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Land [45] **Mar. 7, 1972**

[54] INTEGRAL NEGATIVE/POSITIVE COLOR DIFFUSION TRANSFER PROCESS FILM UNIT EMPLOYING IN-SITU GENERATED VISIBLE LIGHT-REFLECTING AGENT

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[52] **U.S. Cl.** ....**96/3,** 96/29 D, 96/84 R, 96/76 C
[51] **Int. Cl.** **G03c 7/00,** G03c 5/54, G03c 1/84
[58] **Field of Search** ....96/3, 29 D, 84 R

[56] **References Cited**

UNITED STATES PATENTS

3,415,644 12/1968 Land..96/3

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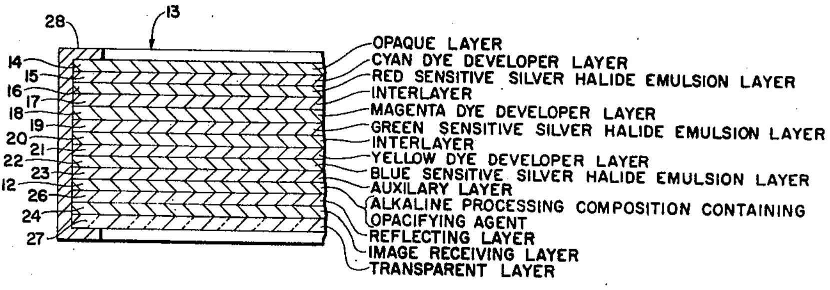
[57] ABSTRACT

This application is directed, in general, to an integral negative/positive color diffusion transfer process film unit which includes, in order, an opaque layer, a photosensitive silver halide layer having associated dye transfer image-forming material, a layer comprising a light-reflecting agent precursor which comprises, upon contact with a processing composition, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light-reflecting agent, a polymeric layer adapted to be dyed by the dye transfer image-forming material, a transparent layer, and means for distributing a processing composition between the dyeable polymeric layer and the photosensitive silver halide layer, and to specified diffusible transfer color processes employing such a film unit.

42 Claims, 7 Drawing Figures



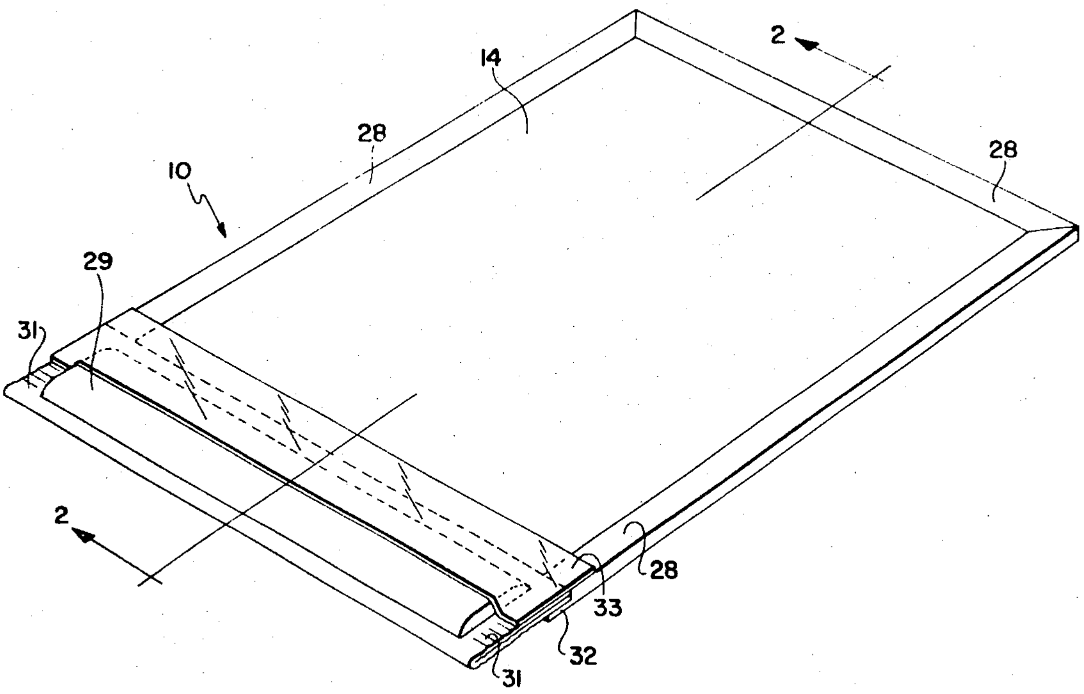


FIG. 1

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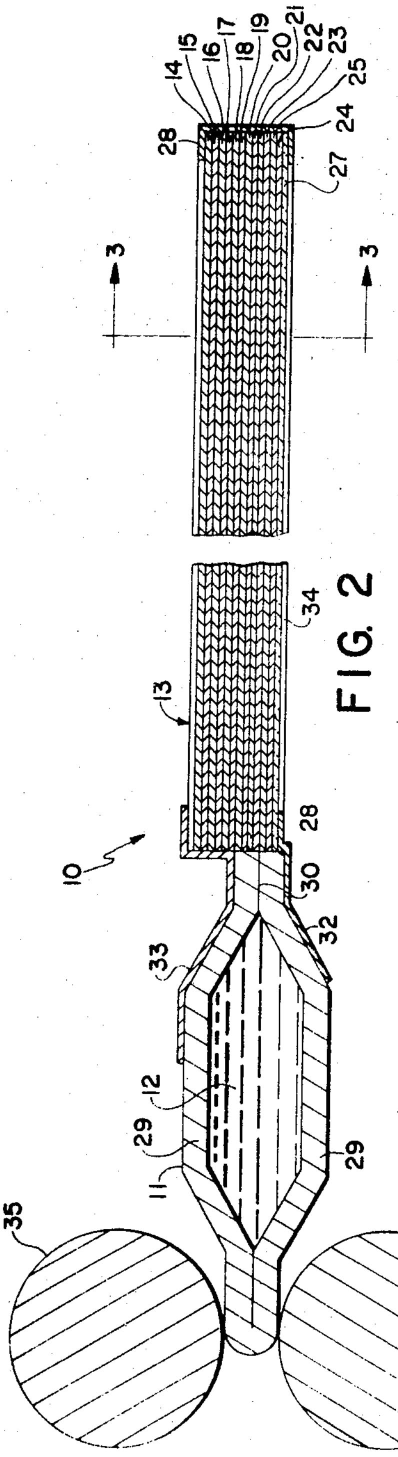

FIG. 2

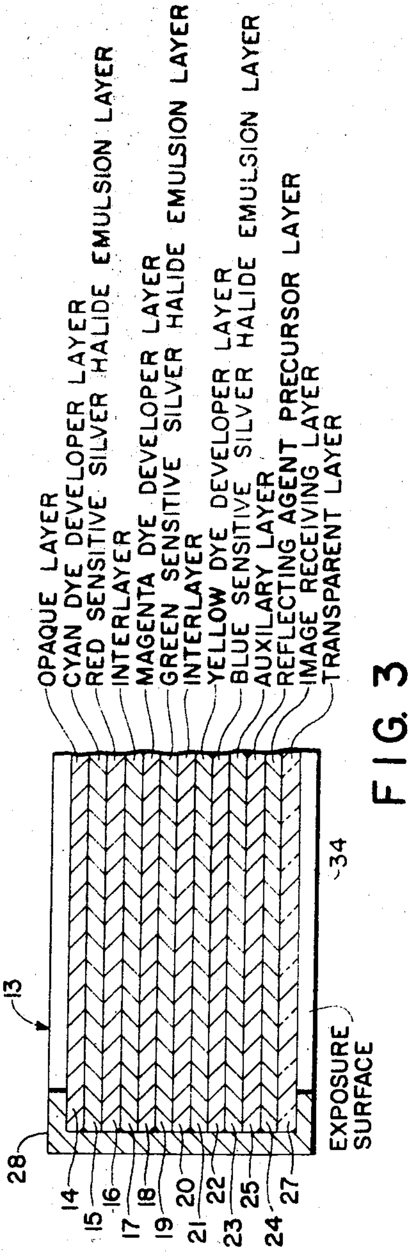

FIG. 3

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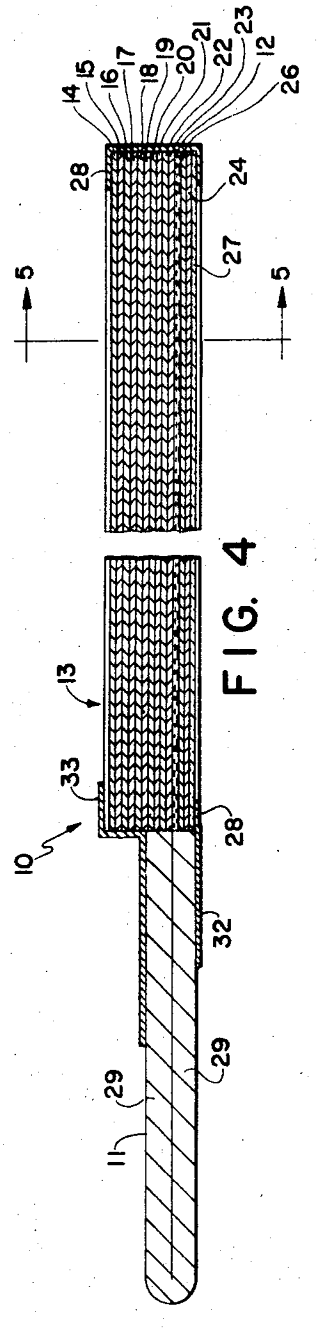

FIG. 4

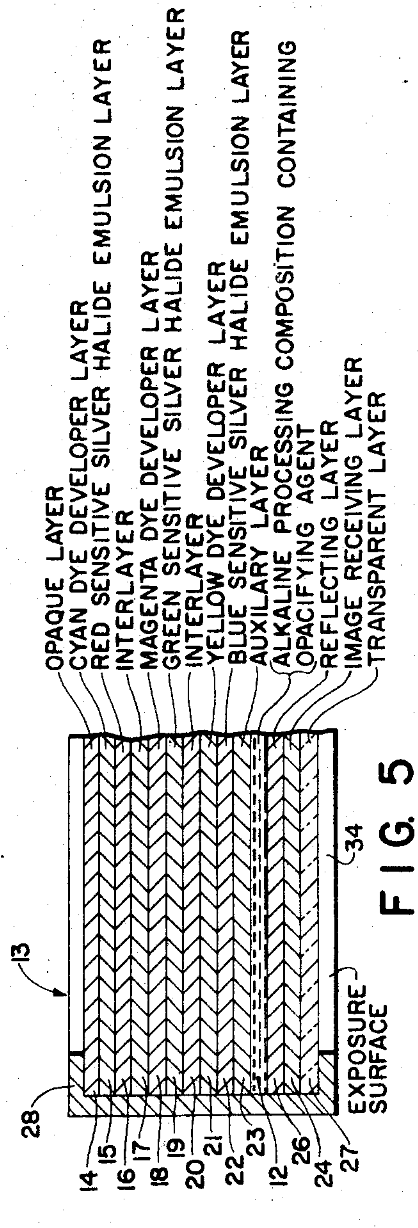

FIG 5

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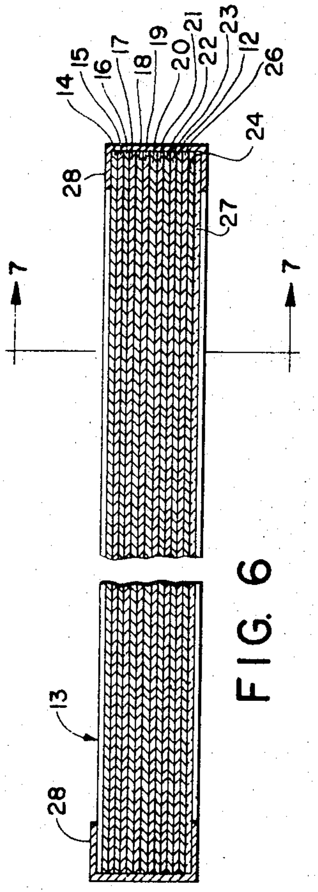

FIG. 6

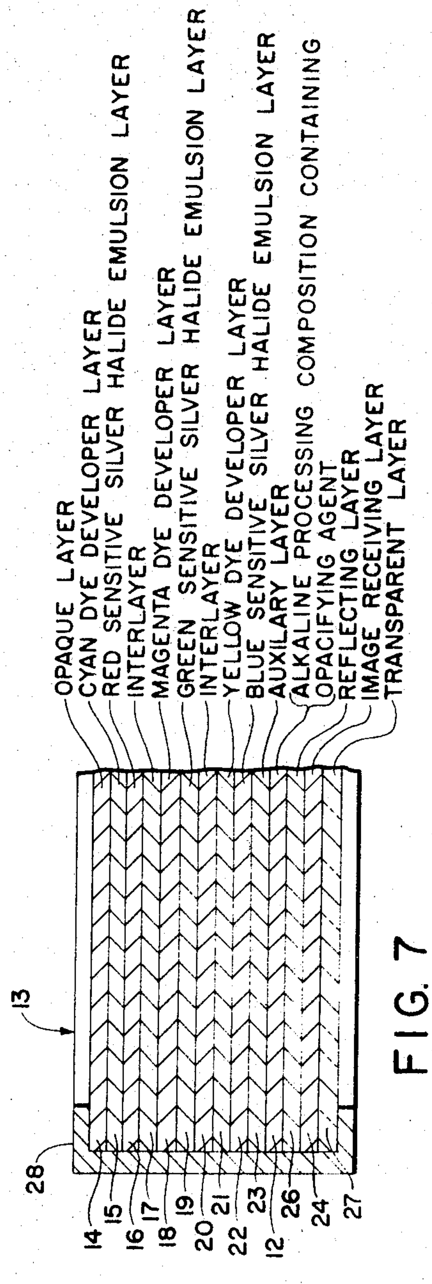

FIG. 7

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INTEGRAL NEGATIVE/POSITIVE COLOR DIFFUSION TRANSFER PROCESS FILM UNIT EMPLOYING IN-SITU GENERATED VISIBLE LIGHT-REFLECTING AGENT

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

The primary objects of the 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 dimensionally stable opaque layer, a photosensitive silver halide emulsion layer having a dye image-forming material associated therewith which is soluble and diffusible in processing composition as a function of exposure of the photosensitive silver halide emulsion layer to incident actinic radiation, a layer permeable to processing composition diffusible dye image-forming material comprising a reflecting agent precursor in a quantity sufficient to mask dye image-forming material associated with the photosensitive silver halide emulsion layer subsequent to and as a function of processing, a polymeric layer dyeable by the dye image-forming material, and a dimensionally stable transparent layer; to provide photographic diffusion transfer products comprising a film unit including a photosensitive laminate, of the last-identified type, in combination with a rupturable container retaining a processing composition and preferably containing dispersed therein an opacifying agent in a quantity effective to prevent exposure of the photosensitive silver halide emulsion layer in the presence of actinic radiation incident on the dimensionally stable transparent layer, the reflecting agent preferably generated in a quantity sufficient to mask both the opacifying agent and dye image-forming material associated with the photosensitive silver halide emulsion layer subsequent to diffusion transfer processing; to provide a diffusion transfer film unit, of the last-identified type, having the container fixedly positioned and extending transverse a leading edge of the photosensitive composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate opposed surfaces of the dyeable polymeric layer and the photosensitive silver halide emulsion and associated dye image-forming material next adjacent thereto, and, in the preferred embodiment, intermediate the opposed surfaces of the processing composition permeable reflecting agent precursor containing layer and the photosensitive silver halide emulsion layer and associated dye image-forming material next adjacent thereto; 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; and

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

As disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961, a photosensitive element containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion may be exposed and wetted by a liquid-processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid-processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid-processing composition, positioned intermediate the photosensitive element and the image-receiving layer, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

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

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

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8 percent, 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 nonimagewise dyeing of the image-carrying layer will 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 U.S. Pat. Nos. 3,415,644; 3,415,645; and 3,415,646, issued Dec. 10, 1969, respectively, in the name of Edwin H. Land.

Specifically an integral photographic film unit particularly adapted for the production of a dye transfer image of unexpectedly improved stability and other properties, by a color diffusion transfer process will be constructed, for example, in accordance with aforementioned U.S. Pat. No. 3,415,644, to include a photosensitive element comprising a laminate having, in sequence, as essential layers, a dimensionally stable opaque layer; a photosensitive silver halide emulsion layer having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH; an alkaline solution permeable polymeric layer dyeable by the dye image-providing material; a polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial transfer dye image formation, of a selected processing solution having the first pH to a second pH at which said dye image-providing material is insoluble and nondiffusible; and a dimensionally stable transparent layer. In combination with the laminate, a rupturable 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.

Film units fabricated in accordance with the parameter set forth above specifically disclose the presence of the stated polymeric acid component to effect in situ process adjustment of the film unit's operational pH range.

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

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

As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14. The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid be accurately so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer must be kept at a functional transfer level, for example, 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to a pH below that at which dye transfer may be accomplished, for example, at least about 11 and preferably about pH 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer.

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

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

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

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

Specifically, it has been quite unexpectedly discovered that an integral photographic film unit of simplified construction and particularly adapted for the production of dye transfer images of unexpectedly improved stability and other desirable properties by a color diffusion transfer process will be constructed to include a photosensitive element comprising a composite structure possessing, in sequence, as essential layers: a dimensionally stable opaque layer; a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is soluble and diffusible in processing composition as a function of the point-to-point degree of exposure of the photosensitive silver halide emulsion layer to incident actinic radiation; a layer permeable to processing composition diffusible dye image-forming material which comprises a reflecting agent precursor present in a concentration sufficient to mask dye image-forming material associated with the photosensitive silver halide emulsion layer subsequent to and as a function of processing; a polymeric layer dyeable by the dye image-forming material; and a dimensionally stable transparent layer. In combination with the composite structure, a rupturable container retaining a processing composition is fixedly positioned and extends transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion layer and associated dye image-forming material next adjacent. In the preferred embodiment of the present invention, an opacifying agent is initially disposed in the processing composition retained by the rupturable container and the container is fixedly positioned and extends transverse the leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate opposed surfaces of the processing composition permeable reflecting agent precursor containing layer and the photosensitive silver halide emulsion layer and associated dye image-forming material next adjacent and the opacifying agent is present in a concentration which is effective, upon distribution, to prevent exposure of the photosensitive silver halide emulsion layer in the presence of actinic radiation incident on the dimensionally stable transparent layer and to mask dye image-forming material associated with the silver halide emulsion layer and the reflecting agent generated is also present in a concentration sufficient to mask distributed opacifying agent.

In a preferred embodiment of the present invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, the dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsion strata each having dye image-providing materials of predetermined color associated therewith which are soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective associated silver halide emulsion strata; a polymeric layer permeable by alkaline processing composition solubilized dye image-providing materials which contain a reflecting agent precursor in a quantity sufficient to mask the dye image-providing materials associated with the selectively sensitized silver halide emulsion strata subsequent to processing; a polymeric layer dyeable by the dye image-providing material; and the dimensionally stable transparent layer.

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.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at a 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 reflecting agent precursor containing layer is about 0.05 to 0.25 micron in thickness; the 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.

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

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

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

Film unit **10** comprises rupturable container **11**, retaining, prior to processing, aqueous alkaline solution **12**, and photosensitive laminate **13** including, in order, dimensionally stable opaque layer **14**, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer **15**; red-sensitive silver halide emulsion layer **16**; interlayer **17**; magenta dye developer layer **18**; green-sensitive silver halide emulsion layer **19**; interlayer **20**; yellow dye developer layer **21**; blue-sensitive silver halide emulsion layer **22**; auxiliary layer **23**, which may contain an auxiliary silver halide developing agent; reflecting agent precursor layer **25**; image-receiving layer **24**; and dimensionally stable transparent layer **27**, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of laminate **13** may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the laminate at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer **24** and the silver halide emulsion layer next adjacent thereto, for example, reflecting agent precursor intermediate layer **25** 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. Pat. Nos. 2,543,181; 2,634,886; 3,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing solution **12** is retained. The longitudinal marginal seal **30** is made weaker than the end seals **31** so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **29** of the container.

As illustrated in FIGS. **1**, **2** and **4**, container **11** is fixedly positioned and extends transverse a leading edge of photosensitive laminate **13** whereby to effect unidirectional discharge of the container's contents **12** between image-receiving layer **24** and the stated layer next adjacent thereto, upon application of compressive force to container **11**. Thus, container **11**, as illustrated in FIG. **2**, is fixedly positioned and extends transverse a leading edge of laminate **13** with its longitudinal marginal seal **30** directed toward the interface between image-receiving layer **24** and auxiliary layer **23**. As shown in FIGS. **1**, **2** and **4**, container **11** is fixedly secured to laminate **13** by extension **32** of tape **28** extending over a portion of one wall **29** of the container, in combination with a separate retaining member such as illustrated retaining tape **33** extending over a portion of the other wall **29** of the container and a portion of laminate **13**'s surface generally equal in area to about that covered by tape **28**.

