July 20, 1971 H. G. ROGERS 3,594,165

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed May 22, 1970 4 Sheets-Sheet 1

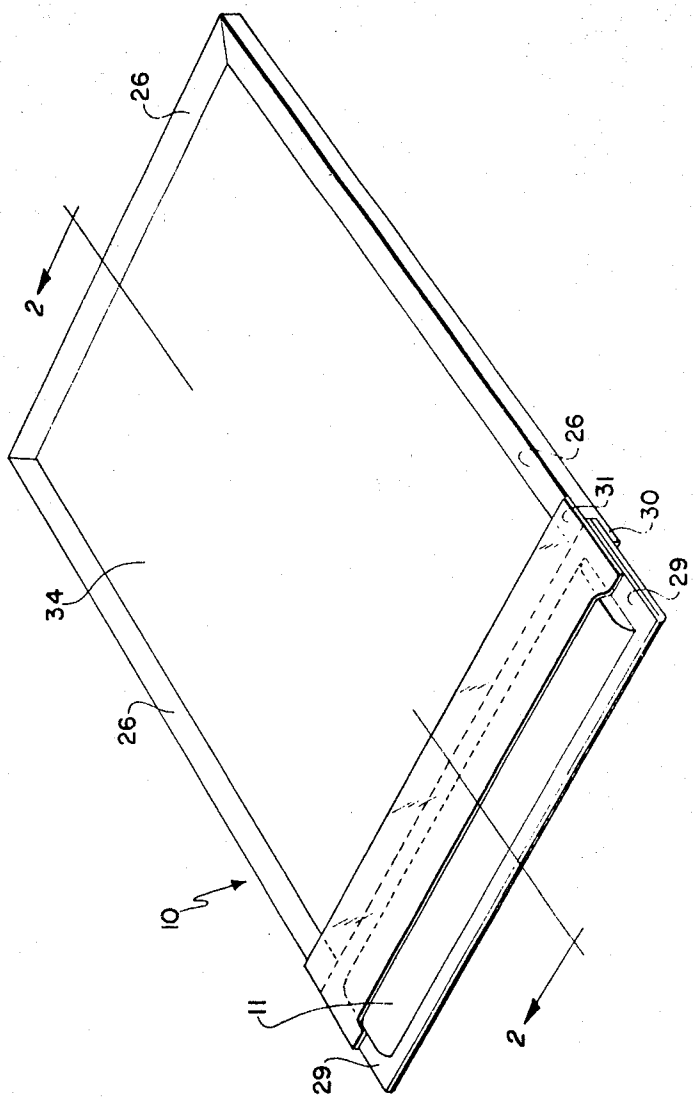


FIG. 1

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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed May 22, 1970 4 Sheets-Sheet 2

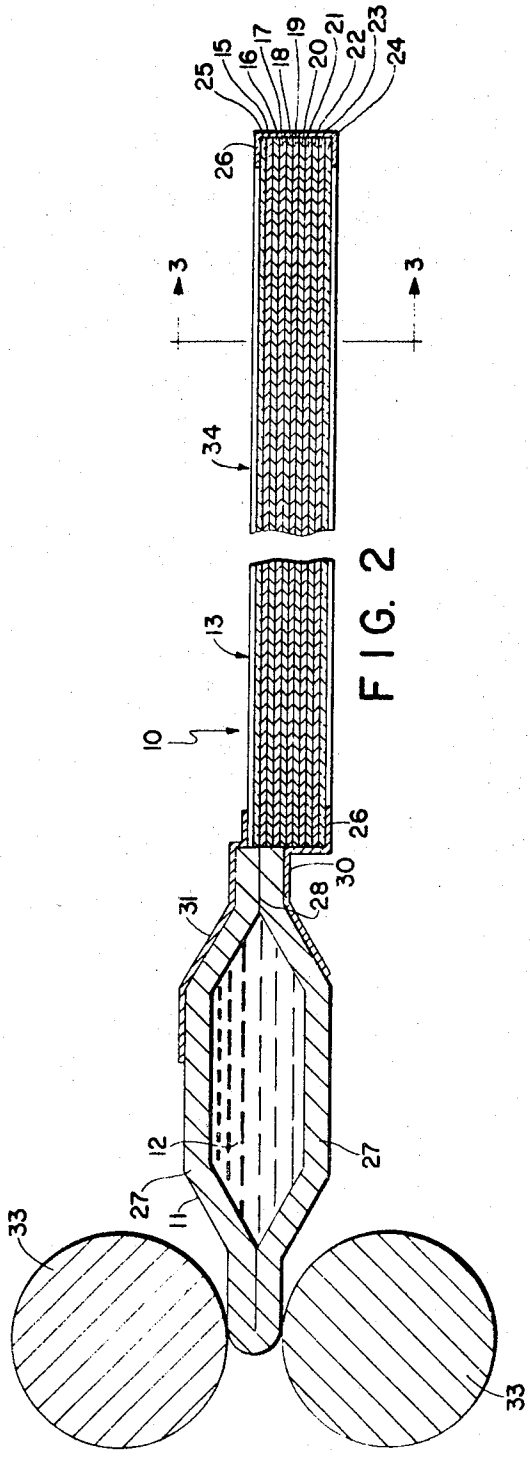


FIG. 2

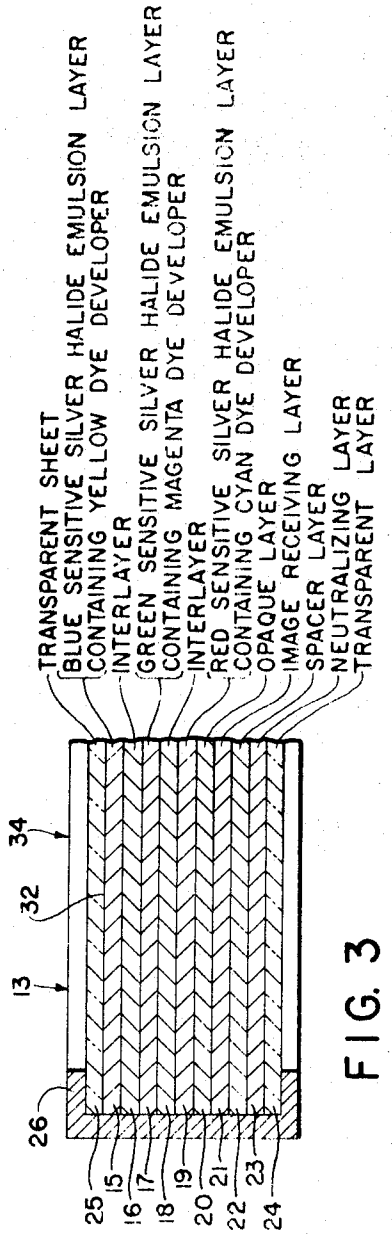


FIG. 3

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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed May 22, 1970 4 Sheets-Sheet 3

