

July 25, 1972

S. A. BUCKLER ET AL
COLOR DIFFUSION TRANSFER PROCESSES AND ELEMENTS FOR
USE THEREON WITH INCORPORATED IMAGE-FORMING
MATERIAL IMPERMEABLE LAYER

3,679,409

Filed June 1, 1971

6 Sheets-Sheet 1

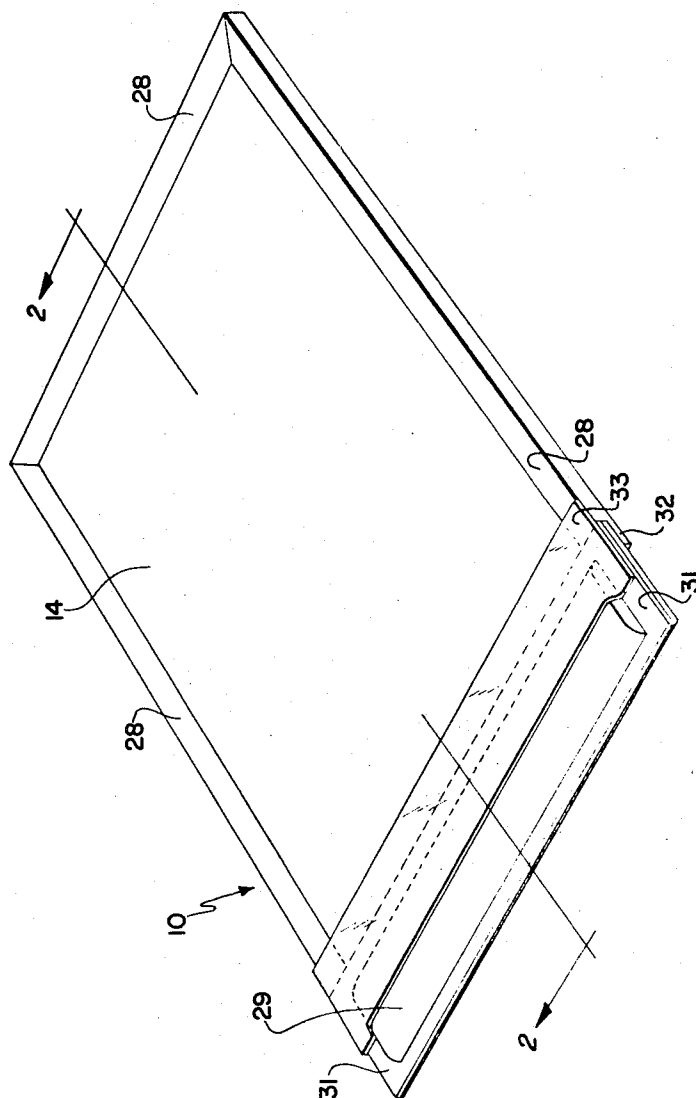


FIG. 1

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6 Sheets-Sheet 2

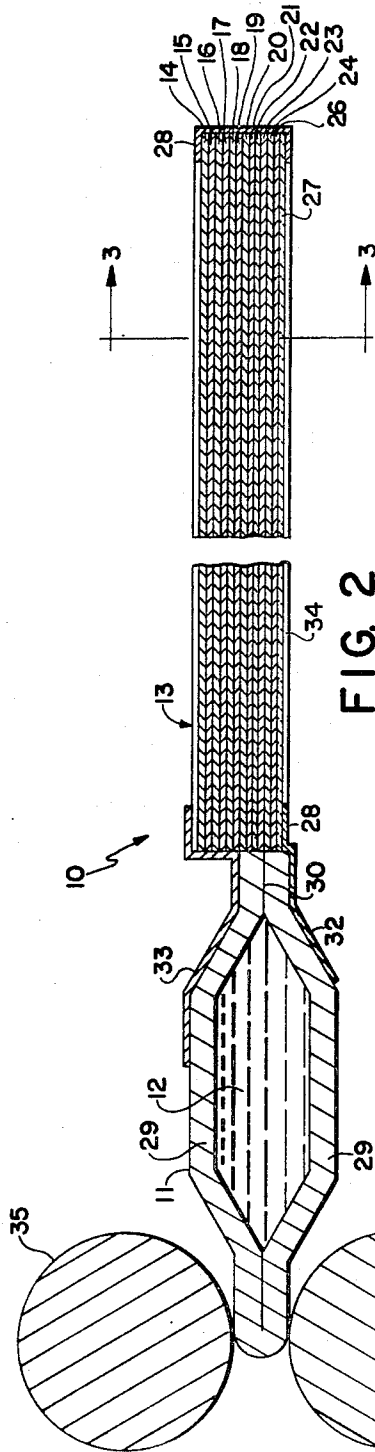


FIG 2

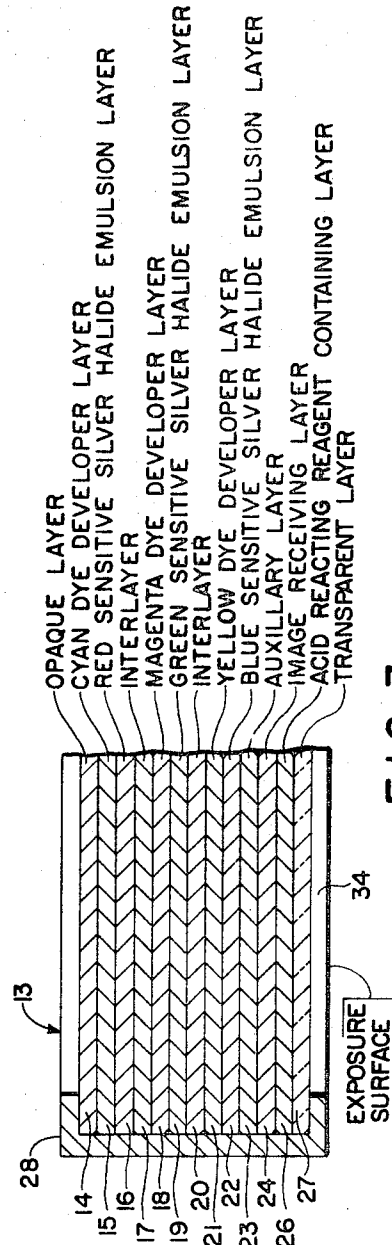


FIG 3

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6 Sheets-Sheet 4

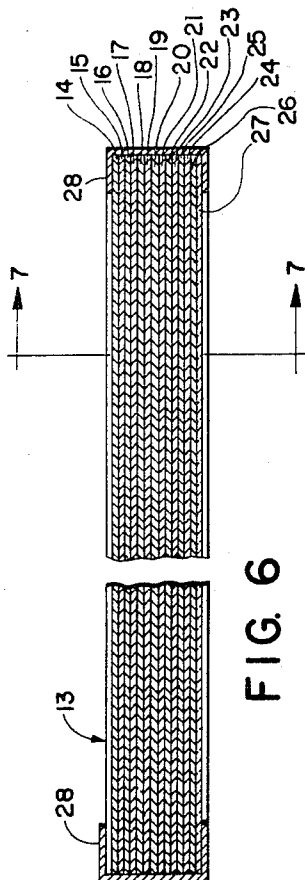


FIG. 6

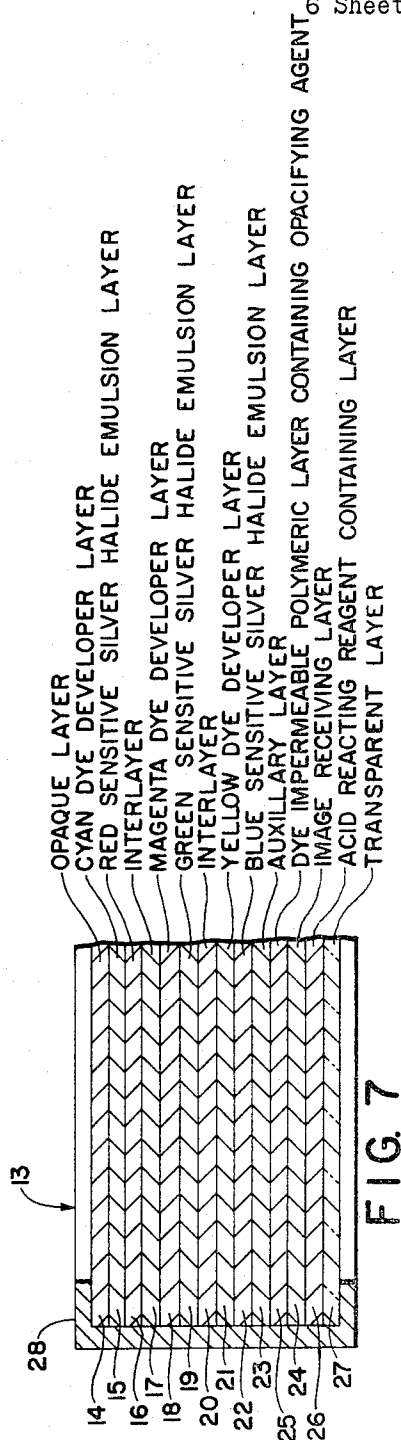


FIG. 7

OPAQUE LAYER