As illustrated in FIG. **6**, extension flap **32** of tape **28** is preferably of such area and dimensions that upon, for example, manual separation of container **11** and tape **33**, subsequent to distribution of processing composition **12**, from the remainder of film unit **10**, flap **32** may be folded over the edge of laminate **13**, previously covered by tape **33**, in order to facilitate maintenance of the laminate's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer **27**.

The fluid contents of the container comprise an aqueous alkaline solution having a pH and solvent concentration at which the dye developers are soluble and diffusible and contains an opacifying agent in a quantity sufficient, upon distribution, effective to prevent exposure of photosensitive silver halide emulsion layers **16**, **19** and **22** by actinic radiation incident on dimensionally stable transparent layer **27** during processing in the presence of such radiation. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of laminate are appropriately protected by incident radiation, at one major surface of 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 reflecting agent generated, 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 reflecting agent may be employed, it is preferred that a reflecting 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 reflecting 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 preferred reflecting agent precursors adapted for employment in the practice of the present invention mention may be made of ionizable, white, inorganic, visible light reflecting pigment generating salts such as barium chloride, zirconium chloride, and the like, the cation of which upon contact with sulfate ions present in the selected processing composition and generally derived from ionizable salts such as sodium sulfate, etc., form reflecting agent pigment salts such as barium sulfate, zirconium sulfate, and the like; ionizable salts such as zinc sulfate and the like, the cation of which upon contact the anion of ionized sodium or potassium hydroxide present in the selected processing composition form reflecting agent pigment such as zinc oxide and the like; ionizable salts such as zinc acetate and the like, the cation of which upon contact with sulfide ions present in the selected processing compositions and generally derived from ionizable salts such as sodium sulfide, etc., form reflecting agent such zinc sulfide and the like; etc. It will be recognized that where desired the functional cation of the exemplary materials may optionally be disposed in the processing composition employed and the anion initially disposed in the processing composition permeable layer; that such adjuncts as are disclosed as initially disposed in the processing composition alternatively may be selectively disposed within the film unit insulated from functional generation of the reflecting agent preceding exposure of the film unit, for example, preceding processing composition solubilization of such adjunct and/or required diffusion and contact between the reactants intermediate the image-receiving layer and next adjacent photosensitive silver halide emulsion layer; and that reflecting agent may be in part generated within the image-receiving and/or next adjacent silver halide emulsion strata of the film unit.

A particularly preferred embodiment of the present invention employs a metathetical reaction between selected precursor salts, the respective exchange of cations or anions of which provide for the simultaneous generation of two separate reflecting agents such as, for example, the metathetical generation of both barium sulfate and zinc sulfide white, inorganic salt pigments by the in situ reaction of substantially colorless barium sulfide and zinc sulfate precursor salts. Such preferred embodiments provide for the in process generation of an increased quantity of reflecting agent per unit volume of precursor salts employed.

A particularly preferred reflecting agent comprises barium sulfate due to its highly effective reflection properties.

In general, in the preferred embodiments, the reflecting agent precursor selected will, as previously denoted, comprise a precursor specifically adapted to provide a substantially white inorganic pigment which reflects visible light and, in particularly preferred embodiments, will be coated at a coverage effective to provide 200 to 1,000 mgs./ft.^{2} reflecting agent, as a result of processing, which coverage is generally sufficient, subsequent to processing, to mask opacifying agent distributed in the processing composition and any residual dye developer present intermediate the image-receiving layer and the dimensionally stable opaque layer.

Where desired, reflecting agent precursor or precursors may be distributed in whole or in part within a processing composition permeable polymeric matrix such as gelatin and/or any other such polymeric matrixes as are specifically denoted throughout the specification as suitable for employment as a matrix binder and may be distributed in one or more of the film unit layers which may be separated or contiguous and should be intermediate the image-receiving layer and dimensionally stable opaque layer, provided that its distribution and concentration is effective to provide the denoted post processing masking function, and that in whole or in part the resultant generated reflecting agent may be ultimately disposed within the processing composition residuum located intermediate the image-receiving layer and next adjacent silver halide emulsion strata and associated dye image-forming material.

As examples of opacifying agents adapted for employment in the practice of the present invention, mention may be made of opacifying pigments and opacifying dyes and mixtures of such dyes and/or pigments preferably dyes and pigments of black coloration and most preferably black pigments such as carbon black, iron oxide, titanium (III) oxide, titanium (III) hydroxide, and the like.

Preferred opacifying agent or agents will possess the maximum opacifying capacity per unit weight, be photographically nondeleterious and substantially nondiffusible during and subsequent to distribution of the processing composition containing same. A particularly preferred opacifying agent has been found to comprise carbon black due to its highly efficient absorption characteristics. In general, a processing composition particularly desired for employment in the practice of the present invention will contain carbon black in a concentration effective, e.g., about 3 to 20 grams of carbon black dispersed in 100 cc. of water, to prevent transmission, through the distributed stratum comprising the composition, of in excess of 95 percent of the actinic radiation incident on the stratum.

In general, preferred agents, both opacifying and reflecting, are those which remain immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible pigment dispersions.

