covering power of the image in FIG. 5, by reason of the aforementioned amplification of the negative image, as compared with the image provided in FIG. 4 by means of the present invention. Thus, FIGS. 2, 3, 4 and 5 illustrate not only the greater optical density range to be achieved by means of the present invention in a directly com-

parative situation, that is, an expanded signal to noise ratio but, in addition, the clearly depressed base density or noise level to be achieved by the present invention.

There is directly illustrated by examination of the photomicrograph of FIG. 6, optical density amplifying negative filamentary image silver formation in a minimum density area of the film unit of FIG. 3's silver halide emulsion stratum, at the same magnification as the preceding photomicrographs, which may be positioned in contiguous overlying relationship with the illustrated maximum density area of FIG. 3 to provide a composite silver transfer image.

There is thus provided by means of the present invention 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 present invention 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 by means of the present invention possess 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 a particularly preferred embodiment of the present invention, the emulsion 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 image reproduction, microscopic distortion of image elements is preferably obviated to insure maximization of the accuracy of image integrity. Specifically, it has been found that a photosensitive silver halide emulsion, comprising photosensitive silver halide crystals dispersed in a polymeric binder possessing a lattice effective to substantially prevent microscopic migration or diffusion of image silver, provides image reproduction acuity particularly desired for effective image reproduction in the manner previously described.

The desired polymeric binder lattice property may be readily achieved by selection of a polymeric material possessing the property of sufficiently fixing spacial image components, or a polymeric material, otherwise desired, may be modified, for example, by cross-linking and/or hardening, to the extent necessary to provide the desired spacial maintenance of image components, that is, a rigidity effective to maintain positive image components in the spacial position at which the photosensitive emulsion was exposed. For example, the 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 ad-

vantageously incorporated in the photosensitive element for the purpose of expediting processing of the element.

In a preferred embodiment of the present invention, the photosensitive silver halide emulsion will be fabricated, as further specifically detailed hereinafter, to provide a differential of 1.5 density units between the maximum image density of the developed negative silver image and the maximum image density of the developed positive silver image. In a particularly preferred embodiment, the photosensitive silver halide emulsion will be fabricated to provide a maximum image density of less than about 0.5 and, more particularly, less than about 0.3 density units upon development of completely exposed areas of the emulsion and will possess silver precipitating nuclei in a concentration effective to provide a maximum image density in excess of about 2.0 and, most preferably, in excess of about 2.4 density units upon development of unexposed areas of the emulsion. In such preferred embodiment, the silver halide emulsion will ordinarily comprise not less than 50 milligrams per foot square silver halide, based on weight of silver, preferably, as mixed silver halide and more preferably, as silver iodobromide, particularly that containing about 1 to 9 percent iodide, by weight of silver, dispersed in a permeable colloid binder which, in the preferred embodiment, comprises gelatin sufficiently hardened to provide the last-mentioned optical parameters and a hydration factor, upon contact of aqueous processing composition preferably possessing a pH in excess of about 12, effective to prevent swelling in excess of a magnitude equal to its ambient size within a period of less than about 15 seconds.

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 film base or support member 10 carrying on one surface a photosensitive silver halide emulsion 11 containing dispersed therethroughout silver precipitating nuclei.

The photoresponsive material of photographic emulsion 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 mixed silver halides, such as silver chlorobromide or silver iodobromide, of varying halides ratios and varying silver concentrations 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 precipitating environment which causes the 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 IB, IIB IVA, VIA, and VIII and the reaction products of Groups IB, IIB, IVA and VIII metals with elements of Group VIA, and may be effectively employed in a relatively low concentration in the order of about $1-25 \times 10^{18}$ moles/ft.³.

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^{123} and 10^{130} , 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 polymeric material such as albumin; casein; or zein; or resins such as cellulose derivative, as described in U.S. Pat. Nos. 2,322,085, and 2,541,474; vinyl polymers such as described in U.S. Pat. Nos. 2,253,078; 2,276,322; 2,276,323; 2,281,703; 2,310,223; 2,311,058; 2,311,059; 2,414,208; 2,461,023; 2,484,456; 2,538,257; 2,579,016; 2,614,931; 2,624,674; 2,632,704; 2,642,420; 2,678,884; 2,691,582; 2,725,296; 2,753,264; and the like.

Support or film base 10 may comprise any of the various types of opaque and transparent ridged or flexible supports, for example, glass, paper, metal, and polymeric films of both the synthetic type and those derived from naturally occurring products, etc. Especially suitable materials, however, comprise flexible opaque and transparent papers and 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; 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.

On the surface of a polyester film base may be coated a composition comprising gelatin, deacetylated chitin and 4,6-diamino-ortho cresol at a coverage of 3.75 mgs./ft.² gelatin, 3.75 mgs./ft.² deacetylated chitin and 0.7 mgs./ft.² 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.² gelatin, 100 mgs./ft.² silver, 0.97 mgs./ft.² cadmium sulfide, 0.026 mgs./ft.² chrome alum, 0.78 mgs./ft.² algin, and 200 mgs./ft.² silica. The resultant film unit may then be advantageously overcoated with a hardened gelatin composition at a coverage of 25 mgs./ft.² gelatin, 0.013 mgs./ft.² chrome alum, 0.39 mgs./ft.² algin, and 50 mgs./ft.² silica.