CYAN DYE DEVELOPER LAYER
RED SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
MAGENTA DYE DEVELOPER LAYER
GREEN SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
YELLOW DYE DEVELOPER LAYER
BLUE SENSITIVE SILVER HALIDE EMULSION LAYER
AUXILIARY LAYER
DYE IMPERMEABLE POLYMERIC LAYER CONTAINING OPACIFYING AGENT
IMAGE RECEIVING LAYER
ACID REACTING REAGENT CONTAINING LAYER
TRANSPARENT LAYER

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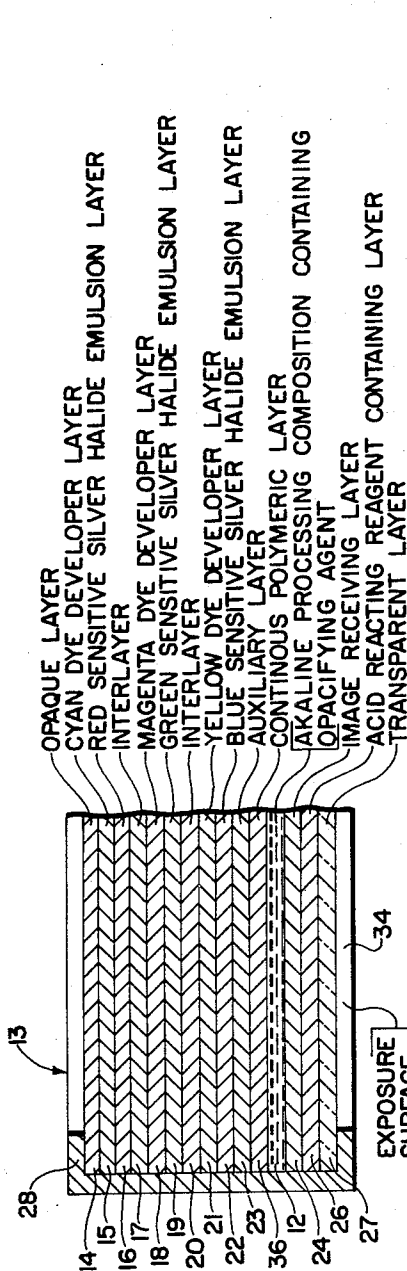
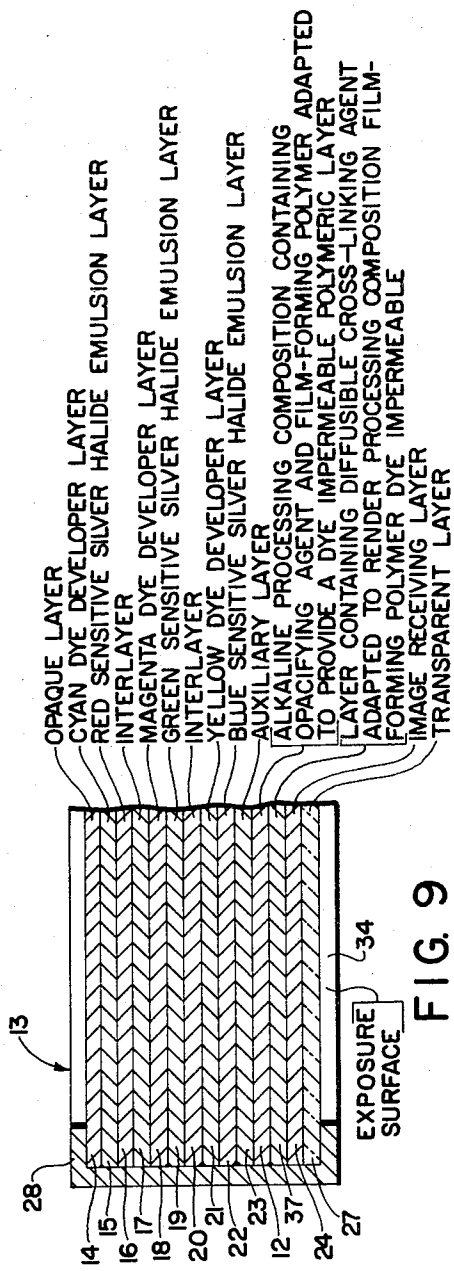
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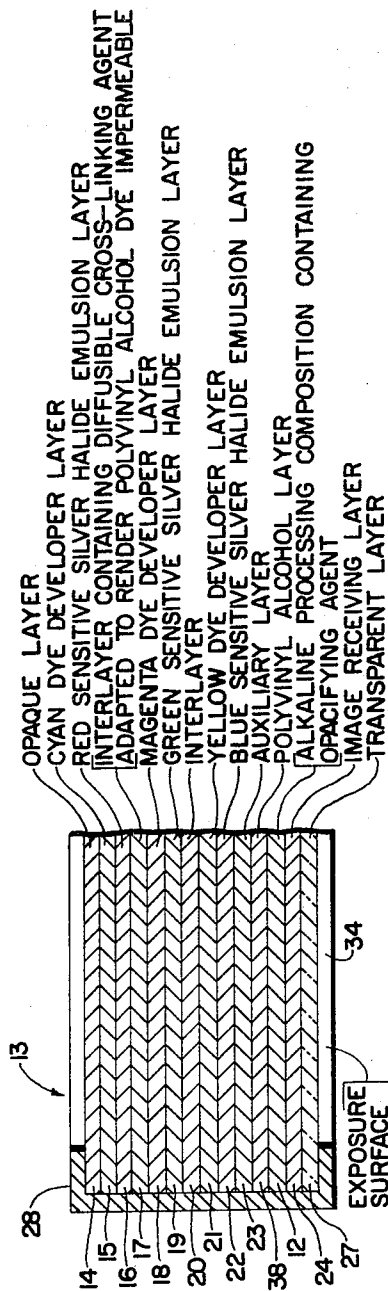


FIG. 10

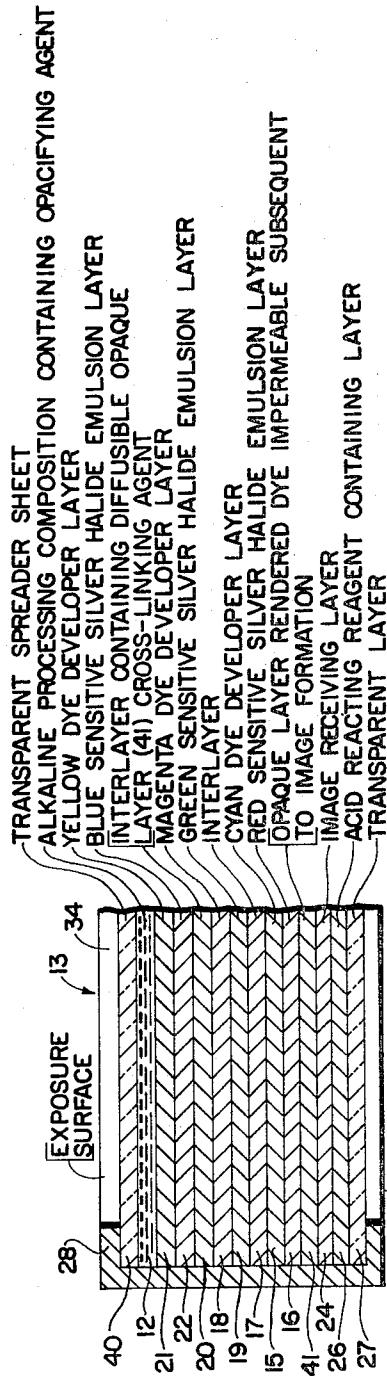


FIG. 11

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COLOR DIFFUSION TRANSFER PROCESSES AND ELEMENTS FOR USE THEREON WITH INCORPORATED IMAGE-FORMING MATERIAL IMPERMEABLE LAYER

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Continuation-in-part of application Ser. No. 867,583, Oct. 20, 1969. This application June 1, 1971, Ser. No. 148,349

Int. Cl. G03c 5/54, 1/48, 1/32

U.S. Cl. 96—3

52 Claims

ABSTRACT OF THE DISCLOSURE

Diffusion of undesirable image-forming materials to the image-receiving element of a multicolor diffusion transfer photographic product is inhibited by incorporating in such product an image-forming material impermeable layer between the image-receiving element and the next adjacent silver halide emulsion layer subsequent to substantial image formation.

This application is a continuation-in-part of application Ser. No. 867,583 filed on Oct. 20, 1969 and now abandoned.

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 given pH, 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 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 said first and second dimensionally stable layers and preferably intermediate the dyeable polymeric layer and photosensitive silver halide emulsion next adjacent thereto, in consequence of which a continuous layer is interposed between said dyeable polymeric layer and said silver halide emulsion next adjacent thereto, said continuous layer being substantially impermeable to dye image-forming materials after substantial image formation in said dyeable polymeric layer; to provide a diffusion transfer color film unit of the last-identified type including an opacifying agent disposed, preferably, 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 possessing the opacifying agent initially present in the processing composition for discharge preferably 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.

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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 preferred photographic film unit embodying the present 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 a typical association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a multicolor transfer image according to the invention, the thickness of the various materials being exaggerated, and wherein FIG. 2 represents an exposure stage, FIG. 4 represents a processing stage and FIG. 6 represents a product of the process;

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 various photosensitive laminates comprising the present invention during the illustrated stages of the transfer process;

FIGS. 8, 9, and 10 are diagrammatic, enlarged cross-sectional views similar to FIGS. 3, 5, and 7, but being directed toward embodiments of the instant invention other than the above-denoted preferred embodiment, and illustrating, in detail, the arrangement of layers comprising alternate photosensitive laminates of the present invention subsequent to exposure and distribution of processing composition; and

FIG. 11 is a diagrammatic enlarged cross-sectional view directed toward another embodiment of the instant invention and illustrating, in detail, the arrangement of layers comprising an alternate photosensitive laminate subsequent to exposure and distribution of processing composition.