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

Subsequent to exposure, as illustrated by FIGS. **2** and **4**, film unit **10** is processed by being passed through opposed suitably gapped rolls **35** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **30** and distribution of alkaline processing composition **12**, possessing an opacifying agent and a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible as a function of the point-to-point degree of exposure of red-sensitive silver halide emulsion layer **16**, green-sensitive silver halide emulsion layer **19** and blue-sensitive silver halide emulsion layer **22**, respectively, intermediate reflecting agent precursor layer **25** 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 and reflecting agent precursor layer **25** to initiate generation of reflecting agent. The cyan, magenta and yellow dye developers, of layers **15, 18** and **21**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to dyeable polymeric layer **24** to provide a multicolor dye transfer image to that layer which is viewable against the background provided by the in situ generated reflecting agent layer **26** which layer effects masking of opacifying agent present in processing composition residuum **12** and cyan, magenta and yellow dye developer remaining associated with blue-sensitive emulsion layer **22**, green-sensitive emulsion layer **19** and red-sensitive emulsion layer **16**.

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

1. a layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl-α-methyl]-ethylamino)-5,8-dihydroxy-anthraquinone dispersed in gelatin and coated at a coverage of about 150 mgs./ft.^{2} of dye and about 200 mgs./ft.^{2} of gelatin;
2. a red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 200 mgs./ft.^{2} of silver and about 100 mgs./ft.^{2} of gelatin;
3. a layer of gelatin coated at a coverage of about 200 mgs./ft.^{2};
4. a layer of the magenta dye developer 2-(p-[β-hydroquinonylethyl]-phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of 70 mgs./ft.^{2} of dye and about 100 mgs./ft.^{2} of gelatin;
5. a green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 100 mgs./ft.^{2} of silver and 60 mgs./ft.^{2} of gelatin;
6. a layer containing 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 25 mgs./ft.^{2} of 4'-methyl-phenyl hydroquinone and about 150 mgs./ft.^{2} of gelatin;
7. a layer of the yellow dye developer 4-(p-[β-hydroquinonylethyl]-phenylazo)-3-(N,n-hexylcarboxamido)-n1-phenyl-5-pyrazolone dispersed in gelatin and coated at a coverage of about 40 mgs./ft.^{2} of dye and 50 mgs./ft.^{2} of gelatin;

8. a blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 60 mgs./ft.^{2} of silver and about 50 mgs./ft.^{2} of gelatin; and
9. a layer of gelatin coated at a coverage of about 30 mgs./ft.^{2} of gelatin.

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

1. the partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 grams of high viscosity poly-(ethylene/maleic anhydride), 140 grams of *n*-butyl alcohol and 1 cc. of 85 percent phosphoric acid to provide a polymeric acid layer approximately 0.75 mils. thick;
2. a 2:1 solution of hydroxypropyl cellulose and polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.25 mil. thick;
3. a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs./ft.^{2}, to provide a polymeric image-receiving layer approximately 0.40 mil. thick; and
4. a dispersion of barium chloride in gelatin at a coverage of approximately 900 mgs./ft.^{2} barium chloride and of approximately 150 mg./ft.^{2} gelatin to provide a polymeric reflecting agent precursor layer approximately 0.25 mil. thick.

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

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

Water	100	cc.
Potassium hydroxide	11.2	g.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4	g.
N-benzyl-α-picolinium bromide	1.5	g.
Benzotriazole	1.0	g.
Titanium dioxide	40.0	g.
Carbon black	6.0	g.
Sodium sulfate	10.7	g.

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 reflecting layer.

The photosensitive laminates may then be exposed through step wedges to selectively filtered radiation incident to the transparent polyethylene terephthalate layer and initially processed, in the absence of actinic radiation, by passage of the exposed film unit through suitably gapped opposed rolls, to effect rupture of the container and distribution of its contents. During processing, the multicolor dye transfer image formation may be viewed through the transparent polyethylene terephthalate film base against the in situ generated barium sulfate reflecting agent 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 90 seconds.

As an illustrative construction of the novel film units of the present invention employing the aforementioned metathetical generation of reflecting agent in situ, the barium chloride precursor of layer 4 immediately above may be replaced with a dispersion of barium sulfide in gelatin coated, as above, at an average of approximately 725 mgs./ft.^{2} barium sulfide and of approximately 150 mgs./ft.^{2} gelatin and the sodium sulfate precursor of the processing composition may be replaced with 12.2 grams of zinc sulfate to effectively provide the simultaneous in situ generation of both barium sulfate and zinc sulfide reflecting agent pigments, intermediate the image-receiving layer of the film unit and auxiliary layer 9, during processing of a photoexposed film unit.

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.

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

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

However, as disclosed in copending U.S. Pat. application Ser. No. 664,503, filed Aug. 30, 1967 in the names of Leonard C. Farney, Howard G. Rogers and Richard W. Young, now U.S. Pat. No. 3,455,686, issued July 15, 1969 preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer-processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

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

It is further stated in the last-mentioned copending application Ser. No. 664,503 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quanternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

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

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1,000, preferably of about 1,000 to 50,000 , possessing a degree of acetalation within about 10 to 30 percent, 10 to 30 percent, 20 to 80 percent, and 10 to 40 percent, of the polyvinyl alcohol's theoretical polymeric hydroxy groups, respectively, and including mixed acetals where desired.

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

Employment of the detailed and preferred film units of the present invention, according to the herein described color diffusion transfer process, specifically provides for the production of a highly stable 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 conditions from those at which dye diffusion or transfer is operative to conditions 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.