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 1,200 grams of water may be added a solution comprising 200 grams of silver nitrate in 1,600 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. 95 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 grams of ammonium thiocyanate in 9.9 cc. of water and 0.4 cc. of a solution containing 0.097 grams 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 percent, 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. 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 antiswelling 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 grams 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 manner detailed above exhibited a D_{max} silver coverage of 160 mgs./ft.² and a D_{min} silver coverage of 166 mgs./ft.² and a optical density of 2.90 and 0.65, respectively. The covering power of the film equaled a D_{max} 179 and at D_{min} 37.5 calculated as C. P. = Optical Density/g. Ag/dm.².

Comparison of a film unit fabricated and processed in the manner detailed above, versus a film unit fabricated and processed in the same manner with the exception that the stated silver precipitating nuclei were dispersed in a separate processing composition permeable layer coated on the surface of the photosensitive silver halide emulsion opposite that of the transparent support and from which film unit the photomicrograph denoted as FIGS. 3, 5 and 6 may be provided, clearly illustrates the highly efficient utilization of silver provided by means of the present invention. Specifically a film unit fabricated and processed in accordance with the present invention, possessing an initial silver coverage of 128 mgs./ft.² prior to exposure and processing, provided subsequent to exposure and processing in image D_{max} areas 118 mgs./ft.² of positive and negative image silver for a percent silver utilization in the order of 92 percent. In contradistinction, a com-

parative film unit possessing the silver precipitating nuclei disposed in a separate layer contiguous the photosensitive silver halide emulsion layer, possessing an initial silver coverage of 133 mgs./ft.² prior to exposure and processing, exhibited subsequent to exposure and processing in areas of maximum positive image density 61 mgs./ft.² of positive image silver and an overlying negative image silver coverage of 40 mgs./ft.² for a total percent silver utilization of 76 percent.

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 employment parameters, a $D_{max.}$ of 4.0 and a $D_{min.}$ of 0.3 to provide a differential of 3.8 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 as providing the photomicrographs of FIGS. 3, 5 and 6, 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 ciné film for motion picture projection, in addition to slide transparency and reflection print 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 may have advantageously incorporated therein discrete particulate materials providing increased porosity to the emulsion, without deleterious effect on the dimensional stability of the emulsion binder lattice, in particular, those materials which additionally act as an antishrinkage agent for the emulsion's polymeric binder material and, accordingly, act to facilitate the prevention of the polymer carried image's microscopic distortion such as discrete silica particles dispersed, for example, in a concentration of about 0.3 to 1.5 parts silica per part polymer, for the purpose of facilitating processing composition permeation of the emulsion. In addition, the emulsion stratum may be advantageously overcoated with a processing composition permeable polymeric material such as a hardened gelatin pad or the like to advantageously promote uniformity in processing composition permeation of the emulsion, 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 the illustrative example employed chrome alum and particularly algin as hardening agents for the polymeric gelatin emulsion binder and a hardening agents for the polymeric gelatin overcoat, it will be recognized that substantially any hardening or cross-linking agent may be employed, where necessary which does not provide deleterious photographic effects, to the extent required to provide a polymeric 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 cross-linking 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 cross-linking 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 cross-linking to be effected. The specific concentration of a selective hardening or cross-linking 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 material, gelatin, provided that such selected polymer provides a matrix which is not deleterious to photosensitive silver halide crystals and possesses a lattice allowing development 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 carbonate, 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 or agents may be disposed within the film unit, for example, in the emulsion and/or a permeable layer directly associated therewith such as intermediate the emulsion and the support.

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 preferably possess a solvent capacity which does not deleteriously hydrate the selected emulsion polymer's lattice 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 preferred image formation.

Although the preceding description of the invention has been couched in terms of the preferred photoresponsive material, that is, a photosensitive salt of silver and particularly, a photosensitive silver halide, it will be recognized that the photosensitive component of the film unit may comprise photosensitive metal salts, other than the specifically denoted silver halides, traditionally employed in nonsilver halide photographic processes, in combination with requisite catalytic reduction nuclei and solvent, in accordance with the teachings of the present invention. An enumeration of photosensitive heavy metal salts other than photosensitive silver halide salts is set forth in Chapter I of Light-Sensitive Systems: Chemistry and Application of Nonsilver Halide

Photographic Processes, Jaromir Kosar, 1965, John Wiley & Sons, Inc., New York, New York, and it is intended that the substitution of nonsilver halide photosensitive salts, in replacement of the illustrative photosensitive silver halides, in the practice of the present invention be considered to be a substitution specifically within the spirit and scope of the annexed claims.

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 comprises a support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei present in a concentration effective to provide, upon contact with a processing composition which includes a silver halide developing agent and a silver halide solvent, a silver image possessing optical density inversely proportional to exposure of the emulsion to radiation actinic.

