

Aug. 3, 1971

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3,597,197

DIFFUSION TRANSFER COLOR PROCESS AND ELEMENT UTILIZING
A PROCESSING COMPOSITION COMPRISING A COALESCING

LATEX DISPERSION

4 Sheets-Sheet 1

Filed Oct. 20, 1969

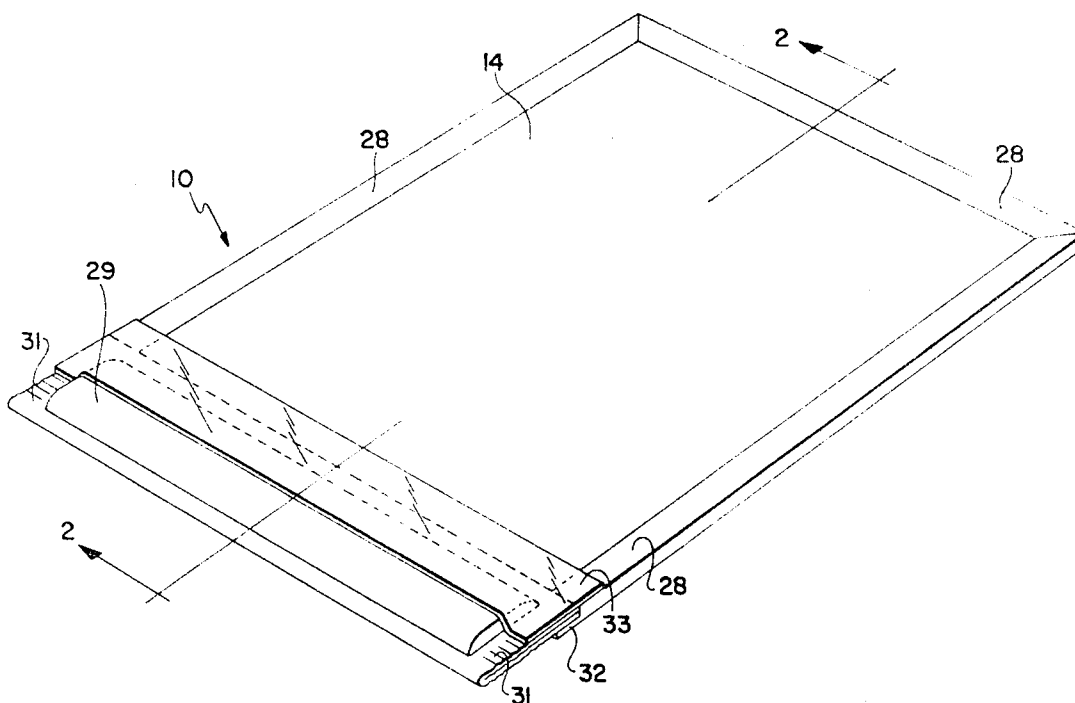


FIG. 1

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4 Sheets-Sheet 2

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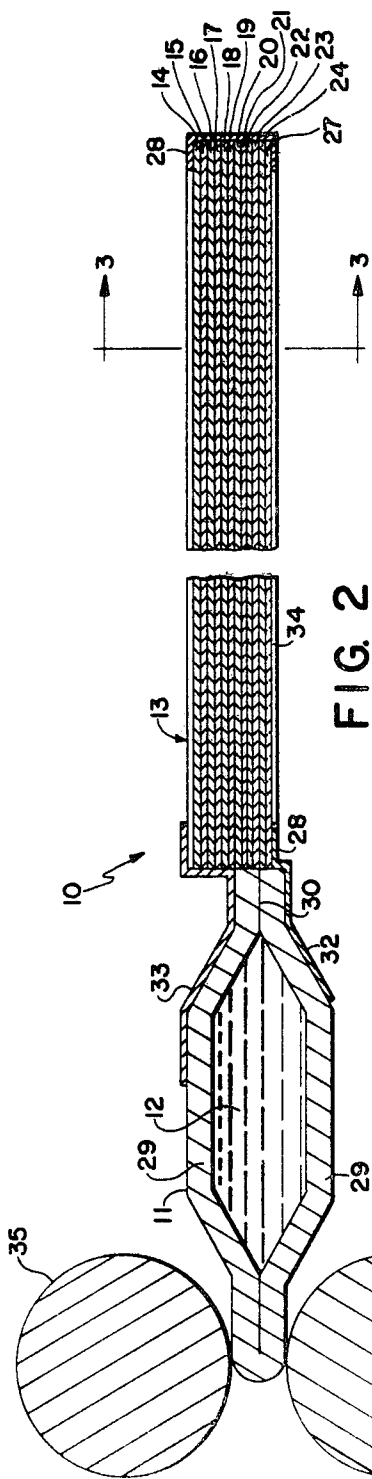


FIG. 2

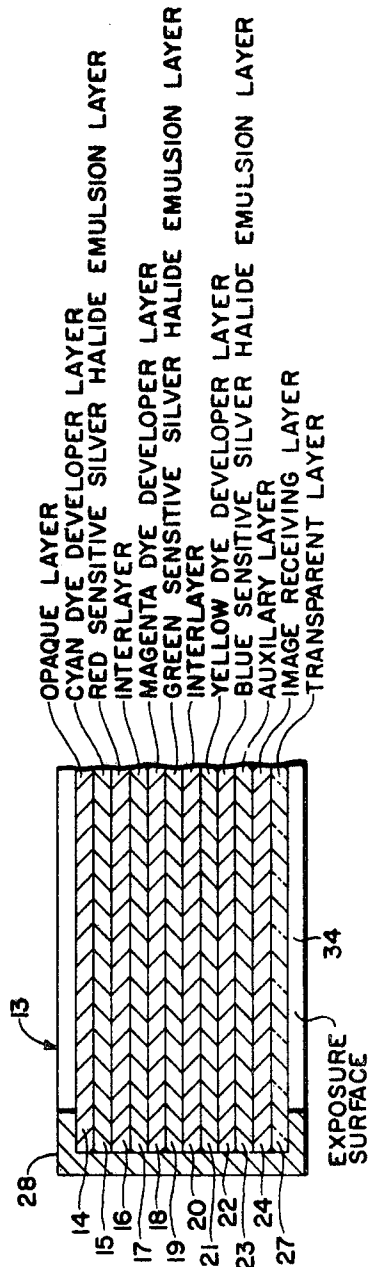


FIG. 3

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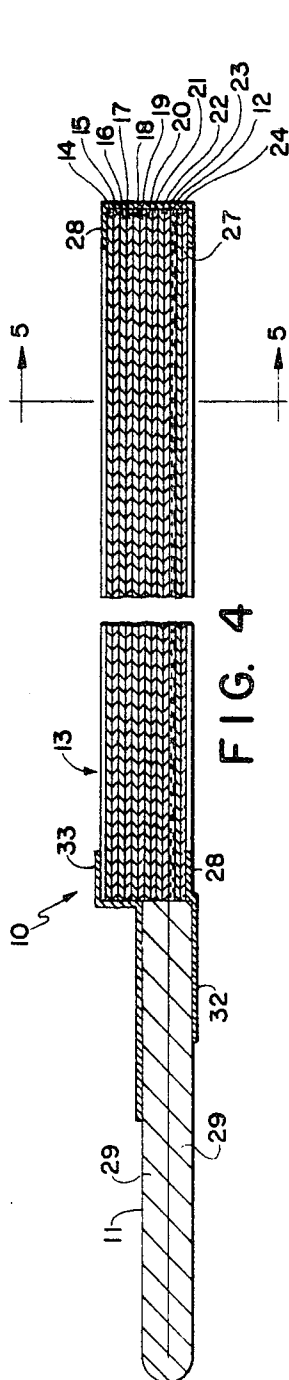


FIG. 4

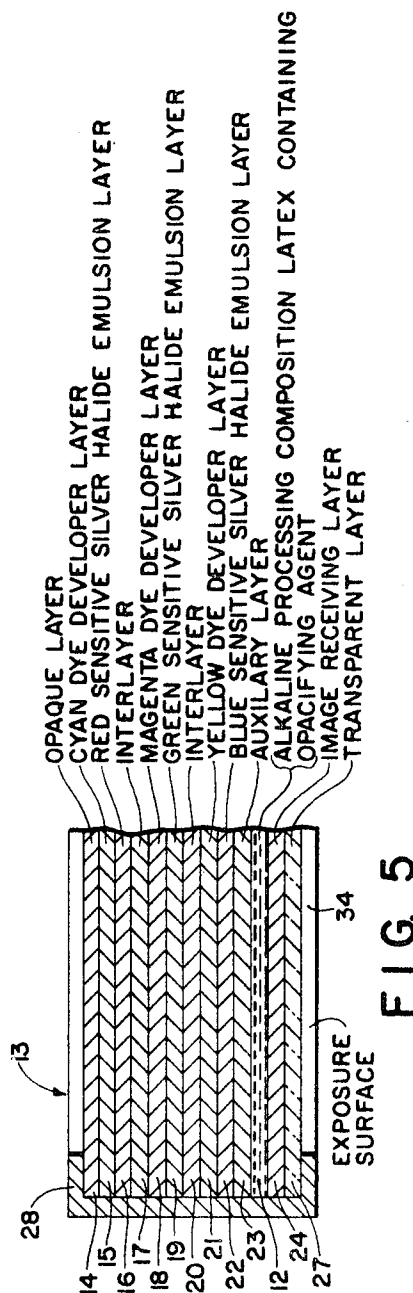


FIG. 5

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4 Sheets-Sheet 4

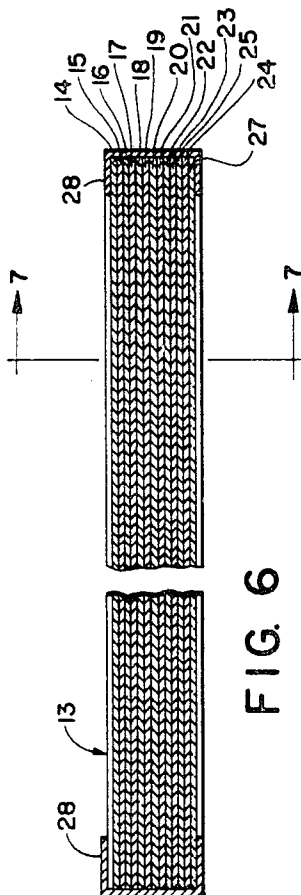


FIG. 6

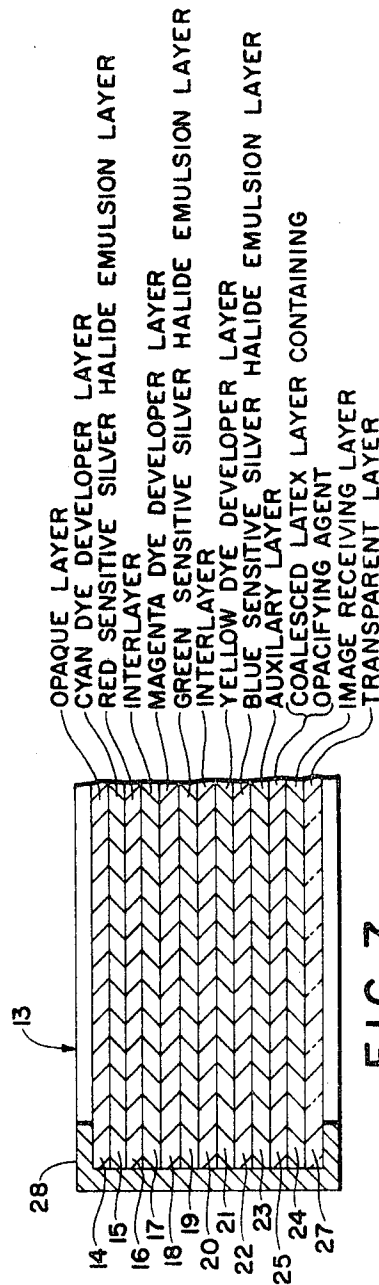


FIG. 7

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3,597,197

DIFFUSION TRANSFER COLOR PROCESS AND ELEMENT UTILIZING A PROCESSING COMPOSITION COMPRISING A COALESCING LATEX DISPERSION

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U.S. Cl. 96—3

44 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a composite photographic diffusion transfer process color film unit which includes rupturable container means retaining processing composition containing an insoluble polymeric dispersion adapted upon loss of processing composition solvent to coalesce at ambient temperatures for distribution between photosensitive and image receptive elements of the unit.

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

The primary objects of the present invention are to provide photographic products particularly adapted for employment in diffusion transfer color processes; to provide photographic products which comprise a photosensitive composite structure which contains a plurality of essential layers including a first dimensionally stable, liquid impermeable layer, a photosensitive silver halide emulsion layer having a dye image-forming material associated therewith which is soluble and diffusible at a first processing composition solvent concentration, a polymeric layer dyeable by the dye image-forming material, and a second dimensionally stable, liquid impermeable layer, transparent to incident radiation, in combination with a rupturable container retaining a processing composition containing dispersed therein a processing composition insoluble particulate polymeric dispersion adapted upon loss of processing composition solvent to coalesce at ambient temperatures fixedly positioned and extending transverse a leading edge of the composite photosensitive structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and photosensitive silver halide emulsion next adjacent thereto containing a quantity of the polymeric dispersion sufficient upon coalescence to provide a substantially continuous, diffusible dye image-forming material impermeable polymeric layer disposed intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent; to provide a diffusion transfer color film unit of the last-identified type including an opacifying agent disposed intermediate the dyeable polymeric layer and the photosensitive emulsion next adjacent thereto in a quantity sufficient to mask the dye image-forming material; to provide a diffusion transfer color film unit of the last-identified type processing the opacifying agent initially present in the processing composition for discharge intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent thereto upon application of compressive pressure to the container and distribution of its contents intermediate the layers; 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 a photographic film unit embodying 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 multi-color 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 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 depth-wise 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 benzenoid 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 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 ex-

ample, 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 diffusion transfer processes comprises an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

In accordance with aforementioned U.S. Pat. No. 2,983,606, an image-receiving layer of the type disclosed in that patent need not be separated from its superposed contact with the photosensitive element, subsequent to transfer image formation, if the image-receiving element is transparent and a processing composition containing a substance rendering the processing composition layer opaque is spread between the image-receiving layer and the silver halide emulsion or emulsions.

However, it has been found, if the image-receiving element is maintained in contact with the photosensitive element, subsequent to dye developer transfer image formation, and includes the presence of an alkaline processing composition, necessarily having a pH at which dye developer, for example, in reduced form, diffuses to form the dye transfer image, intermediate the elements, the transfer image thus formed is unstable over an extended period of time. The dye image instability is due, at least in part to the presence of what is, in general, a relatively high pH alkaline composition in intimate contact with the dye or dyes forming the image. This contact itself provides instability to the molecular structure of dye by, for example catalyzing degradation and undesirable structural shifts effecting the spectral absorption characteristics of the image dye. In addition, the presence of an alkaline composition, possessing a pH at which the dye, for example, in reduced form, diffuses, also provides an integral dynamic system wherein oxidized dye, immobilized in areas of the photosensitive element, as a function of its development, with the passage of time attempts to generate, in such areas, an equilibrium between oxidized and reduced dye. In that the pH of the dynamic system is such that diffusion of the reduced form of the dye will occur, such reduced dye will, at least in part, transfer to the image-receiving layer and the resultant diffusion will imbalance the equilibrium, in such areas of the photosensitive element, in favor of additional formation of reduced dye. As a function of the efficiency of the image-receiving layer, as a dye sink, such nonimagewise dyeing of the image-carrying layer still further imbalances the equilibrium in favor of the additional formation of dye in reduced, diffusible form. Under such circumstances, the transfer image definition, originally carried by the image-receiving layer, will suffer a continuous decrease in the delta between the image's maximum and minimum densities and may, ultimately, result in the image-receiving element's

loss of all semblance of image definition; merely becoming a polymeric stratum carrying a relatively uniform overall dyeing.

Any attempt to decrease the dye sink capacity of the image-carrying layer, for example, by reduction of its mordant capacity, in order to alleviate, at least to an extent, the action of the image-receiving layer as a dye sink, however, will enhance diffusion of the dye, comprising the transfer image, from the image-carrying layer, to the remainder of the element due, at least in part, to the continued presence of the alkaline composition having a pH at which the reduced form of the dye, forming the transfer image, is diffusible. The ultimate result is substantially the same overall image distortion as occurs when the image-receiving layer acts as a dye sink, with the exception that the dye is more extensively distributed throughout the film unit and the ultimate overall dyeing of the image-receiving layer itself is of lower saturation.

The problems inherent in fabricating a film unit of the type wherein the image-receiving element, the alkaline processing composition and the photosensitive element are maintained in contiguous contact subsequent to dye transfer image formation, for example, a film unit of the type described hereinbefore with reference to aforementioned U.S. Pat. No. 2,983,606, may be effectively obviated by fabrication of a film unit in accordance with the physical parameters specifically set forth in copending U.S. Pats. Nos. 3,415,644; 3,415,645; and 3,415,646, issued Dec. 10, 1969, respectively, in the name of Edwin H. Land.

Specifically an integral photographic film unit particularly adapted for the production of a dye transfer image of unexpectedly improved stability and other properties, by a color diffusion transfer process will be constructed, for example, in accordance with aforementioned U.S. Pat. No. 3,415,644, to include a photosensitive element comprising a laminate having, in sequence, as essential layers, a dimensionally stable opaque layer; a photosensitive silver halide emulsion layer having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH; an alkaline solution permeable polymeric layer dyeable by the dye image-providing material; a polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial transfer dye image formation, of a selected processing solution having the first pH to a second pH at which said dye image-providing material is insoluble and nondiffusible; and a dimensionally stable transparent layer. In combination with the laminate, a rupturable containing retaining an aqueous alkaline processing composition having the first pH and containing an opacifying agent, in a quantity sufficient to mask the dye image-providing material, is fixedly positioned and extends transverse a leading edge of the laminate whereby to effect unidirectional discharge of the container's contents between the alkaline solution permeable and dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto, upon application of compressive force to the container.

It will also be recognized that the dimensionally stable polymeric support layer next adjacent the photosensitive silver halide emulsion layer or layers may be transparent, as disclosed in aforementioned U.S. Pat. No. 3,415,646, and that in such instance the opacifying agent may be initially dispersed in the composite film unit intermediate the dyeable polymeric layer and the silver halide emulsion layer next adjacent, as disclosed in aforementioned U.S. Pat. No. 3,415,645.

Employment of the last-mentioned film units, according to the described color diffusion transfer photographic process, specifically provides for the production of a highly stable color transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by 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 inoperative

subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during exposure, processing, viewing, and storage of the unit, which transfer image exhibits the required maximum and minimum dye transfer image densities, dye saturation, hues and definition.

However, film units fabricated in accordance with the parameters set forth above specifically require the presence of the stated polymeric acid component to effect in situ process adjustment of the film units' operational pH range.

Specifically, the film units require the presence of a polymeric acid layer such as, for example, of the type set forth in U.S. Pat. No. 3,362,819 which, most preferably, includes the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the image-receiving layer.

As set forth in the last-mentioned patent, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such 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. The acid-reacting group is, of course, nondiffusible from the acid polymer layer. 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 or 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 methylvinyl ether/maleic anhydride copolymers; etc.

As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14. The acid 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 12 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, thus requiring, of course, that the action of the polymeric acid be accurately 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 must be kept at a functional transfer level, for example, 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to a pH below that at which dye transfer may be accomplished, for example, at least about 11 and

preferably about pH 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, for example, 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.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the acid polymer layer that the rate of their 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 groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the 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 there disclosed that the layer containing the polymeric acid 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 polymer 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 are employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the last-mentioned patent, 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 is there 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.

It has now been quite unexpectedly discovered that the problems inherent in fabricating a film unit of the type where the image-receiving element, the alkali processing composition and the photosensitive element are maintained in contiguous contact during processing and subsequent to dye transfer image formation, for example, a film unit of the type described, with reference to aforementioned U.S. Pat. No. 2,983,606, may be effectively obviated in a considerably simplified manner by fabrication of a film unit in accordance with the physical parameters detailed below.

Specifically, it has been quite unexpectedly discovered that an integral photographic film unit of simplified construction and particularly adapted for the production of dye transfer images of unexpectedly improved stability and other desirable properties by a color diffusion transfer process will be constructed to include a photosensitive element comprising a composite structure possessing, in sequence, as essential layers, a first dimensionally stable layer, a photosensitive silver halide emulsion layer hav-

ing associated therewith a dye image-forming material which is soluble and diffusible as a function of the point-to-point degree of emulsion photoexposure, a polymeric layer dyeable by the dye image-forming material, and a second dimensionally stable layer transparent to incident actinic radiation. In combination with the composite structure, a rupturable container retaining a processing composition containing a particulate dispersion of processing composition insoluble polymer, as a discontinuous phase, which is adapted in the absence of processing composition solvent, the continuous phase, to coalesce at ambient temperature, is fixedly positioned and extends transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion and associated dye image-forming material next adjacent, in a quantity sufficient upon loss of processing composition solvent to provide a substantially continuous, dye image-forming material impermeable polymeric layer, upon coalescence of processing composition retained polymeric dispersion, intermediate the dyeable polymeric layer and next adjacent photosensitive silver halide emulsion. Although both dimensionally stable layers may be transparent and in such instance, an opacifying agent may be initially dispersed intermediate the dyeable polymeric layer and the next adjacent silver halide emulsion layer, in a quantity sufficient to mask the dye image-forming material, such opacifying agent will preferably be disposed within the processing composition, in a quantity sufficient to mask the dye image-forming material upon distribution of the processing composition intermediate the last-stated layers, and, most preferably, the dimensionally stable layer next adjacent the photosensitive silver halide emulsion layer will be opaque with respect to externally derived incident actinic radiation.

In view of the fact that the preferred dye image-providing materials comprise dyes which are silver halide developing agents, as stated above, for purposes of simplicity and clarity, the present invention will be further described hereinafter in terms of such dyes, without limitation of the invention to the illustrative dyes denoted, and, in addition, the photographic film unit structure will be detailed hereinafter employing the last-mentioned preferred structural embodiment, without limitation of the invention to the preferred structure denoted.

In a preferred embodiment of the present invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, the dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsion strata each having dye image-providing materials of predetermined color associated therewith which are soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective associated silver halide emulsion strata; an alkaline solution permeable polymeric layer dyeable by the dye image-providing materials; 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 a selected pH possessing subsequent to processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

In the preferred embodiment, each of the emulsion strata, and its associated dye, is separated from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers.

In such preferred embodiment 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 is dispersed in an aqueous alkaline solution 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 dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; and each of the dimensionally stable opaque and transparent layers are alkaline solution impermeable, most preferably processing composition vapor permeable 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 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 cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable opaque layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the opaque layer and the 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.

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 members, 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, and photosensitive laminate 13 including, in order, dimensionally stable opaque layer 14, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer 15; red-sensitive silver halide emulsion layer 16; interlayer 17; magenta dye developer layer 18; green-sensitive silver halide emulsion layer 19; interlayer 20; yellow dye developer layer 21; blue-sensitive silver halide emulsion layer 22; auxiliary layer 23, which may contain an auxiliary silver halide developing agent; image-receiving layer 24; and dimensionally stable transparent layer 27, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of laminate 13 may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the laminate at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer 24 and the silver halide emulsion layer next adjacent thereto, for example, intermediate image-receiving layer 24 and auxiliary layer 23 as illustrated in FIGS. 2 through 7, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the laminate, in order to facilitate distribution of processing solution 12 intermediate the stated image-receiving layer 24 and the silver halide emulsion layer next adjacent thereto. The laminate's structural integrity may also be enhanced or provided, in whole or in part, by providing a binding member extending around, for example, the edges of laminate 13, and maintaining the layers comprising the laminate intact, except at the interface between layers 23 and 24 during distribution of alkaline solution 12 intermediate those layers. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape 28 securing and or maintaining the layers of laminate 13 together at its respective edges.

Tape 28 will also act to maintain processing solution 12 intermediate image-receiving layer 24 and the silver emulsion layer next adjacent thereto, upon application of compressive pressure to pod 11 and distribution of its contents intermediate the stated layers. Under such circumstances, binder tape 28 will act to prevent leakage of fluid processing composition from the film unit's laminate 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; 3,056,492; 3,056,491; 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 29 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 30 is made weaker than the end seals 31 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 29 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 between image-receiving layer 24 and the stated layer next adjacent thereto, 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 30 directed toward the interface between image-receiving layer 24 and auxiliary layer 23. As shown in FIGS. 1, 2 and 4, container 11 is fixedly secured to laminate 13 by extension 32 of tape 28 extending over a portion of one wall 29 of the container, in combination with a separate retaining member such as illustrated retaining tape 33 extending over a portion of the other wall 29 of the container and a portion of laminate 13's surface generally equal in area to about that covered by tape 28.

As illustrated in FIG. 6, extension flap 32 of tape 28 is preferably of such area and dimensions that upon, for example, manual separation of container 11 and tape 33, subsequent to distribution of processing composition 12, from the remainder of film unit 10, flap 32 may be folded over the edge of laminate 13, previously covered by tape 33, 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 27.

The fluid contents of the container comprise an aqueous alkaline solution, having a pH and solvent concentration at which the dye developers are soluble and diffusible, which contains an opacifying agent in a quantity sufficient to mask the dye developers associated with the silver halide emulsions subsequent to processing and additionally contains a processing composition insoluble polymeric dispersion adapted upon loss of processing composition solvent to coalesce at ambient temperatures to provide a substantially continuous, dye impermeable polymeric layer.

In general, in a preferred embodiment the concentration of opacifying agent or agents selected will be that sufficient to prevent further exposure of the film unit's silver halide emulsion or emulsions, by actinic radiation traversing through the dimensionally stable transparent layer, subsequent to distribution of the processing solution intermediate the dyeable polymeric layer and the stated layer next adjacent thereto. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions or the laminate are appropriately protected by incident radiation, at one major surface by the opaque processing composi-

tion and at the remaining major surface by the dimensionally stable opaque layer. If the illustrated binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The selected opacifying agent, 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 opacifying agent may be employed, it is preferred that an opacifying agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent 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 opacifying agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially, those agents possessing the optical properties desired for reflection of incident radiation.

As examples of opacifying agents, mention may be made of barium sulfate, zinc oxide, titanium oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

A particularly preferred agent comprises titanium dioxide due to its highly effective reflection properties. In general, based upon percent titanium dioxide (weight volume), a processing composition containing about 40–70 grams of titanium dioxide dispersed in 100 cc. of water will provide a percent reflectance of about 85–90%. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of above 85%.

Where it is desired to increase the radiation filtering capacity of a processing composition containing, for example, titanium dioxide or the like, selected predominantly for its radiation reflecting properties, beyond that ordinarily obtained or required to obscure or mask the dye and/or developed silver associated with the photosensitive silver halide emulsion layers, it may also be desirable to provide an additional opacifying agent, exhibiting more effective filtration of radiation incident on the transparent support layer during processing, such as carbon black, for example, added in a concentration of about one part carbon black to 100 to 500 parts titanium dioxide, in order to further protect the emulsions from physical fog formation during processing.

In general, the concentration of processing composition insoluble polymeric dispersion retained in the processing composition will be that sufficient to provide, upon coalescence at ambient temperatures and decrease of processing composition solvent, a substantially continuous, dye developer impermeable polymeric layer, subsequent to distribution of the processing composition between the dyeable polymeric layer and the stated layer next adjacent thereto.

As examples of processing composition insoluble polymeric materials particularly adapted for dispersion in a preselected processing composition and which will coalesce upon loss of processing composition solvent to provide a film at ambient temperatures, mention may be made of the various polymeric solid and liquid materials which provide a latex when dispersed in a solvent in which they are insoluble and stable and, particularly when dispersed in water possessing a preselected pH, known in the art to coalesce at ambient temperatures and at relatively rapid rates upon loss of dispersant solvent to provide relatively impermeable substantially continuous films or polymeric layers including butadiene/styrene copolymers; polyacrylamides; polymethylmethacrylates; polyvinyl chlorides and copolymers thereof; polyvinyl acetates and copolymers thereof; acrylonitrile/ethyl acrylate copolymers; acrylonitrile/styrene/butadiene terpolymers; and the like.

In general, the polymeric dispersion discontinuous

phase dispersed in an aqueous continuous phase will comprise a concentration of polymer particles adapted to provide a substantially continuous film approximately 5 to 30 microns in thickness upon coalescence subsequent to distribution and transpiration of processing composition solvent water content. For a substantially continuous layer possessing the general dimensions of approximately 4 inches x 5 inches x 20 microns, such concentration will ordinarily be within the range of about 5 to 40 grams of particulate polymer/100 cc. of processing composition water content dependent upon specific polymer selected. Upon coalescence, the substantially continuous polymeric layer may contain entrained or entrapped therein one or more of the components, adjuvants or agents originally retained by the processing composition or the like, such as opacifying agent initially distributed in the processing composition in the preferred film unit embodiments detailed above.

In particularly preferred embodiments of the present invention, the substantially continuous polymeric film provided upon coalescence, in addition to being impermeable to solubilized dye developer, will also be substantially impermeable to solubilized photographic adjuncts, present within the film unit, in general and more particularly those possessing physical dimensions, for example, molecular size, less than that of dye developer such as, for example, antifoggants, development restrainers, quaternary accelerators, emulsion stabilizers and sensitizers, and the like, in order to still further enhance maintenance of dye transfer image stability and acuity.

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 35 in order to apply compressive pressure to frangible container 11 and to effect rupture of longitudinal seal 30 and distribution of alkaline processing composition 12, having a pH and solvent concentration at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer 24 and auxiliary layer 23.

Alkaline processing solution 12 permeates emulsion layers 16, 19 and 22 to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers 15, 18 and 21, 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 non-diffusible 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 transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer 24 to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the solvent comprising aqueous alkaline solution 12 transfers, by osmotic diffusion, through vapor permeable, liquid impermeable polymeric layers 14 and 27 whereby alkaline solution 12 decreases in solvent concentration, as a function of diffusion and transpiration, to a solvent concentration at which the processing composition insoluble polymeric dispersed phase coalesces to provide a substantially continuous dye developer impermeable polymeric layer 25 to provide thereby a stable multicolor dye transfer image.

Subsequent to distribution of processing solution 12, container 11 may be manually dissociated from the remainder of the film unit, as described above, to provide the product illustrated in FIG. 6.

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 therein set forth and are intended to be illustrative only.

Film units similar to that shown in the drawings may be prepared, for example, by coating, in succession, on a gelatin subbed, 4 mil opaque polyethylene terephthalate film base, the following layers:

(1) A layer of the cyan dye developer 1,4-bis-(β -[hydroquinonyl- α -methyl] - ethylamino)-5,8-dihydroxy - anthraquinone dispersed in gelatin and coated at a coverage of about 150 mgs./ft.² of dye and about 200 mgs./ft.² of gelatin;

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 200 mgs./ft.² of silver and about 100 mgs./ft.² of gelatin;

(3) A layer of gelatin coated at a coverage of about 200 mgs./ft.²;

(4) A layer of the magenta dye developer 2-(p-[β -hydroquinonyl-ethyl] - phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of 70 mgs./ft.² of dye and about 100 mgs./ft.² of gelatin.

(5) A green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 100 mgs./ft.² of silver and 60 mgs./ft.² of gelatin;

(6) A layer containing 4'-methylphenyl hydroquinone dispersed in gelatin and coated at coverage of about 25 mgs./ft.² of 4'-methylphenyl hydroquinone and about 150 mgs./ft.² of gelatin;

(7) 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 40 mgs./ft.² of dye and 50 mgs./ft.² of gelatin;

(8) A blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 60 mgs./ft.² of silver and about 50 mgs./ft.² of gelatin; and

(9) A layer of gelatin coated at a coverage of about 30 mgs./ft.² of gelatin.

Then a transparent 4 mil. polyethylene terephthalate film base may be coated, in succession, with the following illustrative layers:

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

(2) A 2:1 solution of hydroxypropyl cellulose and polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.25 mil. thick; and

(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.

The two components thus prepared may then be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant laminate.

A rupturable container comprising an outer 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 grams.

Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250]: 3.4 grams.

N-benzyl- α -picolinium bromide: 1.5 grams.

Benzotriazole: 1.0 gram.

Titanium dioxide: 50.0 grams.

Carboxylated (<5% COOH) styrene/butadiene copolymer [commercially available from W. R. Grace Co., New York, N.Y., under the trade name Darex 526-L]: 20.0 grams.

may then be fixedly mounted on the leading edge, of each of the laminates, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that upon application of compressive pressure to a container its contents would be distributed, upon rupture of the container's marginal seal, between layer 9 and the polymeric image-receiving layer.

The photosensitive laminates may then be exposed through step wedges to selectively filtered radiation incident on the transparent polyethylene terephthalate layer and initially processed, in the absence of actinic radiation, by passage of the exposed film unit through suitably gapped opposed rolls, to effect rupture of the container and distribution of its contents. The multicolor dye transfer image formation may be viewed through the transparent polyethylene terephthalate film base and such image formation is found to be substantially completed and exhibiting the required color brilliance, hues, saturation, stability and isolation, within a period of approximately 2 minutes.

The pH and solvent concentration of the processing solution initially employed must be a pH at which the dye developers employed are soluble and diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer, or groups of dye developers, most particularly desirable dye developers are soluble at pH's above 9 and relatively insoluble at substantially any alkaline pH, in oxidized 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 facilitate maintenance of the spread composition as a structurally stable layer of the laminate, during distribution, it is not necessary that such agent be employed as a component of the composition.

Where desired, a polymeric acid layer, for example, of the type discussed above, may be additionally incorporated, as stated, in the film unit of the present invention, to provide reduction of the alkalinity of the processing solution from a pH at which the dyes are soluble to a pH at which the dyes are substantially nondiffusible, in order to advantageously further stabilize the dye transfer image. In such instance, the polymeric acid layer may be positioned intermediate the transparent support and image-receiving layer, and/or the opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

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 effected 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 copending U.S. Patent application Ser. No. 664,503, filed Aug. 30, 1967 and now U.S. Pat. No. 3,455,686 in the names of Leonard C. Farney, Howard G. Rogers and Richard W. Young, 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 effected 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 diffusion barrier time-wise preventing 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 the last-mentioned copending application Ser. No. 664,503 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 oxazolidone, 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 hydroxy 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.

Employment of the detailed and preferred film units of the present invention, according to the herein described color diffusion transfer process, specifically provides for the production of a highly stable dye transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by in situ generation of a substantially continuous, dye image-forming material impermeable polymeric layer or stratum intermediate the dye image-carrying layer and the photosensitive silver halide emulsion and associated dye image-forming material layers of the film unit, subsequent to substantial dye transfer image formation. The stable dye transfer image is obtained irrespective of the fact that the film unit is maintained as

an integral laminate unit during exposure, processing, viewing and storage of the unit, and undesired dye image-forming material transfer, of the type previously discussed in detail, subsequent to substantial dye transfer image formation, is effectively prevented by the in situ generated physical barrier polymeric layer. Accordingly, by means of the present invention, multicolor dye transfer images may be provided which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation. 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.

The dimensionally stable support layers referred to may comprise any of the various types of conventional opaque and transparent rigid or flexible materials possessing the requisite liquid impermeability and vapor transmissivity denoted above, and may comprise polymeric films of both synthetic types and those derived from naturally occurring products. Particularly suitable materials include aqueous alkaline solution impermeable, water vapor permeable, flexible polymeric materials such as vapor permeable polymeric films derived from ethylene glycol terephthalic acid, vinyl chloride polymers; polyvinyl acetate; polyamides; polymethacrylic acid methyl and ethyl esters; cellulose derivatives such as cellulose, acetate, triacetate, nitrate, propionate, butyrate acetate-propionate, or acetate-butyrate; alkaline solution impermeable, water vapor permeable papers; crosslinked polyvinyl alcohol; regenerated cellulose; and the like.

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-benzylaminophenyl, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, 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 quaternary 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 op-

erator. 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 and solvent concentration require. 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.

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. An examples of additional U.S. patents detailing 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 nitro-carboxymethyl 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 vinylphthalimide 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 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 dye image-providing materials, it will be readily recognized that other, less preferred, dye 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, issued July 28, 1953; 2,666,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,788, issued Jan. 4, 1955; and 2,802,735, issued Aug. 13, 1957, 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 formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. No. 2,774,668, issued Dec. 18, 1956, 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.

For the production of the photosensitive gelatin 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 dispersion to remove undesirable reaction products and residual 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 or silver iodobromide, of varying halide ratios and varying silver concentrations.

The emulsions may include the various adjuncts, or addenda, according to the techniques disclosed in the art.

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, re-

placed with some other colloidal material such as albumin; casein; or zein; or resins such as cellulose derivatives, as described in U.S. Pats. Nos. 2,322,085, and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; 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 tri-pack 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, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will 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, a cyan, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye developer and the use of a mixture of dye developers adapted to provide a black and white transfer image, for example, the employment of dye developers of the three subtractive 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.

It will be recognized that, by reason of the preferred film unit's structural parameters, the transfer image formed upon direct exposure of the film unit to a selected subject and processing, will be a geometrically reversed image of the subject. Accordingly, to provide transfer image formation geometrically nonreversed, exposure of such film unit should be accomplished through an image reversing optical system such as a camera possessing an image reversing optical system.