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 is immobilized or precipitated in exposed areas as a result of development. In unexposed and partially exposed

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

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

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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 example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor 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. Furthermore, it has been found that even systems which possess pH reducing mechanisms may be somewhat prone to the described undesirable dye migration in certain instances due to the inherent solvent content of such systems which may add to stimulated dye migration between the photosensitive and image receptive components thereof.

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. Pat. Nos. 2,415,644; 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 container 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, in order to provide a commercially acceptable product, 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 methyl-vinyl 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 sub-coats 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 having 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 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 said first and said second dimensionally stable layers, and preferably intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion and associated dye image-forming material next adjacent thereto. In addition, the aforementioned integral photographic film unit possesses means for forming, in situ, between said dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent thereto, a continuous dye image-forming material impermeable polymeric layer after substantial image formation has been accomplished in said dyeable polymeric layer in order to obviate further dye migration.

Means for the formation of such a continuous polymeric layer include, for example, incorporation in the processing composition of a particulate dispersion of a processing composition insoluble polymer as a discontinuous phase, said polymer being adapted, upon decrease in processing composition solvent subsequent to distribution, to coalesce at ambient temperature to provide a dye image-forming material impermeable polymeric stratum intermediate the dyeable polymeric layer and next adjacent photosensitive silver halide emulsion subsequent to substantial dye transfer image formation.

Additional means for the formation of a continuous dye image-forming material impermeable stratum intermediate the dyeable polymeric layer and next adjacent photosensitive silver halide emulsion include the disposition of a polymeric material in the processing composition wherein the dye image-forming material permeability of the polymeric layer formed upon distribution of the processing composition is a direct function of the pH of the photographic system, for example, at a preselected first or initial pH the resultant polymeric stratum is dye image-forming material permeable and is dye image-forming material impermeable at an in situ provided second pH. Alternatively, such polymeric material may be initially disposed intermediate the dyeable polymeric and next adjacent photosensitive silver halide emulsion layer; the dye image-forming material permeability of such polymeric layer being a direct function of the pH of the photographic system during processing, for example, at the pH of the system provided by contact of such layer with alkaline processing composition, the permeability

of the layer is such that dye image-forming material freely passes therethrough. However, as the pH of the system is decreased, during processing, from an initial preselected pH, for example, in the manner previously discussed, the permeability of such polymeric layer decreases to an ultimate point at which dye image-forming material is incapable of passing through such layer. Such a system is generally visualized as a "pH valve" operative in accordance with selected pH criterion.

Further means effective in the practice of the present invention are to provide to the composite photosensitive unit a diffusible crosslinking agent for a polymeric material such as, for example, a viscosity increasing agent, etc., carried by the processing composition which, subsequent to predetermined transfer image formation, diffuses from its initial position in the photosensitive unit to the polymeric material, distributed as a component of the processing composition intermediate the dyeable polymeric layer and next adjacent photosensitive silver halide emulsion, to provide the requisite crosslinking of the thus formed polymeric stratum and thereby inhibiting further transfer of additional dye image-forming material. Alternatively, the last-mentioned in situ barrier formation of the present invention may be provided by initially disposing a dye image-forming material permeable polymeric layer intermediate the dyeable polymeric layer and next adjacent photosensitive silver halide emulsion and a crosslinking agent for such polymeric layer disposed in an element of the composite film unit and/or incorporated in the selected processing composition to provide during processing, subsequent to substantial dye transfer image formation, crosslinking agent contact with the polymeric layer in a concentration effective to render such polymeric layer substantially impermeable to further dye image-forming material transfer. This latter alternative, it will be appreciated, is applicable to the situation wherein the in situ formation of a dye image-forming material impermeable layer is desired, subsequent to substantial image formation, at a situs other than the layered position in which the processing composition is discharged (see FIG. 11).

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.

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 0.26 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 numbers, appearing in the various figures, refer to like components.

As illustrated in the drawings, FIG. 1 sets forth a perspective view of a preferred film unit according to the present invention, designated 10, and each of FIGS. 2 through 7 illustrate diagrammatic cross-sectional views of a preferred embodiment 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, and FIGS. 8 through 11 depict cross-sectional views of alternate embodiments of the present invention after rupture of the processing composition retaining container and substantial subsequent development.

Film unit 10 comprises rupturable container 11, retaining, prior to processing, aqueous alkaline solution 12, and photosensitive laminate 13 including, in order, dimensionally stable, preferably 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; acid reacting reagent-containing layer 26; 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 5, or, for that matter, intermediate any two layers between which processing composition is to be discharged, 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, for example, 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 halide 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. With the exception of the opaque spreader sheet configuration described with reference to FIG. 11, all the lamina of the denoted photosensitive elements are generally fixedly coextensive.

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 member 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 polymeric material adapted, upon pH reduction below about 11, and preferably below about 9, to form a continuous image-forming material 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 of the laminate are appropriately protected by incident radiation, at one major surface by the opaque processing composition 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 photosensitive emulsions from physical fog formation during processing.

In the preferred embodiment of the present invention detailed above with reference to FIGS. 1 through 7, the concentration of the polymeric film-former solution retained in the processing composition will be that sufficient to provide, upon reduction in pH below about 11, a substantially continuous, dye image-forming material impermeable polymeric layer, subsequent to distribution of the processing composition between the dyeable polymeric layer and the photosensitive emulsion layer next adjacent thereto.

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%.

As examples of alkaline solutions of polymeric materials which may be disposed in the processing composition for subsequent formation of a continuous dye image-forming material impermeable stratum between the image-receiving layer and the photosensitive silver halide emulsion layer next adjacent thereto upon reduction in the pH of the photographic system, mention may be made of the various polymeric materials which are known to act as a "pH valve," as aforementioned. Such materials will, when cast in a film, allow free permeation of image-forming substances as long as the pH remains above a predetermined datum level but will form a substantially continuous dye image-forming material impermeable barrier at such time as the pH is reduced to below the datum; the preferred pH level for impermeable barrier formation in the present invention being between about pH 9-11. These materials include, for example, polyphenolic polymers such as the acetal of hydroxybenzaldehyde and polyvinyl alcohol, and preferably the compound produced when said hydroxybenzaldehyde is a meta compound; sulfonamides, such as, for example, the acetal of a primary formyl benzene sulfonamide and polyvinyl alcohol; polymers comprising α -trifluoromethylvinyl alcohol segments; the benzene sulfonamide of deacetylated chitin; polyhydroxymethylene; the acetal of 3-hydroxybenzaldehyde and a vinyl alcohol- α -trifluoromethylvinyl alcohol copolymer; novolactic phenol formaldehyde polymers; Santolite MHP (trade name of Monsanto Chemical Company for a formaldehyde benzenesulfonamide condensation polymer); poly- α,α -bis(hydroxyethyl) methylene; etc. With regard to many other materials which may be used in the denoted format the disclosure of U.S. Pat. No. 3,362,822 is incorporated herein by reference. In addition it will be evident to those of ordinary skill in the art that various and sundry other polymeric materials possessing the properties denoted may be utilized in the context of the present invention for the denoted purpose.