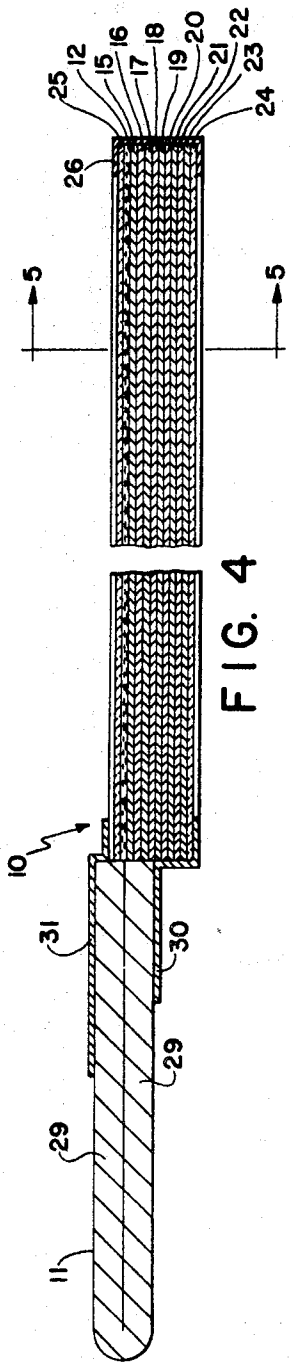


FIG. 4

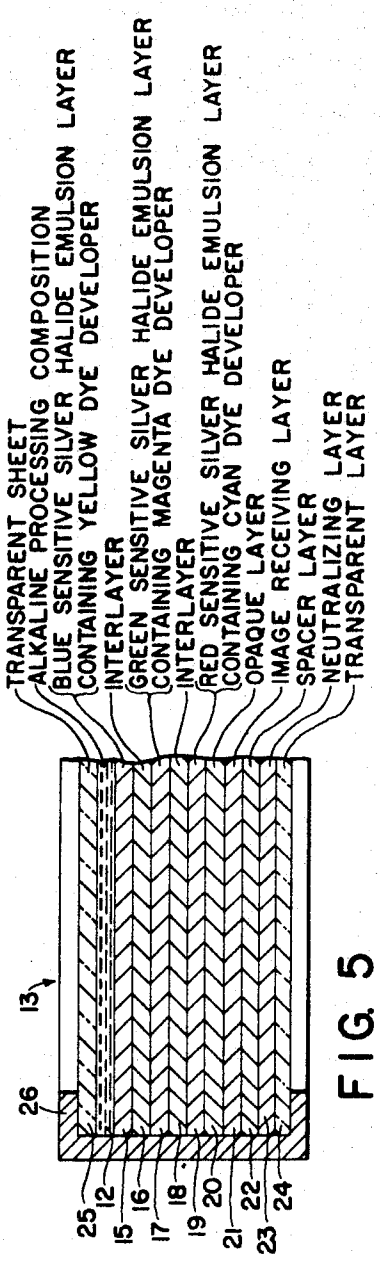


FIG. 5

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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed May 22, 1970 4 Sheets-Sheet 4

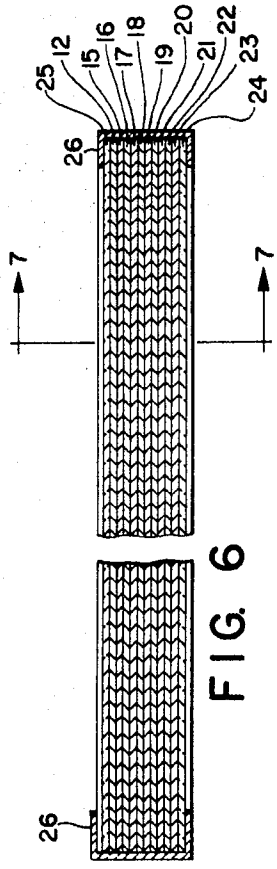


FIG. 6

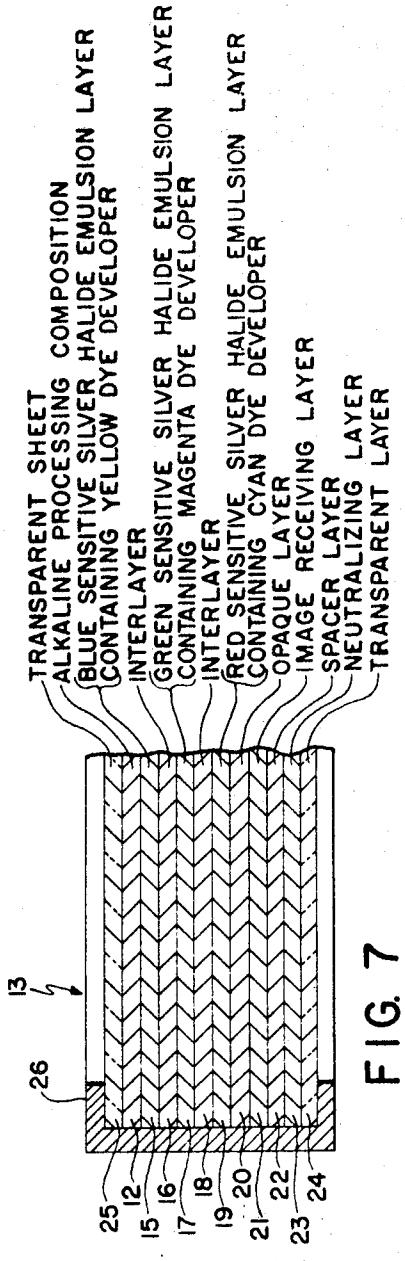


FIG. 7

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United States Patent Office 3,594,165 Patented July 20, 1971

3,594,165

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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Continuation-in-part of application Ser. No. 815,585, Apr. 14, 1969, which is a continuation-in-part of application Ser. No. 728,535, May 13, 1968. This application May 22, 1970, Ser. No. 39,646

Int. Cl. G03c 1/48, 7/00

U.S. Cl. 96—3 19 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to photography, particularly, to photographic products specifically adapted for employment in specified photographic diffusion transfer color processes and, more particularly, to photographic products which comprise a composite photosensitive structure containing, in combination, a photosensitive laminate including, as essential layers, in sequence, a dimensionally stable layer transparent to actinic radiation; an optional polymeric layer substantially transparent to incident radiation and containing sufficient acidifying capacity to effect reduction of a processing composition having a pH at which a selected dye image-forming material is diffusible to a pH at which such material is substantially nondiffusible; a polymeric layer dyeable by the selected dye image-forming material; a processing composition permeable opaque layer; and a photosensitive silver halide layer having associated therewith a dye image-forming material which is processing composition diffusible, as a function of the point-to-point degree of the silver halide layer's exposure to incident actinic radiation; a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the dimensionally stable transparent layer; and a rupturable container retaining a processing composition containing an opacifying agent positioned extending transverse a leading edge of the film unit to effect unidirectional discharge of the container's contents intermediate the dimensionally stable sheet and the laminate; and to specified photographic diffusion transfer color processes employing such products.