2. A photographic film unit as defined in claim 1 which comprises a transparent support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei in a concentration effective to provide upon development in the presence of a silver halide solvent, as a function of exposure to incident actinic radiation, a silver image derived from development of exposed silver halide crystals possessing a maximum image density at least 1.5 density units less than the maximum density of a silver image derived from development of unexposed silver halide crystals.

3. A photographic film unit as defined in claim 2 which comprises a transparent support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei dispersed in a processing composition permeable polymeric binder effective to substantially prevent microscopic diffusion of image components, said 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 of the unit to incident actinic radiation, a minimum image density not in excess of about 0.5 and a maximum image density of not less than about 2.0.

4. A photographic film unit as defined in claim 1 wherein said silver halide crystals comprise silver iodobromide crystals.

5. A photographic film unit as defined in claim 4 wherein said silver iodobromide crystals comprise about 1 to 9 percent, by weight, iodide.

6. A photographic film unit as defined in claim 4 which comprises a transparent support carrying on one surface a photosensitive silver halide emulsion consisting essentially of panchromatically sensitized silver iodobromide crystals and metallic sulfide, metallic selenide or colloidal noble metal silver precipitating nuclei dispersed in a gelatin binder 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 ex-

posure to actinic radiation, a maximum silver image density of developed silver derived from exposed silver halide crystals 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 2.4.

7. A photographic process which comprises, in combination, the steps of exposing a photographic film unit comprising a support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei in a concentration effective to provide a silver image possessing optical density inversely proportional to exposure of the emulsion and contacting said silver halide emulsion with an aqueous processing composition containing a silver halide developing agent and a silver halide solvent to provide a visible silver image to said emulsion possessing optical density inversely proportional to exposure of the emulsion.

8. A photographic process as defined in claim 7 which comprises, in combination, the steps of exposing a photographic film unit containing a transparent support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei dispersed in a processing composition permeable polymeric binder in a 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 1.5 density units greater than the maximum density of the silver image derived from development of exposed silver halide crystals and 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 emulsion 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 1.5 density units greater than the maximum density of developed silver derived from development of exposed silver halide crystals.

9. A photographic process as defined in claim 8 which comprises, in combination, the steps of exposing a photographic film unit which comprises a transparent support carrying on one surface a photosensitive silver halide emulsion consisting essentially of photosensitive silver halide crystals which contain at least two halides selected from the group consisting of iodide, bromide and chloride and silver precipitating nuclei dispersed in a processing composition permeable polymeric binder in a concentration effective to provide upon development of exposed silver halide crystals a maximum silver image density not in excess of about 0.5 and a maximum silver image density derived from unexposed silver halide crystals of not less than about 2.0 and contacting said silver halide emulsion with an aqueous processing composition containing a silver halide developing agent and a silver halide solvent for a sufficient time to provide a silver image to said emulsion comprising a maximum density of image silver derived from development of unexposed silver halide crystals of not less than about 2.0 and a maximum density of image silver derived from development of exposed silver halide crystals not in excess of about 0.5.

10. A photographic process as defined in claim 7 wherein said silver halide emulsion consisting essentially of a silver iodobromide emulsion.

11. A photographic process as defined in claim 10 wherein said silver iodobromide emulsion is panchromatically sensitized.

12. A photographic process as defined in claim 11 wherein said silver iodobromide emulsion consisting essentially of iodobromide crystals containing about 1 to 9 percent, by weight, iodide.

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13. A photographic process which comprises, in combination, the steps of exposing a photographic film unit comprising a support carrying on one surface a photosensitive silver halide emulsion consisting essentially of panchromatically sensitized silver iodobromide crystals and silver precipitating nuclei dispersed in a processing composition permeable gelatin binder in a concentration effective to provide, upon development in the presence of a silver halide solvent and as a function of exposure, image silver derived from development of exposed silver iodobromide crystals possessing a maximum silver image density less than about 0.3 and a maximum silver image density derived from development of unexposed silver iodobromide crystals greater than about 2.4 and contacting said exposed emulsion with an aqueous processing composition containing a silver halide developing agent and a silver

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halide solvent for a time sufficient to provide a silver image to said emulsion in terms of the unexposed areas of said emulsion possessing a maximum silver image density of not less than about 2.4 and a silver image to said emulsion in terms of the exposed areas of said emulsion possessing a maximum silver image density not in excess of about 0.3.

14. A photographic process as defined in claim 13 wherein said silver precipitating nuclei comprises metallic sulfides, metallic selenides or colloidal noble metals.

15. A photographic process as defined in claim 14 wherein said silver precipitating nuclei are dispersed in said silver iodobromide emulsion in a concentration of about 1 to 25×10^4 moles/ft.².

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,520 Dated October 26, 1971

Inventor(s) Edwin H. Land

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

Column 8, line 62 " $1 - 25 \times 10^{16}$ " should be $--1 - 25 \times 10^{-6}--$;

Column 8, line 70 " 10^{123} " should be $--10^{-23}--$ and " 10^{130} " should be $--10^{-30}--$.

Column 16, claim 15, line 13 " $25 \times 10'$ " should be $--25 \times 10^{-6}--$.

Signed and sealed this 16th day of May 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents