

April 27, 1971

E. H. LAND

3,576,625

PHOTOGRAPHIC DIFFUSION TRANSFER COLOR PROCESS
AND FILM UNIT FOR USE THEREIN

Filed July 31, 1969

4 Sheets-Sheet 1

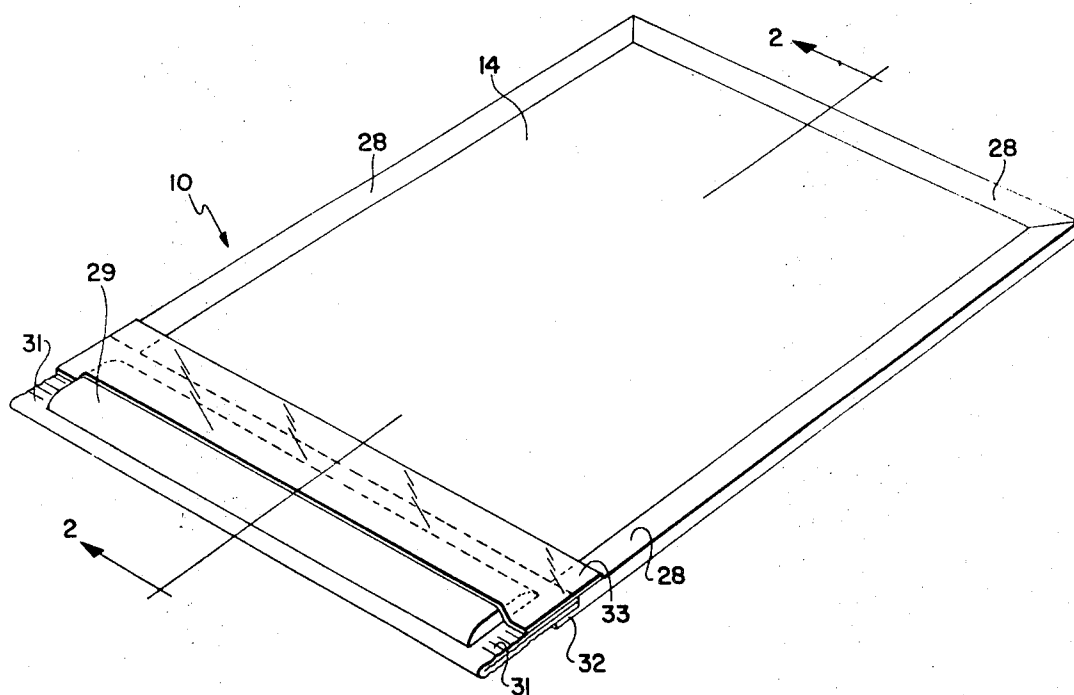


FIG. 1

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4 Sheets-Sheet 2

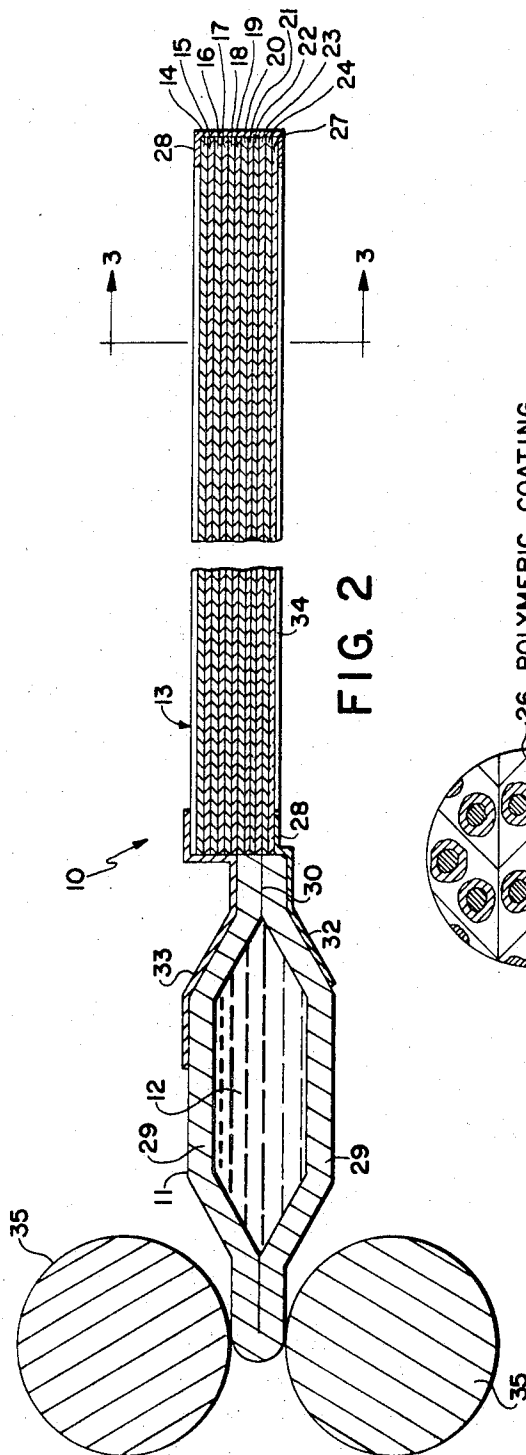


FIG. 2

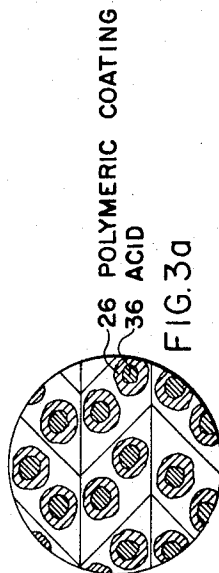


FIG. 3a

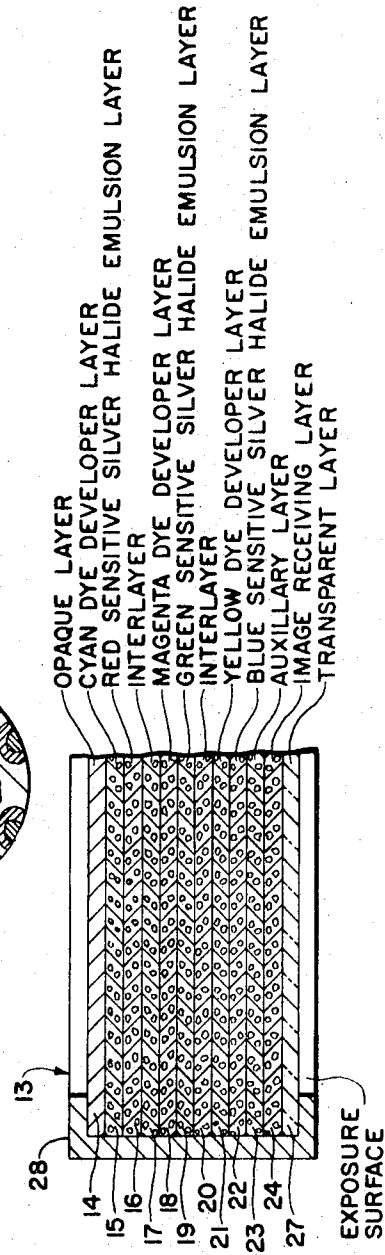


FIG. 3

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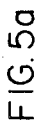
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4 Sheets-Sheet 4

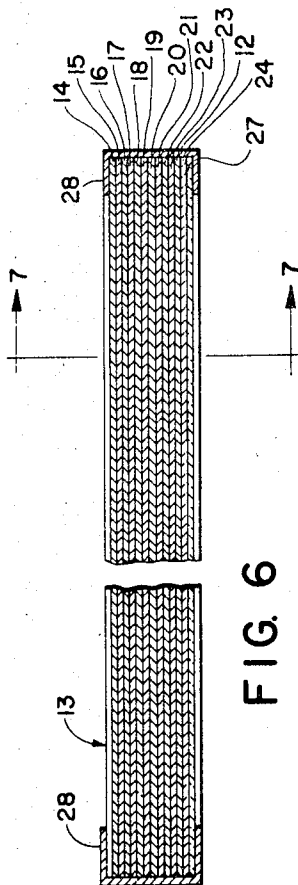


FIG. 6

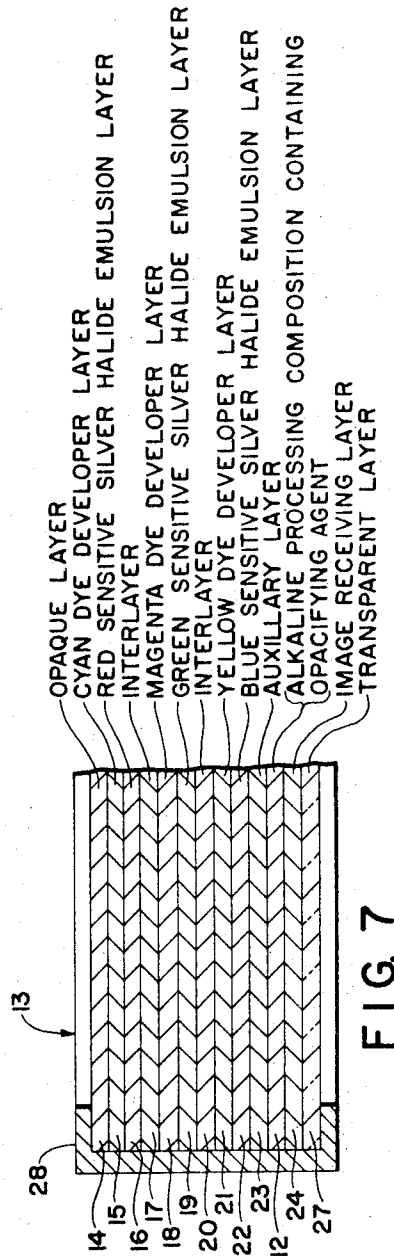


FIG. 7

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3,576,625

PHOTOGRAPHIC DIFFUSION TRANSFER COLOR PROCESSES AND FILM UNIT FOR USE THEREIN

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Int. Cl. G03c 1/40, 7/00

U.S. Cl. 96—3

39 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a permanently structured composite photographic film unit, adapted to provide a color diffusion transfer image, which includes a first dimensionally stable layer; a photosensitive silver halide layer having associated dye image-forming material which is soluble and diffusible, in alkali, at a first pH, as a function of photoexposure of the silver halide layer; a polymeric layer dyeable by the dye image-forming material; a second dimensionally stable layer transparent to incident actinic radiation; and a particulate dispersion of acid material, disposed in an alkaline processing composition permeable layer of the film unit, in a concentration effective to reduce, subsequent to substantial dye transfer image formation, a selected alkaline processing composition possessing the first pH to a second pH at which the dye image-forming material is substantially nondiffusible.

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, in alkaline processing composition, at a first pH, a polymeric layer dyeable by the dye image-forming material, a second dimensionally stable, liquid impermeable layer, transparent to incident radiation and, disposed in an alkaline processing composition permeable layer of the structure, a particulate dispersion of acid material in a concentration effective to reduce a processing composition possessing said first pH to a second pH at which the dye image-forming material is substantially nondiffusible, wherein said acid particles are individually disposed within a polymeric coating permeable to alkaline processing composition at a rate effective to provide contact between said acid and said alkali sufficient to reduce said processing composition from said first pH to said second pH subsequent to substantial transfer image formation; to provide photographic diffusion transfer products comprising a film unit including a composite photosensitive structure of the last-identified type in combination with a rupturable container retaining an aqueous alkaline processing composition; to provide a diffusion transfer film unit of the last-identified type having the container fixedly positioned and extending transverse a leading edge of the composite photosensitive structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and photosensitive silver halide emulsion next adjacent thereto; to provide a diffusion transfer color film unit of the last-identified type including an opacifying agent disposed intermediate the dyeable polymeric layer and the photo-

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sensitive 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 intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent thereto upon application of compressive pressure to the container and distribution of its contents intermediate the layers; and to provide photographic diffusion transfer color processes employing such products.

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

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

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

FIG. 1 is a perspective view of a photographic film unit embodying the invention;

FIGS. 2, 4 and 6 are diagrammatic enlarged cross-sectional views of the film unit of FIG. 1, along section line 2—2, illustrating the association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a 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, and further illustrating, in detail, the arrangement of layers comprising the photosensitive laminate during the three illustrated stages of the transfer process; and

FIGS. 3a and 5a are diagrammatic, still further enlarged cross-sectional views of a functional layer constituting the photosensitive laminate of FIGS. 3 and 5, respectively.

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

unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depth-wise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the image-wise 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-dihydrophenyl 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 process by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, wherein at least two selectively sensitized photosensitive strata, superposed on a single support, are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Specifi-

cally, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for 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 at least 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 preferred 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 non-image-wise dyeing of the image-carrying layer still further imbalances the equilibrium in favor of the additional formation of dye in reduced, diffusible form. Under such circumstances, the transfer image definition, originally carried by the image-receiving layer, will suffer a continuous decrease in the delta between the image's maximum and minimum densities and may, ultimately, result in the image-receiving element's loss of all semblance of image definition; merely becoming a polymeric stratum carrying a relatively uniform overall dyeing.

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

The problems inherent in fabricating a film unit of the type wherein the image-receiving element, the alkaline processing composition and the photosensitive element are maintained in contiguous contact subsequent to dye transfer image formation, for example, a film unit of the type described hereinbefore with reference to aforementioned U.S. Pat. No. 2,983,606, may be effectively obviated by fabrication of a film unit in accordance with the physical parameters specifically set forth in copending U.S. applications Ser. Nos. 622,283; 622,298 and 638,817, filed Mar. 10, Mar. 10 and May 16, 1967, respectively, in the name of Edwin H. Land, now U.S. Pats. Nos. 3,415,644; 3,415,645; and 3,415,646, issued Dec. 10, 1968.

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 specifically require the presence of the stated polymeric acid layer 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 alkaline 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; corbaxymethyl 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 subcoats are employed to help the various polymeric layers adhere to each other during storage and use.

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

It has now been quite unexpectedly discovered that the problems inherent in fabricating a film unit of the

type where the image-receiving element, the alkali processing composition and the photosensitive element are maintained in contiguous contact during processing and subsequent to dye transfer image formation, for example, a film unit of the type described, with reference to aforementioned U.S. Pat. No. 2,983,606, may be effectively obviated in a 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, in alkali, at a first pH, a polymeric layer dyeable by the dye image-forming material, a second dimensionally stable layer transparent to incident actinic radiation, and disposed in an alkaline processing composition permeable layer of the element, a particulate dispersion of acid material in a concentration effective to reduce a processing composition possessing the first pH to a second pH at which the dye image-providing material is substantially nondiffusible, coated with a polymeric coating permeable to alkaline processing composition at a rate effective to provide contact between the acid material and the alkali of the processing composition sufficient to reduce the processing composition, subsequent to substantial dye transfer image formation, from the first pH, at which the dye image-forming material is soluble and diffusible, to the second pH, at which the dye image-forming material is substantially nondiffusible. In combination with the composite structure, a rupturable container retaining a processing composition comprising the first pH is fixedly positioned and extends transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion next adjacent. Although both dimensionally stable layers may be transparent and in such instance, an opacifying agent may be initially dispersed intermediate the dyeable polymeric layer and the next adjacent silver halide emulsion layer, in a quantity sufficient to mask the dye image-forming material, such opacifying agent will preferably be disposed within the processing composition, in a quantity sufficient to mask the dye image-forming material upon distribution of the processing composition intermediate the last stated layers, and, most preferably, the dimensionally stable layer next adjacent the photosensitive silver halide emulsion layer will be opaque with respect to externally derived incident actinic radiation.

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

In general, the acid material may comprise any photographically nondeleterious acid material in solid or liquid state encapsulated within a polymeric wall material permeable to alkaline processing composition at a rate effective to reduce, subsequent to substantial dye transfer image formation, a processing composition possessing the first pH to the second pH. As examples of the extensive number of inorganic, organic and polymeric

acid materials contemplated for employment in the practice of the present invention, mention may be made of: citric acid, succinic acid, oxalic acid, ethylene/maleic anhydride copolymer, sulfonated polystyrene, phosphoric acid, polyphosphoric acid, etc.

Where desired, the acid material selected may comprise an acid precursor which is adapted to generate the requisite acid function during photographic processing as, for example, acid ester, anhydride, lactone, etc., materials which will generate the requisite acid capacity, for example, as a function of hydrolysis upon contact with alkaline photographic processing composition during processing.

The encapsulation with which the preferred embodiment of the present invention is concerned includes all procedures for effectively packaging solid and liquid acid material within a polymeric shell or overcoating comprising a polymeric material possessing the photographically required alkaline processing composition permeation rate and may comprise capsule sizes within arbitrarily set maximum and minimum limits ranging from that of less than micron size to that of several mils depending upon the thickness of the various photographic element layers within which the capsules are to be distributed. In general, the capsule size distribution preferred for employment within the practice of the present invention will generally fall within the range of about 0.1 to 10 microns in diameter and the thickness of the polymeric wall or overcoating will be a function of the permeability characteristics of the polymeric material selected. The choice of polymeric material, which may be made from an extensive number of substances, will be selected according to its compatibility with and retention characteristics for the particular acid material or materials selected, the process of encapsulation chosen and the permeation time delay characteristics required by the elected transfer process.

Among the various encapsulation procedures well known in the art as adapted to effect packaging of liquids and solids as capsular material, mention may be made of: coacervation procedures with respect to the specific details of which an extensive number of patents and literature articles have been published by, for example, National Cash Register Co.; physical procedures such as the well-known spray-coating and drying processes extensively employed in, for example, the pharmaceutical industry and with respect to which extensive technical and industrial literature is available, see, for example, "Spray Drying Principles and Application," E. M. Cook, Drug and Cosmetic Industry, January 1965, 96, 1, pgs. 45-48 and 87-97; interfacial polymerization procedures; and the like; for a compilation of which see, for example, "What Is Happening in Microencapsulation," Flinn et al., Chemical Engineering, Dec. 4, 1967, pgs. 171-178, and the extensive bibliography there set forth and incorporated herein by reference.

As examples of the extensive number of polymeric wall materials contemplated for employment in the practice of the present invention, mention may be made of: polyvinyl alcohols such as cyanoethyl polyvinyl alcohol, hydroxy propyl polyvinyl alcohol, polyvinyl alcohol, etc.; polyvinyl acetals such as polyvinyl formyl, polyvinyl acetal, polyvinyl propional, polyvinyl butyral, p-hydroxyphenyl benzaldehyde acetal of polyvinyl alcohol, β -methoxypropionaldehyde acetal of polyvinyl alcohol, β -ethoxypropionaldehyde acetal of polyvinyl alcohol; cellulose esters such as cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate; cellulose ethers such as hydroxypropylmethyl cellulose, hydroxypropyl cellulose, etc.; sulfonamide/formaldehyde resins; polyvinyl sulfonamides; cellulose tolulenesulfonyl urethanes; etc.

Employing any of the elected procedures for the production of the acid material containing capsules, the photographic effectiveness of the resultant capsules may

be readily determined empirically by distribution of capsules within one or more processing composition permeable layers of the photographic film unit and processing the film unit with alkaline processing composition processing a pH indicator system denoting the requisite alkali concentration change during processing and visibly measuring, through the transparent base, the processing time interval required to effect the requisite dye transfer control pH change. Where desired, opacifying agent, image dyes and the like may be temporarily deleted from the system during such screening in order to obviate, where necessary, masking of a pH indicator system selected.

It will be recognized that the acid material dispersion must remain insulated to a substantial extent from the remainder of the photographic system during storage, exposure and initial processing of the film unit, by means of the polymeric coating, in order to prevent premature pH reduction during processing and, accordingly, the selected acid material must not diffuse out of its encapsulated situs, in a concentration effective to deleteriously effect processing, during the expected life span of the film unit within which it is incorporated.

Although the acid material is preferably dispersed in each alkaline processing composition permeable layer of the film unit in order to prevent a plurality of pH gradients existing in the film unit during processing, if acid material compositions are selected which exhibit undesired residual optical effects with respect to the viewing of a dye transfer image, such compositions will be disposed in the photosensitive element layers masked by the selected opacifying agent. Analogously, structural and/or functional incompatibility with, for example, photosensitive silver halide, sensitizing adjunct, image dye, etc., may be avoided by selective disposition of the elected acid material, such as within the confines of an interlayer or auxiliary layer.

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 alkali, at a first processing composition solvent concentration; 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 the first pH possessing subsequent to processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

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

In such preferred embodiment of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; and each of the dimensionally stable opaque and transparent layers are alkaline solution impermeable, 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.

The selected acid material may be diffusible or non-diffusible, subsequent to substantial transfer image formation, at the election of the operator, and the encapsulating polymeric material may comprise a discontinuous or continuous phase of the layer or layers of which it is a constituent component. Where the polymeric material comprises a continuous phase, the layer containing such should be positioned intermediate the support and associated image-receiving layer and/or intermediate the support and next adjacent associated silver halide/image-dye forming unit, in the optional presence or absence of an alkaline processing composition permeable polymeric spacer intermediate such layer and the respective image-receiving and silver halide/image-dye unit as the case may be as last designated and a polymeric spacer layer possess and expedite development and transfer processing of the film unit. It will be recognized, that in such instances as where a discrete layer of particulate acid material is disposed in the substantial absence of interstitial polymeric material, the spacial location of such layer or layers must be as last designated and a polymeric spacer layer possessing the required hydratability must be present to prevent premature processing composition contact.

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.

Employment of the detailed film unit of the present invention, according to the hereinafter described color diffusion transfer process, specifically provides for the production of a highly stable 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 processing composition pH from a pH at which dye diffusion or transfer 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. Accordingly, by means of the present invention, multicolor transfer images may be provided over an extended processing temperature range which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

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

As illustrated in the drawings, FIG. 1 sets forth a perspective view of the film unit, designated 10, and each of FIGS. 2 through 7 illustrate diagrammatic cross-sectional views of film unit 10, along the stated section lines 2—2, 75

3—3, 5—5, and 7—7, during the various depicted stages in the performance of a photographic diffusion transfer process as detailed hereinafter.

Film unit 10 may comprise rupturable container 11, retaining, prior to processing, aqueous alkaline solution 12 possessing a first pH at which the selected dye developers are soluble and diffusible, and photosensitive laminate 13 including, in order, dimensionally stable, liquid impermeable opaque layer 14, preferably an actinic radiation-opaque vapor permeable flexible sheet material; an alkaline solution permeable cyan dye developer layer 15; an alkaline solution permeable red-sensitive silver halide emulsion layer 16; an alkaline solution permeable interlayer 17; an alkaline solution permeable magenta dye developer layer 18; an alkaline solution permeable green-sensitive silver halide emulsion layer 19; an alkaline solution permeable interlayer 20; an alkaline solution permeable yellow dye developer layer 21; an alkaline solution permeable blue-sensitive silver halide emulsion layer 22; an alkaline solution permeable layer 23, which may contain an auxiliary silver halide developing agent; an alkaline solution permeable image-receiving layer 24; and dimensionally stable, liquid impermeable transparent layer 27, preferably an actinic radiation-transmissive vapor permeable flexible sheet material. Each of alkaline solution permeable layers 15, 16, 17, 18, 19, 20, 21, 22, 23 and 24 possesses a dispersion of particulate acid material 36, the total concentration of which is adapted to effect reduction in the alkalinity of processing solution 12 from the first pH at which the cyan, magenta and yellow dye developers are soluble and diffusible to a second pH at which the dye developers are substantially nondiffusible to image-receiving layer 24, the particles of which comprise polymeric coating 26 permeable by alkaline solution 12 at a rate effective to provide the reduction subsequent to substantial dye transfer image formation in image-receiving layer 24.

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

Rupturable container 11 may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls 29 which are sealed to one another along their longitudi-

dinal 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 at which the dye developers are soluble and diffusible and contains an opacifying agent in a quantity sufficient to mask the dye developers associated with the silver halide emulsions subsequent to processing. In general, in a preferred embodiment the concentration of opacifying agent or agents selected will be that sufficient to prevent further exposure of the film unit's silver halide emulsion or emulsions, by actinic radiation traversing through the dimensionally stable transparent layer, subsequent to distribution of the processing solution intermediate the dyeable polymeric layer and the stated layer next adjacent thereto. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions or the laminate are appropriately protected by incident radiation, at one major surface by the opaque processing 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 emulsions from physical fog formation during processing.

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

Subsequent to exposure, as illustrated by FIGS. 2 and 4, film unit 10 is processed by being passed through opposed suitably gapped rolls 35 in order to apply compressive pressure to frangible container 11 and to effect rupture of longitudinal seal 30 and distribution of alkaline processing composition 12, having a pH and solvent concentration at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer 24 and auxiliary layer 23.

Alkaline processing solution 12 permeates emulsion layers 16, 19 and 22 to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers 15, 18 and 21, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and non-diffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the 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 sufficient portion of the alkali ions comprising aqueous alkaline solution 12 permeates through permeable polymeric coating 26 to contact with acid 36 whereby alkaline solution 12 decreases in pH, as a function of neutralization to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially nondiffusible, to provide thereby a stable multicolor dye transfer image.

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

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

the details therein set forth and are intended to be illustrative only.

Film units similar to that shown in the drawings may be prepared, for example, by coating, in succession, on a gelatin subbed, 5 mil opaque cellulose triacetate 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 and the acid material citric acid encapsulated in cellulose acetate dispersed in gelatin and coated at a coverage of about 150 mgs./ft.² of dye, about 110 mgs./ft.² of acid and about 200 mgs./ft.² of gelatin;

(2) A red-sensitive gelatino-silver iodobromide emulsion and the acid material citric acid encapsulated in cellulose acetate coated at a coverage of about 200 mgs./ft.² of silver, about 110 mgs./ft.² of acid and about 100 mgs./ft.² of gelatin;

(3) A layer of the acid material citric acid encapsulated in cellulose acetate and dispersed in gelatin and coated at a coverage of about 110 mgs./ft.² of acid and about 200 mgs./ft.² of gelatin;

(4) A layer of the magenta dye developer 2-(p-[β -hydroquinonyl-ethyl] - phenylazo)-4-isopropoxy-1-naphthol and the acid material citric acid encapsulated in cellulose acetate, dispersed in gelatin and coated at a coverage of 70 mgs./ft.² of dye, about 110 mgs./ft.² of acid and about 100 mgs./ft.² of gelatin;

(5) A green-sensitive gelatino-silver iodobromide emulsion and the acid material citric acid encapsulated in cellulose acetate coated at a coverage of about 100 mgs./ft.² of silver, about 110 mgs./ft.² of acid and about 60 mgs./ft.² of gelatin;

(6) A layer containing 4'-methylphenyl hydroquinone and the acid material citric acid encapsulated in cellulose acetate, dispersed in gelatin and coated at a coverage of about 25 mgs./ft.² of 4'-methylphenyl hydroquinone, about 110 mgs./ft.² of acid 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 - hexylcarbox-amido)-1-phenyl-5-pyrazolone and the acid material citric acid encapsulated in cellulose acetate, dispersed in gelatin and coated at a coverage of about 40 mgs./ft.² of dye, about 110 mgs./ft.² of acid and about 50 mgs./ft.² of gelatin;

(8) A blue-sensitive gelatino-silver iodobromide emulsion and the acid material citric acid encapsulated in cellulose acetate coated at a coverage of about 60 mgs./ft.² of silver, about 110 mgs./ft.² of acid and about 50 mgs./ft.² of gelatin;

(9) A layer of the acid material citric acid encapsulated in cellulose acetate and dispersed in gelatin and coated at a coverage of about 110 mgs./ft.² of acid and about 30 mgs./ft.² gelatin; and

In each instance the cellulose acetate capsular wall thickness may comprise about 0.1-5 microns.

Then a transparent 5 mil. cellulose triacetate film base may be coated with 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:

Grams

Water—100 cc.

Potassium hydroxide ----- 11.2

Grams

Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name	
Natrasol 250]	3.4
N-benzyl- α -picolinium bromide -----	1.5
Benzotriazole -----	1.0
Titanium dioxide -----	40.0

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 cellulose triacetate 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. Subsequent to processing, the multi-color dye transfer image formation may be viewed through the transparent cellulose triacetate 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 ninety seconds.

The pH and solvent concentration of the alkaline processing solution initially employed must be an alkaline 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 group of dye developers, most particularly desirable dye developers are soluble at pH's above 9 and relatively insoluble at pH's below 9, in reduced form, 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 provide maintenance of the spread composition as a structurally stable layer of the laminate, subsequent to distribution, it is not necessary that such agent be employed as a component of the composition.

The dimensionally stable support layers referred to may comprise any of the various types of conventional opaque and transparent rigid or flexible materials possessing the requisite liquid impermeability and vapor transmissivity denoted, 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; and cellulose derivatives such as cellulose, acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

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-benzyl-

aminophenol 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, alkalies, 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 nitro-carboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfolbenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl- α,β -unsaturated carboxamides and copolymers of N-alkyl- α,β -carboxamides with N-hydroxyalkyl - α,β - unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinylphthalimide and α,β -unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β -unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α,β -unsaturated carboxylic acids and alkyl esters of α,β -unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl- α,β -unsaturated carboxamides with α,β -unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl- α,β -unsaturated carboxamides with

α,β -unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,264; and the like.

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

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

Although the invention has been discussed in detail throughout employing dye developers, the preferred dye image-providing materials, it will be readily recognized that other, less preferred, dye image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049, issued July 28, 1953; 2,661,293, 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 described in U.S. Pats. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography, Its Materials and Processes*, 6th ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the se-

lected 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*.

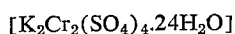
Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion 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, such as speed-increasing compounds of the quaternary ammonium type, as described in U.S. Pats. Nos. 2,271,623; 2,288,226; and 2,334,864; or of the polyethyleneglycol type, as described in U.S. Pat. No. 2,708,162; or of the preceding combination, as described in U.S. Pat. No. 2,886,437; or the thiopolymers, as described in U.S. Pats. Nos. 3,046,129 and 3,046,134.

The emulsions may also be stabilized with the salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, as described in U.S. Pats. Nos. 2,566,245 and 2,566,263; the mercury compounds of U.S. Pats. Nos. 2,728,663; 2,728,664 and 2,728,665; the triazoles of U.S. Pat. No. 2,444,608; the azindines of U.S. Pats. Nos. 2,444,605; 2,444,606; 2,444,607; 2,450,397; 2,444,609; 2,713,541; 2,743,181; 2,716,062; 2,735,769; 2,756,147; 2,772,164; and those disclosed by Burr in "Zwiss, Pot.," volume 47, 1952, pages 2-28; the disulfides of Belgian Pat. No. 569,317; the benzothiazolium compounds of U.S. Pats. Nos. 2,131,038 and 2,694,716; the zinc and cadmium salts of U.S. Pat. No. 2,839,405; and the mercapto compounds of U.S. Pat. No. 2,819,965.

Hardening agents such as inorganic agents providing polyvalent metallic atoms, specifically polyvalent aluminum or chromium ions, for example, potash alum $[K_2Al_2(SO_4)_4 \cdot 24H_2O]$ and chrome alum



and inorganic agents of the aldehyde type, such as formaldehyde, glyoxal, mucochloric, etc.; the ketone type such as diacetyl; the quinone type; and the specific agents described in U.S. Pats. Nos. 2,080,019; 2,725,294; 2,725,295; 2,725,305; 2,726,162; 2,732,316; 2,950,197; and 2,870,013, may be incorporated, where desired and compatible, in the selected coating solution compositions.

Coating solution compositions employed to fabricate the respective strata of the film unit may contain one or more coating aids, where desired and compatible, such as saponin; a polyethyleneglycol of U.S. Pat. No. 2,831,766; a polyethyleneglycol ether of U.S. Pat. No. 2,719,087; a taurine of U.S. Pat. No. 2,739,891; a maleopimarate of U.S. Pat. No. 2,823,123; and amino acid of U.S. Pat. No. 3,038,804; a sulfosuccinamate of U.S. Pat. No. 2,992,108; or a polyether of U.S. Pat. No. 2,600,831; or a gelatin plasticizer such as glycerin; a dihydroxyalkane of U.S. Pat. No. 2,960,404; a bis-glycolic acid ester of U.S. Pat. No. 2,904,434; a succinate of U.S. Pat. No. 2,940,854; or a polymeric hydrosol of U.S. Pat. No. 2,852,386.

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in U.S. Pats. Nos. 2,253,078; 2,276,322; 2,276,323; 2,281,703; 2,310,223; 75

2,311,058; 2,311,059; 2,414,208; 2,461,023; 2,484,456; 2,538,257; 2,579,016; 2,614,931; 2,624,674; 2,632,704; 2,642,420; 2,678,884; 2,691,582; 2,725,296; 2,753,264; and the like.