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 same, or different, components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

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 photographic film unit 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 element comprising a composite structure containing, as essential layers, in sequence, a first dimensionally stable layer opaque to incident actinic radiation; a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is processing composition soluble and diffusible as a function of exposure of the photosensitive silver halide emulsion layer to incident actinic radiation; a polymeric layer dyeable by said dye image-providing material; a second dimensionally stable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining a processing composition containing an opacifying agent in a quantity sufficient to mask said dye image-providing material and a processing composition insoluble polymeric dispersion adapted upon loss of processing composition solvent to coalesce at ambient temperatures, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto, said polymeric dispersion present in a quantity sufficient upon coalescence to provide a dye image-forming material impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

2. A photographic film unit as defined in claim 1 wherein said first dimensionally stable layer is transparent to incident actinic radiation.

3. A photographic film unit as defined in claim 2 wherein said opacifying agent is initially present intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto in a quantity sufficient to mask said dye image-providing material.

4. A photographic film unit as defined in claim 1 wherein said composition is an aqueous alkaline composition.

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

6. A photographic film unit as defined in claim 1 wherein said opacifying agent is present in a quantity sufficient to prevent exposure of said silver halide emulsion during processing in the presence of radiation actinic thereto and incident on said distributed processing solution.

7. A photographic film unit as defined in claim 1 wherein said opacifying agent is actinic radiation reflective.

8. A photographic film unit as defined in claim 7 wherein said opacifying agent is titanium dioxide.

9. A photographic film unit as defined in claim 5 wherein said photosensitive element comprises 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 alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

10. A photographic film unit as defined in claim 9 wherein each of said selectively sensitized photosensitive silver halide emulsions has predominant spectral sensitivity to separate regions of the spectrum and the dye associ-

ated with each of said silver halide emulsion layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion layer.

11. A photographic film unit as defined in claim 10 wherein each of said silver halide emulsion layers and its associated dye is separated from the next adjacent silver halide emulsion layer and its associated dye by an alkaline solution permeable polymeric interlayer.

12. A photographic film unit as defined in claim 5 including at least one polymeric acid layer positioned intermediate at least one of said first dimensionally stable layers and the photosensitive silver halide emulsion layer next adjacent thereto, and said second dimensionally stable layer and the dyeable polymeric layer next adjacent thereto.

13. A photographic film unit as defined in claim 12 wherein said polymeric acidic layer contains sufficient acidifying groups to effect reduction of said processing composition from a first pH at which said dye is substantially soluble and diffusible to a second pH at which said dye is substantially nondiffusible.

14. A photographic film unit as defined in claim 5 wherein said processing composition insoluble polymeric dispersion comprises carboxylated styrene/butadiene copolymer.

15. A photographic film unit as defined in claim 14 wherein said processing composition insoluble polymeric dispersion is present in a quantity sufficient to provide upon distribution intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto and coalescence upon loss of dispersant solvent a dye impermeable polymeric layer within the range of about 5 to 30 microns in thickness.

16. A photographic film unit as defined in claim 15 wherein said processing composition insoluble polymeric dispersion is present in a concentration of about 5 to 40 g. of polymer/100 cc. of processing composition water.

17. A photographic film unit as defined in claim 10 which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination, a composite structure containing, as essential layers, in sequence, a dimensionally stable, liquid impermeable opaque layer; an alkaline solution permeable polymeric layer containing cyan dye; a red-sensitive silver halide emulsion layer; an alkaline solution permeable polymeric layer containing magenta dye; a green-sensitive silver halide emulsion layer; an alkaline solution permeable polymeric layer containing yellow dye; a blue-sensitive silver halide emulsion layer, each of said cyan, magenta and yellow dyes being silver halide developing agents and being soluble and diffusible, in an aqueous alkaline solution at a first pH; an alkaline solution permeable transparent polymeric layer dyeable by said dyes; an alkaline solution permeable transparent polymeric acidic 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; a dimensionally stable, liquid impermeable transparent layer; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition possessing said first pH and an opacifying agent in a quantity sufficient to mask said dyes and a processing composition insoluble particulate polymeric dispersion adapted upon transpiration of processing composition water content to coalesce at ambient temperatures, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer upon application of compressive forces to said container, said polymeric dispersion present in a quantity sufficient upon coalescence

to provide a substantially continuous dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer.

18. A photographic film unit as defined in claim 17 wherein said first pH is above 9 and said second pH is below 9.

19. A photographic film unit as defined in claim 18 wherein said opacifying agent is actinic radiation reflective.

20. A photographic film unit as defined in claim 19 wherein said opacifying agent is titanium dioxide.

21. A photographic film unit as defined in claim 20 wherein said processing composition insoluble polymeric dispersion comprises carboxylated styrene-butadiene copolymer.

22. A photographic film unit as defined in claim 21 wherein said processing composition insoluble polymeric dispersion is present in a concentration of about 5 to 40 g. of polymer/100 cc. of processing composition water.

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

(a) exposing a photographic 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 composite structure comprising a first dimensionally stable layer opaque to incident actinic radiation; a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is processing composition soluble and diffusible as a function of exposure of the photosensitive silver halide emulsion layer to incident actinic radiation; a polymeric layer dyeable by said dye image-providing material; a second dimensionally stable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining a processing composition containing an opacifying agent in a quantity sufficient to mask said dye image-providing material and a processing composition insoluble polymeric dispersion adapted upon loss of processing composition solvent to coalesce at ambient temperatures, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to said container, said polymeric dispersion present in a quantity sufficient upon coalescence to provide a dye image-forming material impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent thereto;

(b) applying compressive force to said rupturable container to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;

(c) effecting thereby development of said silver halide emulsion and forming, as a result of said development, an imagewise distribution of mobile dye image-providing material as a function of the point-to-point degree of emulsion exposure;

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

(e) transferring, by osmotic transpiration of processing composition solvent from said composite structure, subsequent to substantial dye transfer image formation and preceding substantial environmental dye transfer image degradation, a sufficient portion of the

solvent of said processing composition to thereby reduce said solvent concentration intermediate said dyeable polymeric layer and said silver halide emulsion layer next adjacent to a concentration at which said processing composition insoluble polymeric dispersion coalesces at ambient temperatures;

(f) coalescing said processing composition insoluble polymeric dispersion as a result of said osmotic transpiration of processing composition solvent;

(g) forming thereby a dye image-forming material impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the silver halide emulsion next adjacent thereto; and

(h) maintaining said composite structure intact subsequent to said processing.

24. A process as defined in claim 23 wherein said first dimensionally stable layer is transparent to actinic radiation.

25. A process as defined in claim 24 wherein said opacifying agent is initially present intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

26. A process as defined in claim 23 wherein said solvent is water.

27. A process as defined in claim 26 wherein said dye image-providing material is a dye which is a silver halide developing agent.