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

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

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

It will be apparent that the relative proportions of the agents of the diffusion transfer-processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, 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. Pat. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402, 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

As additional examples of synthetic, film-forming, permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. **3,043,692**; polymers of N-alkyl-α,β-unsaturated carboxamides and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinylphthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terepolymers 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. Pat. 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. Pat. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color-developing agents and one or more color 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 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

For the production of the photosensitive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant 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 or undesired components, for example, the procedures described in U.S. Pat. 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. Pat. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography Its Materials and Processes*, 6th Ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of the art, as described in Hammer, F. M., *The Cyanine Dyes and Related Compounds*.

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

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

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. Pat. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack-type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye developer.

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

Where in the specification, the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used 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, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

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

What is claimed is:

1. In a photographic film unit which comprises, in combination:

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

the improvement which comprises a layer permeable to processing composition solubilized dye image-forming material which comprises light reflecting agent precursor which includes, upon contact with a processing composition, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light reflecting agent intermediate said dyeable polymeric layer and said photosensitive silver halide layer.

2. A photographic film unit as defined in claim 1 wherein said reflecting precursor is present in a quantity sufficient to provide, upon contact with said processing composition, said substantially white, inorganic visible light reflecting agent effective to mask said dye image-forming material associated with said photosensitive silver halide layer subsequent to processing.

3. A photographic film unit as defined in claim 1 wherein said means for distributing a processing composition comprises container means fixedly positioned extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said layer containing said reflecting agent precursor and the photosensitive silver halide layer next adjacent thereto and said processing composition contains an opacifying agent in a quantity sufficient upon distribution between said layer containing said reflecting agent precursor and the photosensitive silver halide layer next adjacent thereto to prevent exposure of said silver halide layer in the presence of actinic radiation incident on said dimensionally stable transparent layer.

4. A photographic film unit as defined in claim 3 wherein said reflecting agent precursor is present in a quantity sufficient upon conversion to reflec,ing agent to mask said distributed opacifying agent subsequent to processing.

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

6. A photographic film unit as defined in claim 5 wherein said opacifying agent is carbon black.

7. A photographic film unit as defined in claim 6 wherein said carbon black is present in said processing composition in a concentration within the range of about 3 to 20 grams of carbon black per 100 cc. of processing composition.

8. A photographic film unit as defined in claim 5 wherein said aqueous alkaline solution contains a film-forming polymeric material.

9. A photographic film unit as defined in claim 8 wherein said reflecting agent precursor is barium ions and said processing composition contains sulfate ions adapted to react with said barium ions to provide substantially white, inorganic, visible light reflecting barium sulfate pigment.

10. A photographic film unit as defined in claim 9 wherein said barium ions and said sulfate ions are present in substantially stoichiometric quantities sufficient to provide a barium sulfate coverage of from about 200 to 1,000 mgs./ft.^{2} reflecting agent.

11. A photographic film unit as defined in claim 5 wherein said reflecting agent precursor is disposed in a polymeric matrix permeable to processing composition solubilized dye.

12. A photographic film unit as defined in claim 11 wherein said polymeric matrix is gelatin.

13. A photographic film unit as defined in claim 5 wherein said photosensitive element comprises at least two selectively sensitized silver halide emulsion layers each having a dye which dye is a silver halide developing agent of predetermined color associated therewith, each of said dyes soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

14. A photographic film unit as defined in claim 13 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 associate emulsion layer.

15. A photographic film unit as defined in claim 14 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.

16. A photographic film unit as defined in claim 4 wherein said processing composition is an aqueous alkaline processing composition and said film unit additionally contains at least one acidic layer positioned intermediate at least one of said dimensionally stable opaque layer and the photosensitive silver halide emulsion layer next adjacent thereto, and said dimensionally stable transparent layer and the dyeable polymeric layer next adjacent thereto.

17. A photographic film unit as defined in claim **16** wherein said acidic layer comprises a polymeric acid layer containing sufficient acidifying groups to effect reduction of said processing solution from a first pH at which said dye is substantially soluble and diffusible to a second pH at which said dye is substantially nondiffusible.

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

a rupturable container retaining an aqueous alkaline processing solution possessing said first pH and an opacifying agent and adapted 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;

the improvement which comprises an alkaline solution permeable polymeric layer containing light reflecting agent precursor which comprises, upon contact with said processing solution, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light reflecting agent intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, said container fixedly positioned extending transverse a leading edge of said photosensitive element to effect said unidirectional discharge of said processing composition upon application of said compressive force to said container intermediate said polymeric reflecting agent precursor containing layer and said blue-sensitive silver halide emulsion layer, said reflecting agent precursor present in a quantity sufficient upon conversion to said substantially white, inorganic visible light reflecting agent to mask distributed opacifying agent, and said distributed opacifying agent taken together with said reflecting agent present in a quantity sufficient to prevent exposure of said red-, green-, and blue-sensitive silver halide emulsion layers in the presence of actinic radiation incident on said dimensionally stable transparent layer and to mask said cyan, magenta and yellow dyes associated with said red-, green- and blue-sensitive silver halide emulsion layers.

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

20. A photographic film unit as defined in claim **18** wherein said opacifying agent is carbon black.

21. A photographic film unit as defined in claim **18** wherein said reflecting agent precursor is barium ions and said processing solution includes sulfate ions.