The present invention relates to photography and, more particularly, to photographic products particularly adapted for employment in photographic diffusion transfer color processes.

This application is in part a continuation of my copending U.S. application Ser. No. 815,585, filed Apr. 14, 1969 now abandoned, in turn, in part a continuation of my copending U.S. application Ser. No. 728,535, filed May 13, 1968 (now abandoned).

The primary objects of the present invention are to provide photographic products particularly adapted for employment in diffusion transfer photographic color processes; to provide photographic products which comprise a photosensitive laminate which contains a plurality of layers including a photosensitive silver halide layer having a dye image-forming material associated therewith which is processing composition diffusible, as a function of silver halide layer photoexposure, a permeable opaque layer, a polymeric layer dyeable by the dye image-forming material, preferably a polymeric layer containing sufficient acidifying capacity to effect reduction of a selected processing solution having a first pH at which the dye image-forming material is soluble and diffusible as a function of silver halide layer photoexposure to a second pH at which the dye image-forming material is substantially nondiffusible, and a dimensionally stable transparent layer;

to provide photographic diffusion transfer products comprising a film unit including a photosensitive laminate, of the last-identified type, in combination with a transparent dimensionally stable sheet superposed substantially coextensive the surface of the photosensitive laminate opposite the dimensionally stable transparent layer and a rupturable container retaining a processing composition preferably possessing the first pH and containing dispersed therein an opacifying agent; to provide a diffusion transfer film unit, of the last-identified type, having the container fixedly positioned and extending transverse a leading edge of the photosensitive laminate whereby to effect, upon application of compressive pressure, discharge of the processing composition contiguous the surface of the laminate opposite the dimensionally stable transparent layer; and to provide photographic diffusion transfer color processes employing such products.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others 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 perspective view of one embodiment of a photographic film unit in accordance wtih the invention;

FIGS. 2, 4 and 6 are diagrammatic enlarged cross-sectional views of the film unit of FIG. 1, along section line 2—2, illustrating the association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a multicolor transfer image according to the invention, the thickness of the various materials being exaggerated, and wherein FIG. 2 represents an exposure stage, FIG. 4 represents a processing stage and FIG. 6 represents a product of the process; and

FIGS. 3, 5 and 7 are diagrammatic, further enlarged cross-sectional views of the film unit of FIGS. 2, 4 and 6, along section lines 3—3, 5—5 and 7—7, respectively, further illustrating, in detail, the arrangement of layers comprising the photosensitive laminate during the three illustrated stages of the transfer process.

As disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961, a photosensitive element containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion may be exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition, positioned intermediate the photosensitive element and the image-receiving layer, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by

oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, wherein at least two selectively sensitized photosensitive strata, superposed on a single support, are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

As disclosed in U.S. Pat. No. 3,362,819, image-receiving elements, particularly adapted for employment in diffusion transfer processes of the type disclosed in aforementioned U.S. Pat. No. 2,983,606, wherein the image-receiving elements are separated from contact with a superposed photosensitive element, subsequent to substantial transfer image formation, preferably comprise a support layer possessing on one surface thereof, in sequence, a polymeric layer which is acidic in character and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance, and most preferably include an inert timing or spacer layer intermediate the acidic polymeric layer and the image-receiving layer.

As set forth in the last-mentioned U.S. patent, the acid polymeric layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, nuch as sodium potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride, polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

The acidic polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric layer be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidence, for example, by an undesired reduction in positive image density, the acid component is disclosed to be so distributed in the acidic polymer layer that the rate of its availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid material in the polymer layer may be effected, for example, by mixing an acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only an acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the acid component may contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the last-mentioned U.S. patents, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It was stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As disclosed in aforementioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effective at temperatures above room temperature, for example, at 95 to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

However, as disclosed in U.S. Pat. No. 3,445,686, preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective within the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer images' color definition.

It is further stated in last-mentioned U.S. Pat. No. 3,445,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methyl cellulose, isopropyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1000, preferably of about 1000 to 50,000, possessing a degree of acetalation within about 10 to 30%, 10 to 30%, 20 to 80%, and 10 to 40%, of the polyvinyl alcohol's theoretical polymeric hydroxyl groups, respectively, and including mixed acetals where desired.

Where desired, a mixture of the polymers is to be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor

polymeric layer dyeable by the dye image-providing materials; an alkaline solution permeable polymeric layer containing sufficient acidifying capacity to effect reduction, subsequent to substantial multicolor transfer dye image formation, of a processing composition having the first pH to a second pH, at which the dye image-providing material is substantially non-diffusible; and the dimensionally stable transparent layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing subsequent to photoexposure or processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion. Specifically preferred dyes comprise dyes which exhibit major spectral absorption outside of the primary regions of the spectrum to which the associated silver halide emulsion is sensitive and a spectral transmission substantially complementary to the absorption, during exposure of the emulsion, and major spectral absorption within the spectral range to which the associated silver halide emulsion is sensitive and spectral transmission substantially complementary to said absorption, subsequent to exposure or processing of said emulsion, for example, of the type disclosed in U.S. Pat. No. 3,307,947.

In one embodiment each of the emulsion strata, and its associated dye, may be spaced from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers and the dyeable polymeric layer next adjacent the polymeric acid layer may be separated from that layer by an alkaline solution permeable polymeric spacer layer, most preferably a polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

In such preferred embodiments of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself may be dispersed in an aqueous alkaline solution permeable polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; the alkaline solution polymeric spacer layer is transparent and about 0.1 to 0.7 mil in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mils in thickness; and the dimensionally stable transparent layer is alkaline solution impermeable and about 2 to 6 mils in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

In view of the fact that the preferred dye image-providing materials comprise dyes which are silver halide developing agents, as stated above, the present invention will be further described hereinafter in terms of such dyes without limitation of the invention to the illustrative dyes.

In the preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily comprise a yellow dye developer/blue-sensitive emulsion unit, a cyan dye developer/red-sensitive emulsion unit and a magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing that the relative order of such units may be varied in accordance with the desires of the operator.

In those instances, where either or both the respective yellow and magenta dye developers, employed in a preferred tripack configuration which positions the yellow dye developer/blue-sensitive emulsion unit distal the dimensionally stable transparent layer and the cyan dye developer/red-sensitive emulsion unit proximal the transparent layer to provide the multicolor transfer image, comprise a dye developer which exhibits major spectral absorption outside of the primary region of the spectrum to which its associated silver halide emulsion is sensitive and a spectral transmission substantially complementary to that absorption, during exposure of the emulsion, then, in ordinary circumstances, it may be advantageous to incorporate filter agents adapted to insure the correct selective exposure of the respective emulsions less proximal the exposure surface of the laminate. Specifically, in the instance where the yellow dye developer exhibits major spectral absorption outside of the primary regions of the spectrum to which its associated silver halide emulsion is sensitive, that is, the blue region of the visible spectrum, during exposure of the emulsions, then a yellow filter agent may advantageously be incorporated intermediate the blue-sensitive emulsion and the remaining green- and red-sensitive emulsions, in order to prevent undesired exposure of the latter emulsions by reason of their inherent sensitivity to actinic radiation within the blue range of the spectrum generally present. In the instance where the magenta dye developer employed exhibits major spectral absorption outside of the primary region of the spectrum to which its associated silver halide emulsion is sensitive, that is, the green region of the visible spectrum, during exposure of the emulsions, a magenta filter agent may be advantageously incorporated intermediate the green- and red-sensitive emulsions in instances wherein the red-sensitive emulsion possesses sensitivity to actinic radiation within the green region of the spectrum.

Where desired, the yellow dye developer employed in such preferred embodiment also may be disposed in the processing composition retained within the container and distributed contiguous the exposure surface of the blue-sensitive emulsion, subsequent to exposure of the photosensitive laminate, during processing of the exposed film unit, to provide the desired multicolor transfer image formation. In the latter embodiment, it may be desirable to incorporate a yellow filter agent intermediate the blue- and green-sensitive emulsion units of the photosensitive laminate for the reasons stated above.

Employment of the detailed film unit of the present invention, according to the hereinafter described color diffusion transfer photographic process, is specifically adapted to provide for the production of a color transfer image accomplished by a diffusion transfer process which may include in-process adjustment of the environmental pH of the film unit, from a pH at which transfer processing is operative to a pH at which dye transfer is substantially inoperative, subsequent to substantial transfer image formation, in order to obviate the previously discussed disadvantages of the prior art products and processes. The color transfer image is thus obtained and maintained irrespective of the fact that the film unit comprises an integral laminate unit during exposure, processing and subsequent viewing, and storage of the unit. Accordingly, by means of the present invention, color transfer images and specifically multicolor images may be obtained, employing an integral laminate film unit, which exhibit desired maximum and minimum dye densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation, over an extended period of time, as compared with prior art disclosed film materials. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient

utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

Reference is now made to FIGS. 1 through 7 of the drawings wherein there is illustrated a preferred film unit of the present invention and wherein like numbers, appearing in the various figures, refer to like components.

As illustrated in the drawings, FIG. 1 sets forth a perspective view of the film unit, designated **10**, and each of FIGS. 2 through 7 illustrate diagrammatic cross-sectional views of film unit **10**, along the stated section lines **2—2**, **3—3**, **5—5** and **7—7**, during the various depicted stages in the performance of a photographic diffusion transfer process as detailed hereinafter.

Film unit **10** comprises rupturable container **11**, retaining, prior to processing, aqueous alkaline solution **12**, photosensitive laminate **13** including, in order, blue-sensitive silver halide emulsion layer **15** containing yellow dye developer; interlayer **16**; green-sensitive silver halide emulsion layer **17** containing magenta dye developer; interlayer **18**; red-sensitive silver halide emulsion layer **19** containing cyan dye developer; opaque layer **20**; image-receiving layer **21**; spacer layer **22**; neutralizing layer **23**; and dimensionaly stable transparent layer **24**; and dimensionally stable transparent sheet **25**; both layer **24** and sheet **25** preferably comprising an actinic radiation transparent and processing composition impermeable flexible sheet material.

The composite may be provided with a binding member extending around, for example, the specified edges of composite, maintaining the laminate and sheet element comprising the composite intact except at the interface between the elements during distribution of processing composition **12**. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape **26** securing the sheet and laminate elements together at the composite's specified edges. Tape **26** will also act to maintain processing composition **12** intermediate sheet **25** and photosensitive laminate **13** upon application of compressive pressure to container **11** and distribution of its contents intermediate the stated elements. Under such circumstances, binder tape **26** will act to prevent leakage of processing composition from the film unit during and subsequent to photographic processing.

Rupturable container **11** may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,491; 3,056,492; 3,152,515; and the like. In general such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls **27** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing solution **12** is retained. The longitudinal marginal seal **28** is made weaker than the end seals **29** so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **27** of the container.

As illustrated in FIGS. 1, 2 and 4, container **11** is fixedly positioned and extends transverse a leading edge of photosensitive laminate **13** whereby to effect unidirectional discharge of the container's contents **12** intermediate transparent sheet **25** and surface **32** of blue-sensitive silver halide emulsion layer **15**, upon application of compressive force to container **11**. Thus, container **11**, as illustrated in FIG. 2, is fixedly positioned and extends transverse a leading edge of laminate **13** with its longitudinal marginal seal **28** directed toward the leading edge of surface **32**. As shown in FIGS. 1, 2 and 4, container **11** is fixedly secured to laminate **13** by extension **30** of tape **26** extending over a portion of one wall **27** of the container, in combination with a separate retaining member such as illustrated, retaining tape **31** extending over a portion of the other wall **27** of the container and a portion of laminate **13**'s surface **32** generally equal in area to about that covered by tape **26**.

Transparent sheet **25**, as illustrated in the figures in the preferred embodiment, is fixedly maintained superposed on and coextensive with surface **32** of blue-sensitive emulsion layer **15**, at least during processing, to facilitate distribution of processing composition **12** upon compressive rupture of container **11** and unidirectional discharge of its contents on surface **32**.

As illustrated in FIGS. 1, 2 and 4, extension flap **30** of tape **26** may be of such area and dimensions that upon, for example, manual separation of container **11** and tape **31**, subsequent to distribution of the composition, from the remainder of film unit **10**, flap **30** may be folded over the edge of laminate **13**, previously covered by tape **31**, in order to facilitate maintenance of the laminate's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer **24**. Preferably, however, the film unit will be maintained intact subsequent to processing including retention of the exhausted container, the processing composition and transparent sheet in the spacial position assumed during processing. In such instance, the processing composition employed should possess the requisite adhesive capacity, in both the fluid and dry states, to enhance the integrity and stability of the spacial arrangement assumed.

In general, in a particularly preferred embodiment, the opacity of processing composition **12** when distributed will be sufficient to prevent further exposure of the film unit's silver halide emulsion or emulsions, by actinic radiation incident on transparent sheet **25**, during processing of the unit in the presence of radiation actinic to the emulsion or emulsions. Accordingly, the film unit may be processed, subsequent to exposure, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of the laminate are appropriately protected from incident radiation, at one major surface by the opaque layer or layers **20** and at the remaining major surface by opaque processing composition **12** as further described hereinafter. If the illustrated binder tapes are also opaque, as stated above, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The selected opaque layer or layers **20**, however, should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric layer. In general, while substantially any permeable opaque layer may be employed, it is preferred that a layer be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, a layer which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable opaque layers will be those providing a white background, for viewing the transfer image, and specifically those adapted to be employed to provide background for reflection photographic prints and, especially, those layers possessing the optical properties desired for reflectance of incident radiation.

The opaque layer may comprise substantially any opacifying agent compatible with the photographic system, such as, for example, barium sulfate, zinc oxide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica and the like, which may be distributed in a permeable polymeric matrix or binder, such as, for example, gelatin, polyvinyl alcohol, and the like.

A particularly preferred opaque layer comprises titanium dioxide due to its highly effective reflection properties. In general, a coating composition, for example,

hydroxyethylcellulose, containing sufficient titanium dioxide to provide a percent reflectance of about 85 to 99%, respectively, will be employed. In the most preferred embodiments, the percent reflectance desired thus will be in the order of about 85%.

Where it is desired to increase the opacifying capacity of a layer containing, for example, titanium dioxide, beyond that ordinarily obtained, an additional opacifying agent such as carbon black, for example, in a concentration of about 1 part carbon black to 100 to 500 parts titanium dioxide may be provided to the layer. Preferably, however, such additional opacifying capacity will be provided by constituting the opacifying layer as a plurality of more or less discrete layers, the layer next adjacent the transparent support comprising a reflection layer and the succeeding layer or layers comprising one or more opacifying agents possessing greater opacifying capacity than that ordinarily obtained from the reflecting agent or agents employed.

The opacifying agent dispersed in processing composition **12** may be any of the multiplicity of such agents known in the art such as carbon black, iron oxide, titanium (III) oxide, titanium (III) hydroxide, and the like. In preference, the agent or agents should be selected which possess the maximum opacifying capacity per unit weight, is photographically nondeleterious and is substantially nondiffusible throughout the film unit subsequent to distribution. A particularly preferred agent has been found to comprise carbon black employed in a concentration effective to provide the opacity required to prevent undesired physical fogging of the emulsion formulations selected and employed by radiation transmitted through the spread processing composition.

In the performance of a diffusion transfer multicolor process employing film unit **10**, the unit is exposed to radiation, actinic to photosensitive laminate **13**, incident on the laminate's exposure surface **34**, as illustrated in FIG. 2.

Subsequent to exposure, as illustrated by FIGS. 2 and 4, film unit **10** is processed by being passed through opposed suitably gapped rolls **33** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **28** and distribution of processing composition **12**, containing an opacifying agent and having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate transparent sheet **25** and blue-sensitive silver halide emulsion layer **15** on a coextensive surface **32**.

Processing composition **12** permeates emulsion layers **15**, **17** and **19** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **15**, **17** and **19**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfer, by diffusion, to processing composition permeable polymeric layer **21** to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous composition **12** transfer, by diffusion, through permeable polymeric layer **21**, permeable spacer layer **22** and to permeable polymeric acid layer **23** whereby solution **12** decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image viewable through dimensionally stable transparent layer **24**.

Subsequent to distribution of processing solution **12**, container **11**, optionally, may be manually dissociated from the remainder of the film unit, as described above.

As previously stated, the multicolor dye transfer image is viewable through dimensionally stable transparent layer **24** both during and subsequent to transfer image formation, in the preferred embodiment detailed above. In addition, a multicolor dye image, negative with respect to the transfer image, may be viewed subsequent to processing, through surface **34** of the laminate, in embodiments wherein sheet **25** and processing composition are separated from the remainder of the photosensitive laminate subsequent to processing.

The present invention will be further illustrated and detailed in conjunction with the following illustrative constructions which set out representative embodiments and photographic utilization of the novel photographic film units of this invention, which, however, are not limited to the details herein set forth and are intended to be illustrative.

Film units similar to that set forth in the drawings may be prepared, for example, by coating, in succession, on a transparent cellulose triacetate film base:

(1) The partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing for 14 hours, about 300 grams of high viscosity poly-(ethylene/maleic anhydride), about 140 grams of n-butyl alcohol and about 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.75 mil thick;

(2) A solution of hydroxy propyl cellulose in water to provide a polymeric spacer layer approximately 0.075 mils thick;

(3) A 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs./ft.^{2}, to provide a polymeric image-receiving layer approximately 0.40 mil thick;

(4) A layer of titanium dioxide dispersed in hydroxyethyl cellulose and coated at a coverage of about 1200 mgs./ft.^{2} of titanium dioxide and about 30 mgs./ft.^{2} of hydroxyethyl cellulose;

(5) A layer of gelatin coated at a coverage of about 200 mgs./ft.^{2};

(6) A layer of the acrylic latex sold by Rohm and Haas Co., Philadelphia, Pa. under the trade designation Rhoplex AC–61 coated at a coverage of about 110 mgs.ft./^{2};

(7) A layer of carbon black dispersed in hydroxyethyl cellulose coated at a coverage of about 150 mgs./ft.^{2} carbon black and about 3.0 mgs./ft.^{2} hydroxyethyl cellulose;