The above-denoted polymeric compositions whose permeability is directly related to the environmental pH may be utilized by being spread between the image-receiving layer and the next adjacent photosensitive silver halide layer as above denoted in the preferred embodiment referred to above, or such materials may be initially coated intermediate the image-receiving layer and the photosensitive silver halide emulsion next adjacent thereto as a continuous film to be rendered permeable at such time as the processing composition container is ruptured to thereby release an alkaline processing composition possessing a predetermined pH whereby the pH valve is rendered permeable to image-producing materials until such time as the pH of the system is dropped below a datum level. Generally speaking, such materials comprise weakly ion-

ized polymeric acids, for example, those having an ionization constant between about 10^{-4} and 10^{-12} . See, for example, FIG. 8 which denotes a layer of polymeric material capable of reacting as a pH valve precoated over the auxiliary layer adjacent the photosensitive silver halide emulsion layer next adjacent the image-receiving layer just after the processing composition retaining container is ruptured.

In a further embodiment of the present invention, a concentration of processing composition insoluble dispersion of polymeric material may be disposed in the processing composition sufficient to provide, upon coalescence at ambient temperatures and decrease of processing composition solvent, a substantially continuous, dye image-forming material, 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 dispersent 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.

A still further embodiment of the present invention comprises a system whereby well-known viscosity increasing ingredients utilized in the processing composition are cross-linked subsequent to substantial image formation in the image-receiving layer to the extent required to provide an image-forming material impermeable layer between the image-receiving layer and the next adjacent photosensitive silver halide emulsion layer. Such a system may be carried out by incorporating a cross-linking agent in the composite photosensitive structure whereupon said cross-linking agent diffuses into distributed processing composition to thereby cross-link a thickening substance or other polymeric material incorporated in said processing composition in order to form such dye impermeable layer after substantial image formation has taken place. As is denoted above, hydroxyethyl cellulose is commonly utilized as a viscosity increasing agent in conventional diffusion transfer processes as more fully disclosed and discussed in numerous of the aforementioned patents and particularly in U.S. Pat. No. 2,983,606. A well-known cross-linking agent for hydroxy functional compositions as, for example, the above-denoted hydroxyethyl cellulose is divinylsulfone. If, for example, a divinylsulfone precursor such as, for instance, bis-pyridinium ethyl sulfone chloride is dissolved in a solution of, for example, polyacrylamide, and coated over the image-receiving layer as denoted in FIG. 9, upon being contacted with the processing composition which is distributed between the image-receiving layer and the next adjacent photosensitive silver halide layer, it will form divinyl sulfone which will migrate into the processing composition and substantially cross-link the hydroxy-functional material present therein to thereby form a continuous image-forming material impermeable barrier. It will be appreciated that bis-pyridinium ethyl sulfone chloride type cross-linking agents are conventional and well-known in the art and furthermore that one of ordinary skill in the art would naturally be aware of many other such materials which would provide the requisite functionality to the materials which may be utilized in the context of the present invention. For example, reference may be had to U.S. Pat. No. 3,345,177

wherein cross-linking agents comprising β -ketoethyl onium salts are disclosed as cross-linking agents for materials useful in the context of the present invention.

It will be further appreciated that the effect denoted in the paragraph next above can be potentiated by overcoating the negative and/or positive element such as with a thin layer of a polymeric material, for example, polyvinyl alcohol, which will itself be cross-linked by any agent utilized to cross-link hydroxy functional materials which are present in the system. Such a barrier implementation system may be used whether or not cross-linkable processing composition components are employed since the presence of the cross-linking agent in the system may be sufficient to provide the requisite barrier effect to cross-linkable polymeric layer or layers.

Further amplification of the embodiments denoted in the two paragraphs next above and FIG. 9 embraces the utilization of cross-linking agent for the thickener present in the processing composition—such agents being optionally disposed in a layer of the photosensitive element and being capable of providing the requisite cross-linking to the thickener upon solvation by the processing composition and migration to the thickener situs.

In a still further specifically detailed amplification of the embodiments referred to immediately above, a polyvinyl alcohol coating as denoted in FIG. 10 may be utilized intermediate the image-receiving and the next adjacent photosensitive silver halide layers, and a cross-linker therefor which will not have a substantial deleterious effect on other components of the film unit system such as gelatin and the like may be incorporated within one of the layers comprising the negative and/or positive element in the format of the present invention, as, for example, in the denoted interlayer between the red-sensitive silver halide emulsion layer and the magenta dye developer layer. Within such an embodiment, for example, a boric acid cross-linking agent for polyvinyl alcohol may illustratively be incorporated in the above-denoted interlayer. At such time as processing composition is distributed between the image-receiving layer and the negative element, such processing composition would render the boric acid material diffusible within the system. As such material contacts the polyvinyl alcohol overcoat between the image-receiving layer and the next adjacent photosensitive element the polyvinyl alcohol would be cross-linked and would become impermeable to image-forming materials thereby lending a substantial stability to the system of the present invention.

In embodiments of the present invention predicated upon migration of a cross-linking agent to render, for example, a cast layer impermeable to image-forming materials, it may be desirable to incorporate in such embodiments mechanisms particularly designed to inhibit migration of such cross-linking agent, e.g., diffusion delay layers, etc., until image formation has gone to substantial completion. Such techniques are well known in diffusion transfer photographic technology. In addition, where stable, if the dynamics of a particular system are appropriate, the cross-linking agent may be incorporated in the processing composition. Furthermore, in embodiments of the present invention directed toward cross-linking a precast layer of polymeric material not cast from the processing composition, it is preferred that such layer be located intermediate the image-receptive layer and the silver halide emulsion layer next adjacent thereto at a position more distal from the image-receptive layer than the processing composition is to occupy.

In general, the amount of polymeric materials utilized to form the herein denoted barrier layers will be determined empirically since various materials will provide different barrier effects for given concentrations. It has been found that as a rule a sufficient concentration of materials to provide a continuous layer possessing the general dimensions of approximately 20 microns will suffice to provide the designated functionality to the system.