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 primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

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

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

What is claimed is:

1. A photographic film unit which is adapted to be

processed by passing said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive element comprising a composite structure containing a plurality of layers including a first dimensionally stable, liquid impermeable layer opaque to incident actinic radiation; an alkaline processing composition permeable photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is soluble and diffusible, in alkali, at a first pH, as a function of photo-exposure of its associated silver halide emulsion layer; an alkaline processing composition permeable polymeric layer dyeable by said dye image-forming material; a second dimensionally stable, liquid impermeable layer transparent to incident actinic radiation; a dispersion of acid material disposed in an alkaline processing composition permeable layer of the composite structure in a concentration effective to reduce an alkaline processing composition possessing said first pH at which said dye image-forming material is soluble and diffusible to a second pH at which said dye image-forming material is substantially nondiffusible, said acid material particles having associated therewith a polymeric coating permeable to alkaline processing composition at a rate effective to provide contact between alkali of said processing and said acid material sufficient, subsequent to substantial dye transfer image formation by diffusion transfer processing, to decrease said pH at which said dye image-forming material is soluble and diffusible to said second pH at which said dye image-forming material is substantially nondiffusible; and means securing said layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing solution possessing said first pH and an opacifying agent in a quantity sufficient to mask said dye image-providing material fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's alkaline processing solution between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

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

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

4. A photographic film unit as defined in claim 1 wherein said dye image-providing material is a dye which is a silver halide developing agent.

5. A photographic film unit as defined in claim 4 wherein said dye is substantially soluble and diffusible only in the reduced form at said first pH and is substantially nondiffusible in said reduced form at said second pH.

6. A photographic film unit as defined in claim 4 wherein said opacifying agent is present in a quantity sufficient to prevent exposure of said silver halide emulsion during processing in the presence of radiation actinic thereto and incident on said distributed processing solution.

7. A photographic film unit as defined in claim 4 wherein said opacifying agent is actinic radiation reflective.

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

9. A photographic film unit as defined in claim 4 wherein said aqueous alkaline solution contains a film-forming polymeric material.

10. A photographic film unit as defined in claim 4 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 a predetermined color associated therewith, each of said dyes soluble and diffusible, in alkali, at said first pH.

11. A photographic film unit as defined in claim 10 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.

12. A photographic film unit as defined in claim 11 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.

13. A photographic film unit as defined in claim 11 which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination, a composite structure containing a plurality of layers including, as essential layers, in sequence, a dimensionally stable, liquid impermeable opaque layer; an alkaline solution permeable polymeric layer containing cyan dye; an alkaline solution permeable red-sensitive silver halide emulsion layer; an alkaline solution permeable polymeric layer containing magenta dye; an alkaline solution permeable green-sensitive silver halide emulsion layer; an alkaline solution permeable polymeric layer containing yellow dye; an alkaline solution permeable 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; a dimensionally stable, liquid impermeable transparent layer; a dispersion of particulate acid material disposed in at least one alkaline solution permeable polymeric layer in a concentration effective to reduce an alkaline processing solution having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible, to a second pH at which said dyes are substantially nondiffusible, said acid particles possessing a polymeric coating permeable to alkaline processing solution at a rate effective to provide, subsequent to dye transfer image formation by diffusion transfer processing, reduction of alkaline processing solution from said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible to said second pH at which said dyes are substantially insoluble; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing solution possessing said first pH in a quantity sufficient to provide said first concentration of water 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.

14. A photographic film unit as defined in claim 13 wherein said first pH is above 9 and said second pH is below 9.

15. A photographic film unit as defined in claim 14 wherein said opacifying agent is actinic radiation reflective.

16. A photographic film unit as defined in claim 15 wherein said opacifying agent is titanium dioxide.

17. A photographic film unit as defined in claim 13 wherein said particulate acid material is disposed in at least one of said cyan, magenta and yellow dye-containing layers.

18. A photographic film unit as defined in claim 17 wherein said particulate acid material is disposed in each of said cyan, magenta and yellow dye-containing layers and each of said red-sensitive, green-sensitive and blue-sensitive emulsion layers.

19. A photographic film unit as defined in claim 10 wherein said acid material is disposed in at least one of said emulsion layers.

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

- (a) exposing a photographic film unit which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which includes, in combination, a composite structure comprising a first dimensionally stable, liquid impermeable layer opaque to incident actinic radiation; an alkaline processing composition permeable photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is soluble and diffusible, in alkali, at a first pH, as a function of photoexposure of its associated silver halide emulsion layer; an alkaline processing composition permeable polymeric layer dyeable by said dye image-forming material; a dispersion of acid material disposed in an alkaline processing composition permeable layer of the composite structure in a concentration effective to reduce an alkaline processing composition possessing said first pH at which said dye image-forming material is soluble and diffusible to a second pH at which said dye image-forming material is substantially nondiffusible, said acid material particles having associated therewith a polymeric coating permeable to alkaline processing composition at a rate effective to reduce, subsequent to substantial dye transfer image formation by diffusion transfer processing, alkaline processing composition possessing said first pH at which said dye image-forming material is soluble and diffusible to a second pH at which said dye image-forming material is substantially nondiffusible; a second dimensionally stable, liquid impermeable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and a rupturable container retaining an alkaline processing solution possessing said first pH and an opacifying agent in a quantity sufficient to mask said dye image-forming material fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's alkaline processing solution between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to said container;
- (b) applying compressive force to said rupturable container to effect unidirectional discharge of said container's alkaline processing solution between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;
- (c) effecting thereby development of said silver halide emulsion and, as a result of said development, forming an imagewise distribution of mobile dye image-forming material associated with said emulsion as a function of the point-to-point degree of emulsion exposure;
- (d) transferring, by diffusion, at least a portion of said imagewise distribution of said mobile dye image-forming material to said polymeric layer dyeable by said dye image-forming material to provide a dye image thereto in terms of said distribution;
- (e) contacting, subsequent to substantial dye transfer image formation, a sufficient portion of the ions of said alkaline processing solution with said acid material to thereby reduce said first pH at which said dye image-forming material is soluble and diffusible to a

second pH at which said dye image-forming material is substantially nondiffusible; and

- (f) maintaining said composite structure intact subsequent to said processing.

21. A process as defined in claim 20 wherein said first dimensionally stable layer is transparent to actinic radiation.

22. A process as defined in claim 21 wherein said opacifying agent is initially present intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto.