(7) A layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl - α - methyl] - ethyl-amino)-5,8-dihydroxyanthraquinone and carbon black dispersed in gelatin and coated at a coverage of about 50 mgs./ft.^{2} of dye, about 180 mgs./ft.^{2} of carbon black and about 63 mgs./ft.^{2} of gelatin;

(9) A red-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 120 mgs./ft.^{2} of silver and about 22 mgs./ft.^{2} of gelatin;

(10) A layer of Rhoplex AC–61 coated at a coverage of about 80 mgs./ft.^{2};

(11) A layer of the magenta dye developer 4-isopropoxy - 2 - [p - (β - hydroquinonyl ethyl) - phenylazo]-naphthalene-1-ethoxy acetate dispersed in a green-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 80 mgs./ft.^{2} of dye, about 110 mgs./ft.^{2} of silver and about 150 mgs./ft.^{2} of gelatin;

(12) A layer of the last-mentioned magenta dye developer dispersed in gelatin at a coverage of about 20 mgs./ft.^{2} of dye and about 30 mgs./ft.^{2} gelatin;

(13) A layer of Rhoplex AC–61 coated at a coverage of about 110 mgs./ft.^{2};

(14) A layer of the yellow dye developer 4-(p-[β-hydroquinonyl ethyl]-phenylazo) - 3 - (N-n-hexylcarboxamido)-1-phenyl-5-pyrazolone dispersed in gelatin and coated at a coverage of about 140 mgs./ft.^{2} of dye and about 175 mg./ft.^{2} of gelatin;

(15) A blue-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 150 mgs./ft.^{2} of silver and about 28 mgs./ft.^{2} of gelatin; and

(16) A layer containing 4'-methylphenyl hydroquinone dispersed in gelatin at a coverage of about 20 mgs./ft.^{2} of 4'-methylphenyl hydroquinone and about 30 mgs./ft.^{2} of gelatin.

Transparent cellulose triacetate film base may then be superposed on the external surface of coating No. 15 and the two components then taped together, in composite form, at their respective edges by means of opaque pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant film unit.

A rupturable container comprising an outer layer of paper, an intermediate layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising:

Water—100 cc.
Potassium hydroxide—11.2 gms.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250]—3.4 gms.
N-benzyl-α-picolinium bromide—1.5 gms.
Benzotriazole—1.0 gm.
Carbon black—6.4 gms.

may then be fixedly mounted on the leading edge, of each of the composites, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that upon application of compressive pressure to the container, its contents will be distributed, upon rupture of the container's marginal seal, intermediate the cellulose triacetate sheet and the 4'-methylphenyl hydroquinone containing layer.

The photosensitive laminates may be exposed through step wedges to selectively filtered radiation incident on the cellulose triacetate sheet and processed by passage of the exposed film unit through suitably gapped opposed rolls, to effect rupture of the container and distribution of the container's contents between the 4'-methylphenyl hydroquinone layer and the sheet element. During processing, a multicolor dye transfer image formation may be viewed through the cellulose triacetate film base and such image formation is found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation within a period of about 1 to 3 minutes.

The pH of the alkaline processing solution initially employed must be a pH at which the dye developers employed are diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer, or group of dye developers, most particularly desirable dye developers are soluble at pH's about 9 and relatively insoluble at pH's below 9, in reduced form, and the system can be readily balanced accordingly for such dye developers. In addition, although as previously noted, the processing composition, in the preferred embodiment, will include the stated film-forming viscosity-increasing agent, or agents, to facilitate spreading of the composition and to provide maintenance of the spread composition as a structurally stable layer of the laminate, subsequent to distribution, it is not necessary that such agent be employed as a component of the composition. In the latter instance, however, it will be preferred that the concentration of solvent, that is, water, etc., comprising the composition be the minimum amount necessary to conduct the desired transfer processs, in order not to adversely effect the structural integrity of the laminate and that the layers forming the laminate can readily accommodate and dissipate the solvent throughout during processing and drying without effecting undesirable dimensionl changes in the layers forming the laminate.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, tolu-hydroquinone, phenylhydroquinone, 4'-methylphenyl-hydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethylenimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quanternary ammonium compound, in accordance with the processes disclosed in U.S. Pat. No. 3,173,786, issued Mar. 16, 1965.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition 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 substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The dimensionally stable layers and sheet referred to may comprise any of various types of conventional opaque and transparent rigid or flexible materials, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include alkaline solution impermeable materials such as paper; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers, polyvinyl acetal; polyamides such as nylon; polyester such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate or acetate-butyrate. It will be recognized that one or more of the designated layers may not be required when the remaining layers of the laminate are such as to provide the functions of these layers in the absence of same, for example, where the remaining layers of the laminate provide the requisite dimensional stability and radiation filtering properties.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of addi-

tional U.S. patents detailing the specific dye developers for photographic transfer process use, mention may also be made of U.S. Pats. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

As additional examples of synthetic, film-forming, permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl-α,β-unsaturated carboxamides and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinyl phthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,264; and the like.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric, or colloidal, matrix such as ball-milling and the like techniques, the preparation of the dye developer dispersion may also be obtained by dissolving the dye in an appropriate solvent, or mixture of solvents, and the resultant solution distributed in the polymeric binder, with optional subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic color-providing materials in polymeric binders, specifically for the formation of component layers of photographic film units, reference may be made to U.S. Pats. Nos. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171; and the like.

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552 3,227,554 3,243,294 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,433,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color or dye formers or couplers to provide a dye transfer image to a superposed image receiving layer and those disclosed in U.S. Pats. No. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials which, as disposed in the film unit, are initially diffusible or non-diffusible in the processing composition selected and are capable of providing an imagewise distribution of processing composition diffusible dye image-forming material as a direct or indirect function of exposure.

For the production of the photosensitive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pats. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; 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 of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of the art, as described in Hammer, F. M., The Cyanine Dyes and Related Compounds.

Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of silver, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver chloroiodobromide or silver iodobromide, of varying halide ratios and varying silver concentrations.

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; and vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, and appropriate dye image-forming mate-

rial in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen may comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, for example, a cyan, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye image-providing material and the use of a mixture of, for example, dye developers adapted to provide a black-and-white transfer image, for example, the employment of dye developers of the three substractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

Where in the specification, the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

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 improving adhesion, and that any one or more of the described layers may comprise a composite of two or more strata of the same, or different, components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like.