Upon formation of the ultimate film the substantially continuous 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 hereinabove.

In a particularly preferred embodiment of the present invention the substantially continuous polymeric film provided within one or more of the embodiments denoted herein, in addition to being impermeable to solubilized dye developer, will also be substantially impermeable to solubilized photographic adjuncts present in the film unit in general and more particularly those possessing physical dimensions as, for example, molecular size, less than that of dye developer such as, for example, antifoggant, 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 nondiffusible oxidized form, thereby providing image-wise 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 image-wise 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 substantially continuous dye developer impermeable polymeric layer 25 is provided according to the above-denoted preferred embodiment to thereby form 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.

Certain other embodiments of the present invention as discussed above may be more clearly appreciated with reference to FIGS. 8–11. Referring first to FIG. 8, in addition to the various layers described in FIG. 5, it will be noted that layer 36 which comprises a continuous layer of an image-forming material impermeable polymer is coated over the auxiliary layer 23. The polymeric material is pH reactive to the extent that distribution of alkaline processing composition in intimate contact therewith renders such polymeric layer permeable to image-forming materials which are free to diffuse therethrough until such time as acid reacting-reagent containing layer 26 reduces the pH of the system below a value at which said polymeric layer becomes impermeable to further diffusion of image-forming materials.

Referring now to FIG. 9 it will be noted that in addition to the layers discussed relative to FIG. 5, the denoted structure contains a layer 37 which contains a cross-linking agent for a polymeric material utilized in the alkaline processing composition. As more fully described above such polymeric material is generally utilized as a thickener for said processing composition. The various cross-linking agents which may be employed are ordinarily disposed in a polymeric carrier such as, for example, polyacrylamide, and may be cast over, for example, the image-receiving layer and/or disposed in any one or more layers intermediate the transparent support and the situs for distributed processing composition. At such time as the processing composition-retaining container is ruptured and processing composition is distributed between the image-receiving layer and next adjacent emulsion layer, cross-linking agent is slowly diffused into the processing composition to ultimately cross-link the thickener therein and provide the requisite barrier to the system. It will be further noted that layer 26 which comprises an acid-reacting reagent, for illustrative purposes, has not been shown in FIG. 9 since the necessity for having such a reagent present is obviated by the non-pH functionality of the mechanism attributed to the embodiment described in FIG. 9.

Referring now to FIG. 10, it will be noted that, structurally speaking, the embodiment described is similar to that described in FIG. 9 except for the deletion of layer 37 of FIG. 9 and the incorporation of a polyvinyl alcohol overcoat 38 on the auxiliary layer. In addition it will be noted that the interlayer between the magenta dye developer layer and the red-sensitive silver halide emulsion layer has been denoted as containing a polyvinyl alcohol cross-linking agent, as, for example, boric acid. After rupture of the processing composition retaining container alkali diffusion throughout the system will cause the cross linking agent in the interlayer to become mobile and diffuse through the system into the polyvinyl alcohol layer 38 and cause such layer to cross-link at a slower rate than image formation, thereby preventing further transfer of image-producing materials from the negative element to the image-receiving layer and vice versa after substantial image formation.

In a similar context to the specifically detailed embodiment described respecting FIG. 10, attention is directed to U.S. patent applications Ser. Nos. 39,646, now U.S. Pat. 3,594,165 and 39,666, now U.S. Pat. 3,594,164 each filed on May 22, 1970 as continuations-in-part of U.S. patent application Ser. No. 815,581, filed Apr. 14, 1969, which is, in part, a continuation of U.S. patent application Ser. No. 728,353, filed May 13, 1968, both of the latter two applications having been abandoned. The disclosures of aforementioned U.S. patent applications Ser. Nos. 39,646 and 39,666 are incorporated herein by reference and generally relate to composite photographic diffusion transfer color process film units which comprise a laminate including a dimensionally stable transparent support carrying a dyeable polymeric layer, a processing composition permeable opaque layer and a photosensitive silver halide layer having associated therewith a dye transfer image-forming material; a dimensionally stable sheet adapted to be superposed substantially coextensive the surface of the laminate opposite the transparent support, and means for applying a processing composition between the surface of the laminate opposite the transparent support and the superposed sheet, the said means for applying a processing composition preferably comprising a rupturable container fixedly positioned and extending transverse a leading edge of said composite structure. Obviously, in the event the dimensionally stable superposed sheet is transparent, it may be fixedly positioned as part of the composite structure. It will be appreciated, however, that such sheet may comprise a material opaque to incident actinic radiation whereby during exposure it is held out of contact with the surface of the laminate as depicted, for example, in FIG. 1 of the aforementioned

U.S. patent application Ser. No. 39,666 and is, after exposure, brought into intimate contact with the surface of the composite photosensitive unit whereby it masks the photosensitive components thereof from further exposure to actinic radiation. Even when the superposed sheet is opaque to actinic radiation it is still fixed at least along one transverse edge to the photosensitive laminate. FIG. 11 depicts a transparent spreader-sheet embodiment after the spreading of processing composition—the denoted opaque layer 41 between the image-receiving layer and next adjacent silver halide emulsion layer providing the additional function of preventing dye image-forming material permeation subsequent to substantial image formation in the image-receiving layer by a mechanism, for example, as discussed relative to FIG. 10. Referring specifically to FIG. 11, exposure is accomplished through transparent sheet 40 (or through the denoted “exposure surface” 34 if a spreader sheet is not present during exposure) the various other layers being as hereinbefore described and the opaque layer being rendered dye impermeable by, for example, migration of cross-linking agent from layer 20. In contradistinction to the embodiments denoted in FIGS. 2 through 10, the embodiment of FIG. 11 is viewed, after image formation, through the side of unit 13 opposite to the exposure side.

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	cc.	100
Potassium hydroxide	grams	11.2
Hydroxyethyl cellulose (high viscosity) (commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250)	grams	3.4
N-benzyl- α -picolinium bromide	do.	1.5
Benzotriazole	do.	1.0
Titanium dioxide	do.	50.0
Carboxylated (<5% CoOH) styrene/butadiene copolymer (commercially available from W. R. Grace Co., New York, N.Y., under the trade name Darex 526-L)	grams	20.0

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.