28. A process as defined in claim 27 wherein said opacifying agent is present in a quantity sufficient to prevent exposure of said silver halide emulsion during processing in the presence of radiation actinic thereto and incident on said processing solution distributed between said dyeable polymeric layer and said silver halide emulsion layer next adjacent thereto.

29. A process as defined in claim 27 wherein said opacifying agent is actinic radiation reflective.

30. A process as defined in claim 29 wherein said opacifying agent is titanium dioxide.

31. A process as defined in claim 26 wherein said processing composition insoluble polymeric dispersion comprises carboxylated styrene/butadiene copolymer.

32. A process as defined in claim 26 wherein said processing composition insoluble polymeric dispersion is present in a quantity sufficient to provide upon distribution intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto and coalesces a dye image-forming material polymeric layer possessing a thickness within the range of about 5 to 30 microns.

33. A process as defined in claim 32 wherein said processing composition insoluble polymeric dispersion is present in a concentration of about 5 to 40 g. of polymer/100 cc. of processing composition water.

34. A process as defined in claim 23 including the step of separating said container from said composite structure subsequent to substantial transfer image formation.

35. A process as defined in claim 27 which comprises, in combination, the steps of:

(a) exposing a photographic film unit which is adapted to be processed by passage through a pair of juxtaposed pressure-applying members and which includes in combination, a composite structure comprising a first dimensionally stable, liquid impermeable layer opaque to incident actinic radiation at least two selectively sensitized silver halide emulsion layers, 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 aqueous alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsions associated therewith; a polymeric layer dyeable by said dye; a second dimensionally stable, liquid impermeable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition containing an opacifying agent in a quantity sufficient to mask said dyes and an aqueous alkaline processing composition insoluble polymeric dispersion adapted upon loss of processing composition water content to coalesce at ambient temperatures, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect discharge of said container's aqueous alkaline processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to said container, said polymeric dispersion present in a quantity sufficient upon coalescence to provide a dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;

(b) applying compressive force to said rupturable container to effect discharge of said container's aqueous alkaline processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;

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

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

(e) forming thereby 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 dyes to said polymeric layer dyeable by said dyes to provide thereto a dye image;

(g) transferring, by osmotic transmission of aqueous alkaline processing composition solvent from said composite structure, subsequent to substantial dye transfer image formation and preceding said substantial environmental dye transfer image degradation, a sufficient portion of the aqueous solvent of said aqueous alkaline processing composition to thereby reduce said solvent concentration intermediate said dyeable polymeric layer and said silver halide emulsion layer next adjacent to a concentration at which said aqueous alkaline processing composition insoluble polymeric dispersion coalesces at ambient temperatures;

(h) coalescing said aqueous alkaline processing composition insoluble polymeric dispersion as a result of said osmotic transpiration of aqueous solvent;

(i) forming thereby a dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the silver halide emulsion next adjacent thereto; and

(j) maintaining said composite structure intact subsequent to said processing.

36. A process as defined in claim 35 wherein each of said selectively sensitized silver halide emulsion layers possess predominant spectral sensitivity to a separate region of the spectrum and the dye associated with each of said emulsion layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion.

37. A process as defined in claim 36 wherein said composite structure includes at least one polymeric acid layer positioned intermediate at least one of said first dimensionally stable layers and the next adjacent photosensitive silver halide layer, and said second dimensionally stable layer and the next adjacent dyeable polymeric layer and said polymeric acid layers containing sufficient acidifying groups to effect reduction of an aqueous alkaline processing composition possessing a first pH at which said dyes are substantially soluble and diffusible to a second pH at which said dyes are substantially nondif-

fusible and including the step of transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said alkaline processing solution to said polymeric acid layers to thereby reduce the alkalinity of said solution from said first pH to said second pH.

38. A process of forming transfer images in color as defined in claim 37 which comprises, in combination, the steps of:

- (a) exposing a photographic 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 element comprising a laminate containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye; each of said cyan, magenta and yellow dyes being silver halide developing agents and soluble and diffusible in aqueous alkaline solution at a first pH; 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 an alkaline processing solution having said first pH to a second pH at which said dyes are substantially insoluble and nondiffusible; a dimensionally stable, alkaline solution impermeable transparent layer; and

a rupturable container retaining an aqueous alkaline processing solution possessing said first pH, an opacifying agent in a quantity sufficient to mask said dyes and an aqueous alkaline solution insoluble particulate polymeric dispersion adapted upon loss of processing solution water to coalesce at ambient temperatures, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing solution between said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer upon application of compressive force to said container, said exposure effected by actinic radiation incident on said dimensionally stable transparent layer, said polymeric dispersion present in a quantity sufficient upon coalescence to provide a substantially continuous dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer;

(b) applying compressive force to said rupturable container to effect unidirectional discharge of said container's alkaline solution between said alkaline solution permeable and dyeable polymeric layer and said blue-sensitive silver halide emulsion layer;

(c) effecting thereby development of the latent image contained in each of said red, green and blue-sensitive 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 immobile yellow, magenta and cyan dyes 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 from said first pH at which said dyes are soluble and diffusible to said second pH at which said dyes are substantially nondiffusible;

(h) transferring, by diffusion, subsequent to substantial transfer image formation and preceding substantial environmental transfer image degradation, from said laminate to the atmosphere a sufficient portion of the water of the alkaline processing solution to thereby reduce said water concentration intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer to a concentration at which said aqueous alkaline processing solution insoluble polymeric dispersion coalesces at ambient temperatures;

(i) coalescing said aqueous alkaline processing solution insoluble polymeric dispersion as a result of said reduction in said water concentration;

(j) forming thereby a substantially continuous dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer; and

(k) maintaining said laminate intact subsequent to said processing.

39. A process as defined in claim 38 wherein said first pH is above 9 and said second pH is below 9.

40. A process as defined in claim 38 including the step of separating said container from said laminate subsequent to substantial image formation.

41. A process as defined in claim 38 wherein said opacifying agent is radiation reflective.

42. A process as defined in claim 41 wherein said opacifying agent is titanium dioxide.

43. A process as defined in claim 38 wherein said aqueous alkaline processing solution insoluble polymeric dispersion comprises carboxylated styrene/butadiene copolymer.

44. A process as defined in claim 43 wherein said aqueous alkaline processing solution insoluble polymeric dispersion is present in a concentration of about 5 to 40 g. of polymer/100 cc. of processing solution water.

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