In addition, the polymeric neutralizing layer disclosed to be optionally disposed, in a preferred embodiment, intermediate the dimensionally stable transparent support and next adjacent essential layer may, where desired, be disposed carried by the transparent sheet element on the surface of that element next adjacent the photosensitive laminate and adapted to effect the stated in situ process modulation of the environmental pH, subsequent to substantial dye transfer image formation. In such structure, the pH modulating acidic component may be appropriately insulated to a substantial extent from deleterious interaction with the remainder of the photographic system during storage, exposure and initial processing of the film unit by means of, for example, a polymeric diffusion control barrier or spacer timing layer of the general type and design discussed above and may be employed alone or in combination with the polymeric neutralizing layer discussed hereinbefore. The in situ process modulation referred to may also optimally be in whole or in part accomplished by the employment of particulate acidic material distributed within the film unit and selectively available to effect the desired pH reduction in accordance with techniques disclosed in the copending U.S. patent application Ser. No. 846,442 of Edwin H. Land, filed July 31, 1969 and incorporated by reference herein.

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

What is claimed is:

1. A composite photographic diffusion transfer color process film unit which comprises, in combination:

(a) a photosensitive laminate containing, as essential layers, a dimensionally stable transparent support carrying on one surface, in order, a dyeable polymeric layer, a processing composition permeable opaque layer, and a photosensitive silver halide layer having associated therewith a dye image-forming material which is processing composition diffusible, as a function of the point-to-point degree of silver halide layer's exposure to actinic radiation;

(b) a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the dimensionally stable transparent support; and

(c) a rupturable container retaining a processing composition including an opacifying agent positioned extending transverse a leading edge of the film unit to effect unidirectional discharge of the container's contents intermediate the dimensionally stable sheet and the photosensitive laminate.

2. A photographic film unit as defined in claim **1** wherein said dyeable polymeric layer is processing composition permeable and said film unit additionally includes a polymeric layer, containing sufficient acidifying capacity to effect reduction of a processing composition having a first pH at which said dye image-forming material is soluble and diffusible to a second pH at which said material is substantially nondiffusible, positioned intermediate said dimensionally stable transparent support and next adjacent essential layer.

3. A photographic film unit as defined in claim **1** wherein said opacifying agent is present in said processing composition in a quantity effective, upon distribution on the surface of said photosensitive laminate, to prevent exposure of said photosensitive silver halide layer during processing in the presence of radiation actinic thereto and incident on distributed processing composition and said opaque layer is effective to prevent exposure of said photosensitive silver halide layer during processing in the presence of radiation actinic thereto and incident on said opaque layer.

4. A photographic film unit as defined in claim **2** wherein said dye image-providing material is a dye which is a silver halide developing agent.

5. A photographic film unit as defined in claim **3** wherein said processing composition permeable opaque layer is actinic radiation reflective.

6. A photographic film unit as defined in claim **5** wherein said opaque layer comprises titanium dioxide dispersed in a processing composition permeable polymeric binder.

7. A photographic film unit as defined in claim **1** which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination:

a photosensitive laminate containing, as essential layers, at least two selectively sensitized silver halide emulsion layers each having a dye, which dye is a silver halide developing agent, of predetermined color associated therewith, each of said dyes soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable polymeric layer dyeable by said dyes, an alkaline solution permeable opaque layer positioned intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto, a dimensionally stable alkaline solution impermeable transparent layer, and an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are nondiffusible positioned intermediate said dimensionally stable transparent layer and the essential layer next adjacent thereto;

a dimensionally stable transparent sheet superposed coextensive the surface of the laminate opposite said dimensionally stable transparent layer; and

a rupturable container retaining an aqueous alkaline

processing solution containing an opacifying agent, having said first pH, fixedly positioned and extending transverse said leading edge of said laminate to effect unidirectional discharge of the container's contents coextensive the surface of the laminate intermediate said laminate and said transparent sheet.

8. A photographic film unit as defined in claim **7** wherein each of said selectively sensitized photosensitive silver halide emulsion layers has predominant spectral sensitivity to separate regions of the spectrum and subsequent to photoexposure of said laminate the dye associated with each of said silver halide emulsion layers posseses a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion layer.

9. A photographic film unit as defined in claim **7** which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive laminate containing, in sequence, a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye, a red-sensitive silver halide emulsion layer having associated therewith a cyan dye, each of said cyan, magenta and yellow dyes being silver halide developing agents and being soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable opaque layer, an alkaline solution permeable transparent polymeric layer dyeable by said dyes, an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are insoluble and nondiffusible, and a dimensionally stable alkaline solution impermeable transparent support;

a dimensionally stable transparent sheet fixedly maintained superposed substantially coextensive the surface of the laminate opposite said transparent support; and

a rupturable container retaining an aqueous alkaline processing solution, having said first pH and containing dispersed therein an opacifying agent, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of the container's contents intermediate said laminate and said opaque sheet upon application of compressive force to said container.

10. A photographic film unit as defined in claim **9** wherein said opaque layer is actinic radiation reflective.

11. A photographic film unit as defined in claim **9** wherein said opaque layer comprises at least two substantially separate strata wherein the stratum next adjacent the transparent support is actinic radiation reflective and the remaining strata are actinic radiation absorptive.

12. A photographic fim unit as defined in claim **11** wherein said reflecting layer comprises titanium dioxide dispersed in an alkaline solution permeable polymeric matrix.

13. A process of forming transfer images in color which comprises, in combination, the steps of:

(a) exposing a photographic film diffusion transfer color process unit which include, in combination:

a photosensitive laminate containing, as essential layers, a dimensionally stable transparent support carrying on one surface, in order, a dyeable polymeric layer, a processing composition permeable opaque layer, and a photo-sensitvie silver halide layer having associated therewith a dye image-forming material which is processing composition diffusible, as a function of the point-to-point degree of silver halide layer's exposure to actinic radiation;

a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the dimensionally stable transparent support; and

a rupturable container retaining a processing composition including an opacifying agent positioned extending transverse an edge of the film unit to effect unidirectional discharge of the container's contents intermediate the dimensionally stable sheet and the photosensitive laminate;

(b) contacting said exposed photosensitive silver halide emulsion layer with said processing composition;

(c) effecting thereby development of said photoexposed silver halide layer;

(d) forming thereby an imagewise distribution of mobile dye image-forming material, as a function of the point-to-point degree of said silver halide layer's exposure to incident actinic radiation;

(e) transferring, by diffusion, at least a portion of said imagewise distribution of mobile dye image-forming material to said polymeric layer dyeable by said dye image-forming material to provide a dye image thereto in terms of said imagewise distribution; and

(f) maintaining the laminate formed during processing intact subsequent to said processing.