As an illustration of an embodiment employing in situ formation of a polymeric film which is permeable to dye developer as a function of the operative processing pH of the system, the aforementioned carboxylated styrene/butadiene copolymer may be replaced in the denoted construction by 1.5 grams of the acetal of polyvinyl alcohol and p-formylbenzenesulfonamide, which provides the designated advantageous results denoted with respect to the aforementioned embodiment employing in situ generation of a substantially continuous dye developer impermeable carboxylated styrene/butadiene copolymeric layer, subsequent to substantial dye transfer image formation, upon osmotic reduction in the solvent water concentration of the photographic system.

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, unless, of course, it is a functional component of the barrier-formation system as above-denoted.

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.

The presence of such a polymeric acid layer is particularly critical in instances wherein the barrier formation functionality is predicated upon a pH valve mechanism. It will be appreciated that in the absence of a specific mechanism for reducing the pH within the film, the pH will remain at a high level and will militate against formation of a continuous film by the pH valve mechanism described hereinabove. To some limited extent pH reduction is inherent in the described color diffusion transfer system by the oxidation of the dye components which forms the diffusible dye. Such reduction, however, is generally insufficient to reduce the pH of the system to a level whereupon formation of a suitable barrier by the pH valve mechanism is assured. Accordingly, it is considered critical to the utilization of a pH valve in the inventive environment herein disclosed to utilize therewith somewhere within the system a pH reducing mechanism, and particularly those described above.

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 U.S. Pat. No. 3,455,686, preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective within the temperature range of optimum transfer processing. Con-

versely, 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 timewise 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 U.S. Pat. No. 3,455,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl 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 the 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 de-

sign 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 a desired liquid impermeability and vapor transmissivity 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; cross-linked 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 operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalis, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH and solvent concentration required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

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

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the

table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of 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 nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl- α,β -unsaturated carboxamides and copolymers of N-alkyl- α,β -carboxamides with N-hydroxyalkyl- α,β -unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of 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.

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 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; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, 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 gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant 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 flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures de-

scribed in U.S. Pats. Nos. 2,614,928; 3,614,929; 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, replaced 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 tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, 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 pri-

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

Throughout the specification reference has been made toward interposing a barrier layer between the image-receiving layer and the photosensitive emulsion layer next adjacent thereto. By such language it is not intended to connote necessarily the absence of other layers between said interposed barrier layer and either or both of said image-receiving layer or said next adjacent photosensitive emulsion 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:

1. A photographic film unit which comprises, in combination:

a photosensitive element comprising a composite structure containing, as essential layers, in sequence, a first dimensionally stable layer; 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;

means for applying a processing composition, and an opacifying agent in a quantity sufficient to mask said dye image-providing material between said first and said second dimensionally stable layers; and

means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto subsequent to substantial image formation in said dyeable polymeric layer.

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

3. The photographic film unit as defined in claim 2 wherein said means for applying said processing composition is capable of discharging such composition between said first dimensionally stable transparent layer and the next adjacent photosensitive silver halide emulsion layer.

4. The photographic film unit as defined in claim 3 which additionally includes a processing composition permeable actinic radiation opaque layer between said image-receiving layer and the next adjacent photosensitive silver halide emulsion layer.

5. The photographic film unit as defined in claim 4 wherein said means for applying a processing composition comprises a rupturable container fixedly positioned and extending transverse a leading edge of said composite structure.

6. The photographic film unit as defined in claim 1 wherein said first dimensionally stable layer is opaque to incident actinic radiation.

7. The photographic film unit as defined in claim 6 wherein said means for applying said processing composition is capable of discharging such composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

8. The photographic film unit as defined in claim 7 wherein said means for applying a processing composition comprises a rupturable container fixedly positioned and extending transverse a leading edge of said composite structure.

9. A photographic film unit as defined in claim 8 wherein said composition is an aqueous alkaline composition.

10. A photographic film unit as defined in claim 9 wherein said dye image-providing material is a dye which is a silver halide developing agent.

11. A photographic film unit as defined in claim 8 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 composition.

12. A photographic film unit as defined in claim 8 wherein said opacifying agent is actinic radiation reflective.

13. A photographic film unit as defined in claim 12 wherein said opacifying agent is titanium dioxide.

14. A photographic film unit as defined in claim 10 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 being soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

15. A photographic film unit as defined in claim 14 wherein each of said selectively sensitized photosensitive silver halide emulsions has predominant spectral sensitivity to separate regions of the spectrum and the dye associated 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.

16. A photographic film unit as defined in claim 15 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.

17. A photographic film unit as defined in claim 10 including at least one polymeric acid layer positioned intermediate said first dimensionally stable layer and the photosensitive silver halide emulsion layer next adjacent thereto, or intermediate said second dimensionally stable layer and the dyeable polymeric layer.

18. A photographic film unit as defined in claim 17 wherein said polymeric acid layer contains sufficient acid-

fyng 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.

19. A photographic film unit as defined in claim 18 wherein said means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto comprises a polymeric film-forming material contained in said processing composition said material being capable of passing image-forming materials therethrough at said first pH, but being incapable of passing image-forming materials therethrough at said second pH.

20. A photographic film unit as defined in claim 18 wherein said means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto comprises a continuous layer of a polymeric material integrally incorporated in the photographic film unit intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto wherein said polymeric layer comprises a material which is impermeable to image-forming materials at said second pH but is permeable thereto at said first pH.

21. A photographic film unit as defined in claim 10 wherein said processing composition comprises a polymeric thickening agent, which is capable of being cross-linked, in a concentration effective to provide a continuous dye image-forming material permeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent thereto; and a diffusible agent, capable of cross-linking said polymeric thickening agent, in a concentration effective to provide, subsequent to substantial diffusion transfer dye image-formation, a continuous dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto, is disposed in a layer of said photosensitive element.

22. A photographic film unit as defined in claim 10 wherein said means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer adjacent thereto comprises a dye image-forming material permeable polymeric layer which is capable of being cross-linked, intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto; and further, wherein a diffusible cross-linking agent for said polymeric cross-linkable material is positioned in a layer of said photosensitive element or in said processing composition.

23. The invention of claim 22 wherein said cross-linkable polymeric layer is polyvinyl alcohol and said cross-linking agent is boric acid.

24. A photographic film unit which contains 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 acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are substantially nondiffusible; a dimensionally stable liquid impermeable transparent layer and means securing said layer in substan-

tially fixed relationship; a rupturable container retaining an aqueous alkaline processing composition possessing said first pH; and means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto subsequent to substantial image formation in said dyeable polymeric layer.