23. A process as defined in claim 20 wherein said acid material dispersion is disposed in said silver halide emulsion.

24. A process as defined in claim 20 wherein said dye image-forming material is a dye which is a silver halide developing agent.

25. A process as defined in claim 24 wherein said dye is substantially soluble and diffusible only in the reduced form at said first pH and is substantially nondiffusible in said reduced form at said second pH.

26. A process as defined in claim 24 wherein said dye and said acid material are disposed in a separate alkaline processing composition permeable layer contiguous the associated silver halide emulsion layer intermediate that layer and the first dimensionally stable layer.

27. A process as defined in claim 24 wherein said opacifying agent is present in a quantity sufficient to prevent exposure of said silver halide emulsion during processing in the presence of radiation actinic thereto and incident on said processing solution distributed between said dyeable polymeric layer and said silver halide emulsion layer next adjacent thereto.

28. A process as defined in claim 24 wherein said opacifying agent is actinic radiation reflective.

29. A process as defined in claim 28 wherein said opacifying agent is titanium dioxide.

30. A process as defined in claim 28 wherein said aqueous alkaline solution contains a film-forming polymeric material.

31. A process as defined in claim 24 including the step of separating said container from said composite structure subsequent to substantial transfer image formation.

32. A process as defined in claim 24 which comprises, in combination, the steps of:

- (a) exposing a photographic film unit which is adapted to be processed by passage through a pair of juxtaposed pressure-applying members and which includes, in combination, a composite structure comprising a first dimensionally stable, liquid impermeable layer opaque to incident actinic radiation; at least two selectively sensitized, alkaline processing solution permeable 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 alkali, at a first pH; an alkaline processing permeable polymeric layer dyeable by said dye; a particulate dispersion of acid material disposed in an alkaline processing solution permeable layer of the composite structure in a concentration effective to reduce the alkalinity of an alkaline processing solution possessing a first pH at which said dyes are soluble and diffusible to a second pH at which said dyes are substantially nondiffusible, said acid material particles possessing a polymeric coating permeable to alkaline processing solution at a rate effective to reduce, subsequent to substantial dye transfer image formation, the alkalinity of said processing solution from said first pH at which said dyes are soluble and diffusible to said second pH at which said dyes are substantially nondiffusible; a second dimensionally stable, liquid impermeable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an 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 discharge of said container's processing solution between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to said container;

- (b) applying compressive force to said rupturable container to effect discharge of said container's alkaline processing solution between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;
- (c) effecting thereby development of each of said silver halide emulsions;
- (d) immobilizing the dye associated with each of said emulsion layers as a result of development;
- (e) forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of emulsion exposure;
- (f) transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dyes to said polymeric layer dyeable by said dyes to provide thereto a dye image;
- (g) contacting, subsequent to substantial dye transfer image formation and preceding said substantial dye transfer image degradation, a sufficient portion of the ions of said alkaline processing solution with said acid material to thereby reduce said first pH at which said dyes are soluble and diffusible to said second pH at which said dyes are substantially nondiffusible; and
- (h) maintaining said composite structure intact subsequent to said processing.

33. A process as defined in claim 32 wherein each of said selectively sensitized silver halide emulsion layers possess predominant spectral sensitivity to a separate region of the spectrum and the dye associated with each of said emulsion layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion.

34. A process of forming transfer images in color as defined in claim 33 which comprises, in combination, the steps of:

- (a) exposing a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination, a photosensitive element comprising a laminate containing a plurality of layers including a dimensionally stable alkaline solution impermeable opaque layer; an alkaline solution permeable red-sensitive silver halide emulsion layer having associated therewith cyan dye; an alkaline solution permeable green-sensitive silver halide emulsion layer having associated therewith magenta dye; an alkaline solution permeable 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; a dispersion of particulate acid material disposed in at least one alkaline solution permeable polymeric layer in a concentration effective to reduce an alkaline solution having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible to a second pH at which said dyes are substantially nondiffusible, said acid particles possessing a polymeric coating perme-

able to alkaline processing solution, at a rate effective to provide, subsequent to substantial transfer dye image formation, reduction of an alkaline processing solution having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible to a second pH at which said dyes are substantially insoluble and nondiffusible; a dimensionally stable alkaline solution impermeable transparent layer; and a rupturable container retaining an aqueous alkaline processing solution possessing said first pH 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;

- (b) applying compressive force to said rupturable container to effect unidirectional discharge of said container's alkaline solution between said alkaline solution permeable and dyeable polymeric layer and said blue-sensitive silver halide emulsion layer;
- (c) effecting thereby development of the latent image contained in each of said red, green and blue-sensitive silver halide emulsions;
- (d) immobilizing said yellow, magenta and cyan dyes as a result of development of their respective associated silver halide emulsions;
- (e) forming thereby an imagewise distribution of immobile yellow, magenta and cyan dyes as a function of the point-to-point degree of exposure of their respective associated silver halide emulsions;
- (f) transferring, by diffusion, at least a portion of each of said imagewise distributions of mobile dye to said alkaline solution permeable polymeric layer dyeable by said dyes to provide thereto a multicolor dye image;
- (g) transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline solution to said acid material 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; and
- (h) maintaining said laminate intact subsequent to said processing.

35. A process as defined in claim 34 wherein said first pH is above 9 and said second pH is below 9.

36. A process as defined in claim 34 including the step of separating said container from said laminate subsequent to substantial image formation.

37. A process as defined in claim 34 wherein said opacifying agent is radiation reflective.

38. A process as defined in claim 37 wherein said opacifying agent is titanium dioxide.

39. A process as defined in claim 34 wherein said particulate acid material is dispersed in each alkaline solution permeable layer of said photosensitive laminate.

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