14. A process of forming transfer images in color as defined in claim **13** which comprises, in combination, the steps of:

(a) exposing a photographic diffusion transfer color process film unit which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which includes, in combination:

a photosensitive laminate containing, as essential layers, a photosensitive silver halide emulsion layer having associated therewith dye image-providing material which is soluble and diffusible as a function of the point-to-point degree of silver halide emulsion exposure to incident actinic radiation, in alkali, at a first pH, an alkaline solution permeable polymeric layer dyeable by said image-providing material, an alkaline solution permeable opaque layer positioned intermediate said dyeable polymeric layer and said photosensitive silver halide emulsion layer and associated dye image-providing material, a dimensionally stable transparent layer, and an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to said second pH at which said dye image-providing material is substantially nondiffusably positioned intermeidate said dimensionally stable transparent layer and next adjacent essential layer;

a dimensionally stable transparent sheet superposed coextensive the surface of the laminate opposite the dimensionally stable transparent layer; and

a rupturable container retaining an aqueous alkaline processing solution containing an opacifying agent, having said first pH, fixedly positioned and extending transverse a leading edge of said photosensitive laminate to effect unidirectional discharge of the container's contents intermediate said dimensionally stable sheet and said laminate upon application of compressive force to said container, said exposure accomplished by radiation actinic to said film unit incident on said photosensitive silver halide emulsion layer;

(b) applying compressive force to said rupturable container to effect unidirectional discharge of the container's aqueous alkaline processing solution coex-

tensive the surface of said laminate intermediate said laminate and said dimensionally stable sheet;

(c) effecting thereby development of said silver halide emulsion;

(d) forming thereby an imagewise distribution of mobile dye image-providing material, as a function of the point-to-point degree of emulsion exposure;

(e) transferring, by diffusion, at least a portion of said imagewise distribution of mobile dye image-providing material to said alkaline solution permeable polymeric layer dyeable by said dye image-providing material to provide a dye image thereto in terms of said imagewise distribution;

(f) transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said alkaline solution to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said aqueous alkaline solution to said second pH; and

(g) maintaining the laminate formed during processing intact subsequent to said processing.

15. A process as defined in claim **14** including the step of separating said container from the laminate formed during processing subsequent to substantial transfer image formation.

16. A process as defined in claim **14** wherein said opaque layer is actinic radiation reflective.

17. A process as defined in claim **13** wherein said dye image-providing material is a dye which is a silver halide developing agent.

18. A process of forming transfer images in color as defined in claim **13** which comprises, in combination, the steps of:

(a) exposing a photographic diffusion transfer color process film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination:

a photosensitive laminate containing at least two selectively sensitized silver halide emulsion strata, each of said silver halide emulsions having associated therewith a dye, which is a silver halide developing agent, of predetermined color, and is soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable polymeric layer dyeable by said dye, an alkaline solution permeable opaque layer positioned intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto, a dimensionally stable transparent layer, and an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are substantially nondiffusible positioned intermediate said dimensionally stable transparent layer and the essential layer next adjacent thereto;

a dimensionally stable transparent sheet positioned on the surface of the laminate opposite said dimensionally stable transparent layer; and

a rupturable container retaining an aqueous alkaline processing solution containing an opacifying agent, having said first pH fixedly positioned and extending transverse a leading edge of said laminate to effect unidirectional discharge of the container's contents on the surface of said laminate distal said dimensionally stable transparent layer upon application of compressive force to said container;

(b) applying compressive force to said rupturable container to effect unidirectional discharge of the container's aqueous alkaline solution between said sheet and said laminate;

(c) effecting thereby development of each of said silver halide emulsions;

(d) immobilizing the dye associated with each of said emulsions as a result of development;

(e) forming an imagewise distribution of mobile dye, as a function of the point-to-point degree of emulsion exposure;

(f) transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to said alkaline solution permeable polymeric layer dyeable by said dyes to provide thereto a dye image;

(g) transferring, by imbibition, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline solution to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said solution to said second pH; and

(h) maintaining at least the laminate intact subsequent to processing.

19. A process of forming transfer images in color as defined in claim **18** which comprises, in combination, the steps of:

(a) exposing a photographic diffusion transfer color process film unit which is adapted to be processing by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination:

a photosensitive laminate containing, as essential layers, in sequence, a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye, a red-sensitive silver halide emulsion layer having associated therewith a cyan dye, each of said cyan, magenta and yellow dyes being silver halide developing agents and being soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable opaque layer, an alkaline solution permeable polymeric layer dyeable by each of said dyes, an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are insoluble and nondiffusible, and a second dimensionally stable alkaline solution impermeable transparent support layer;

a dimensionally stable transparent sheet fixedly positioned superposed on the surface of the laminate opposite said transparent support layer; and

a rupturable container retaining an aqueous alakline processing composition having said first pH and containing dispersed therein an opacifying agent fixedly positioned and extending transverse said leading edge of said elaminate to effect unidirectional discharge of the container's contents on the surface of said laminate intermediate said transparent sheet and said laminate upon application of compressive force to said container;

(b) applying compressive force to said rupturable container to effect unidirectional discharge of the container's alkaline solution intermediate said superposed transparent sheet and said laminate;

(c) effecting thereby development of the latent image contained in each of said silver halide emulsions;

(d) immobilizing said yellow, magenta and cyan dye, as a result of development of their respective associated silver halide emulsions;

(e) forming thereby an imagewise distribution of mobile yellow, magenta and cyan dye, as a function of the point-to-point degree of exposure of their respective associated silver halide emulsions;

(f) transferring, by diffusion, at least a portion of each of said imagewise distributions of mobile dye to said alkaline solution permeable polymeric layer dyeable

by said dyes to provide thereto a multicolor dye image;

(g) transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline solution to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said solution to said second pH; and

(h) maintaining the laminate intact subsequent to proccessing.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,594,165 Dated July 20, 1971

Inventor(s) Howard G. Rogers

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 22, "fabricating in a film unit" should be --fabricating a film unit--;

line 24, immediately following "are" insert "to be".

Column 14, line 48, "(7)" should be --(8)--.

Column 15, line 67, "processs" should be --process--.

Column 18, line 75, "and" should be --an--.

Column 21, line 57, "fim" should be --film--;

line 64, "include" should be --includes--.

Column 22, line 54, "fusably" should be --fusible--;

line 54, "intermeidate" should be --intermediate--.

Column 24, line 22, "processing" should be --processed--;

line 53, "elaminate" should be --laminate--.

Signed and sealed this 8th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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