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

26. A photographic film unit as defined in claim 15 wherein said opacifying agent is actinic radiation reflective.

27. A photographic film unit as defined in claim 26 wherein said opacifying agent is titanium dioxide.

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

exposing a photographic film unit which includes, in combination, a composite structure containing, as essential layers, in sequence, a first dimensionally stable layer; 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 image-providing material; a second dimensionally stable layer transparent to incident actinic radiation; means for applying a processing composition, and an opacifying agent in a quantity sufficient to mask said dye image-providing material between said first and said second dimensionally stable layers; and means for forming, in situ, a dye image-forming material impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto subsequent to substantial image formation in said dyeable polymeric layer;

applying said processing composition between said first and said second dimensionally stable layers, effecting thereby development of said silver halide emulsion and, as a result of said development, forming an imagewise distribution of mobile dye image-providing material associated with said emulsion as a function of the point-to-point degree of emulsion exposure;

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-providing material to provide a dye image thereto in terms of said distribution;

forming, subsequent to substantial dye transfer image formation and preceding substantial environmental dye transfer image degradation, a dye image-forming material impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the silver halide emulsion next adjacent thereto; and

maintaining said composite structure intact subsequent to said processing.

29. The process as defined in claim 28 wherein said first dimensionally stable layer is transparent to actinic radiation.

30. The process as defined in claim 29 wherein said means for applying said processing composition is capable of discharging said composition between said first dimensionally stable layer and the next adjacent photosensitive silver halide emulsion layer.

31. The process as defined in claim 30 wherein a processing composition permeable actinic radiation opaque layer is positioned between said image-receiving layer and the next adjacent photosensitive silver halide emulsion layer.

32. The process as defined in claim 31 wherein said means for applying said processing composition comprises

a rupturable container fixedly positioned and extending transverse a leading edge of said composite structure.

33. The process as defined in claim 28 wherein said first dimensionally stable layer is opaque to incident actinic radiation.

34. The process as defined in claim 33 wherein said means for applying said processing composition is capable of discharging said composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

35. The process as defined in claim 34 wherein said means for applying said processing composition comprises a rupturable container fixedly positioned and extending transverse a leading edge of said composite structure.

36. A process as defined in claim 35 wherein said composition is an aqueous alkaline composition.

37. A process as defined in claim 36 wherein said dye image-providing material is a dye which is a silver halide developing agent.

38. A process as defined in claim 37 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 composition distributed between said dyeable polymeric layer and said silver halide emulsion layer next adjacent thereto.

39. A process as defined in claim 37 wherein said opacifying agent is actinic radiation reflective.

40. A process as defined in claim 39 wherein said opacifying agent is titanium dioxide.

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

exposing a photographic film unit 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 emulsion 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;

a rupturable container retaining an aqueous alkaline processing composition containing an opacifying agent in a quantity sufficient to mask said dyes 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; and

means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto subsequent to substantial image formation in said dyeable polymeric layer;

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;

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

forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of emulsion exposure;

transferring, by imbibition, and 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;

providing, subsequent to substantial dye transfer image formation and preceding substantial environmental dye transfer image degradation, a dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and the silver halide emulsion next adjacent thereto; and

maintaining said composite structure intact subsequent to said processing.

42. A process as defined in claim 41 wherein each of said selectively sensitized silver halide emulsion layers possesses 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.

43. A process as defined in claim 42 wherein said composite structure includes at least one polymeric acid layer positioned intermediate at least one of said first dimensionally stable layer 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 layer contains 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 nondiffusible and including the step of transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said alkaline processing composition to said polymeric acid layers to thereby reduce the alkalinity of said composition from said first pH to said second pH.

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

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 composite structure 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; and 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;

a rupturable container retaining an aqueous alkaline processing solution possessing said first pH and an opacifying agent in a quantity sufficient to mask said dyes 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; and means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer subsequent to substantial image formation in said dyeable polymeric layer;

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;
 effecting thereby development of the latent image contained in each of said red, green and blue-sensitive silver halide emulsions;
 immobilizing said yellow, magenta and cyan dye as a result of development of their respective associated silver halide emulsions;
 forming thereby an imagewise distribution of mobile yellow, magenta and cyan dyes as a function of the point-to-point degree of exposure of their respective associated silver halide emulsions;
 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;
 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;
 forming, subsequent to substantial transfer image formation and preceding substantial environmental transfer image degradation, a substantially continuous dye impermeable polymeric layer disposed intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer; and
 maintaining said composite structure intact subsequent to said processing.

45. A process as defined in claim 44 wherein said first pH is above 9 and said second pH is below 9.

46. A process as defined in claim 44 including the step of separating said container from said composite structure subsequent to substantial image formation.

47. A process as defined in claim 44 wherein said opacifying agent is radiation reflective.

48. A process as defined in claim 47 wherein said opacifying agent is titanium dioxide.

49. A process as defined in claim 44 wherein said means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, subsequent to substantial image-formation in said dyeable polymeric layer, comprises incorporating in said processing solution a polymeric thickening agent, which is capable of being crosslinked, in a concentration effective to provide a continuous dye permeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer; and further disposing in a layer of said photosensitive element a diffusible agent capable of cross-linking said polymeric thickening agent in a con-

centration effective to provide, subsequent to substantial diffusion transfer dye image-formation, a continuous dye impermeable polymeric layer intermediate said dyeable polymeric layer and the blue-sensitive silver halide emulsion.

50. A process as defined in claim 44 wherein said means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, subsequent to substantial dye image-formation in said dyeable polymeric layer, comprises a layer of dye image-forming material permeable polymeric material which is capable of being cross-linked, positioned intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer; and an agent capable of cross-linking said polymeric cross-linkable material is disposed in a layer of said photosensitive element or in said processing composition, whereupon after substantial image-formation a dye impermeable layer is provided between said dyeable polymeric layer and said blue-sensitive emulsion layer.

51. A process as defined in claim 44 wherein said means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, subsequent to substantial dye image formation in said dyeable polymeric layer, comprises incorporating a polymeric material in said processing composition, a layer of which polymeric material is provided intermediate said blue-sensitive silver halide emulsion layer and said dyeable polymeric layer upon discharge of said processing composition from said rupturable container, wherein said polymeric material is capable of passing image-forming materials therethrough at said first pH, but being incapable of passing image-forming materials therethrough at said second pH.

52. A process as defined in claim 44 wherein said means for forming, in situ, a dye impermeable polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive emulsion layer, subsequent to substantial dye image formation in said dyeable polymeric layer, comprises an integral continuous polymeric layer intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer which continuous polymeric layer is dye permeable at said first pH and dye impermeable at said second pH.

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