22. In a process for forming transfer images in color which comprises, in combination, the steps of:

a. exposing a photographic film unit which includes, in combination, a composite photosensitive structure comprising a first dimensionally stable, liquid impermeable layer opaque to incident actinic radiation, a photosensitive silver halide layer having associated therewith a dye image-forming material which is soluble and diffusible in processing composition as a function of exposure of the silver halide layer to incident actinic radiation; a polymeric layer dyeable by said dye image-providing material; a second dimensionally stable, liquid impermeable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; and means for distributing a processing composition between said dyeable polymeric layer and the photosensitive silver halide layer next adjacent thereto upon application of compressive force to said container;

b. distributing said processing composition intermediate said dyeable polymeric layer and the photosensitive silver halide layer next adjacent thereto;

c. effecting thereby development of said silver halide layer;

d. forming thereby an imagewise distribution of mobile dye image-providing material as a function of the point-to-point degree of silver halide layer exposure;

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

f. maintaining said composite structure intact subsequent to said processing;

the improvement which comprises a layer permeable to processing composition solubilized dye image-forming material which comprises light reflecting agent precursor which includes, upon contact with a processing composition, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and said photosensitive silver halide layer, and effecting thereby interaction between said first and said second ionic species upon contact of said layer including said light-reflecting agent precursor and said distributed processing composition to provide said substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and said photosensitive silver halide layer.

23. A process as defined in claim **22** wherein said means for distributing said processing composition comprises container means fixedly positioned extending transverse a leading edge of said composite photosensitive structure to effect unidirectional discharge of said container's processing composition between said layer containing said reflecting agent precursor and the photosensitive silver halide layer next adjacent thereto and said processing composition contains an opacifying agent in a quantity sufficient upon distribution between said layer containing said reflecting agent and the photosensitive silver halide layer next adjacent thereto to prevent exposure of said silver halide layer in the presence of actinic radiation incident on said dimensionally stable transparent layer.

24. A process as defined in claim **23** wherein said reflecting agent precursor is present in a quantity sufficient upon conversion to reflecting agent to mask said distributed opacifying agent.

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

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

27. A process as defined in claim **24** wherein said opacifying agent is carbon black.

28. A process as defined in claim **27** wherein said carbon black is present in said processing composition in a concentration within the range of about 3 to 20 grams of carbon black per 100 cc. of processing composition.

29. A process as defined in claim **25** wherein said reflecting agent precursor is disposed in a processing composition permeable polymeric matrix.

30. A process as defined in claim **29** wherein said polymeric matrix is gelatin.

31. A process as defined in claim **29** wherein said reflecting agent precursor is barium ions and said processing composition contains sulfate ions adapted to coact with said barium ions to provide substantially white, inorganic visible light reflecting barium sulfate pigment.

32. A process as defined in claim **31** wherein said barium and said sulfate ions are present in stoichiometric quantities sufficient to provide a reflecting pigment coverage within the range of about 200 to 1,000 mgs./ft.^{2} reflecting agent.

33. A process as defined in claim **22** including the step of separating said container from said composite structure subsequent to substantial transfer image formation.

34. In a process as defined in claim **25** 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 layer opaque to incident actinic radiation; at least two selectively sensitized silver halide emulsion layers, each of said silver halide emulsions having associated therewith a dye, which is a silver halide developing agent, of predetermined color, and is soluble and diffusible, in alkaline processing composition as a function of the point-to-point degree of exposure of the respective silver halide emulsion associated therewith; a polymeric layer dyeable by said dye; a second dimensionally stable layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship;

a rupturable container retaining an alkaline-processing composition possessing an opacifying agent 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 composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto;

c. effecting development of each of said emulsion layers as a result of development;

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; and

g. maintaining said composite structure intact subsequent to said processing;

the improvement which comprises a layer permeable to processing composition diffusible dye containing light-reflecting agent precursor which comprises, upon contact with said alkaline processing composition, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto, said container fixedly positioned extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said processing composition upon said application of compressive force to said container intermediate said reflecting agent precursor containing layer and said silver halide emulsion layer next adjacent thereto, and effecting thereby interaction between said first and said second ionic species upon contact of said light reflecting agent precursor layer with said distributed processing composition to provide said substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and distributed processing composition opacifying agent in a quantity effective to mask said distributed opacifying agent.

35. A process as defined in claim **34** 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.

36. A process as defined in claim **35** wherein said composite structure includes at least one polymeric acid layer positioned intermediate at least one of said dimensionally stable opaque layer and the next adjacent photosensitive silver halide layer, and said dimensionally stable transparent layer and the next adjacent dyeable polymeric layer and said polymeric acid layers containing sufficient acidifying groups to effect reduction of an alkaline processing solution possessing a first pH at which said dyes are substantially soluble and diffusible to a second pH at which said dyes are substantially nondiffusible and including the step of transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said alkaline processing solution to said polymeric acid layers to thereby reduce the alkalinity of said solution from said first pH to said second pH.

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

a. exposing a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination, a photosensitive element comprising a laminate containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith a magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye; each of said cyan, magenta and yellow dyes being silver halide developing agents and soluble and diffusible in aqueous alkaline solution at a first pH; an alkaline solution permeable polymeric layer dyeable by said dyes; an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of an alkaline processing solution having said first pH to a second pH at which said dyes are substantially insoluble and nondiffusible; a dimensionally stable, alkaline solution impermeable transparent layer;

a rupturable container retaining an aqueous alkaline-processing solution possessing said first pH and an opacifying agent in a quantity sufficient to prevent exposure of said red-, green- and blue-sensitive silver halide emulsions in the presence of actinic radiation incident on said dimensionally stable transparent layer fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing solution intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer upon application of compressive force to said container; and

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 dyeable polymeric layer and said blue-sensitive silver halide emulsion layer;

c. effecting development of the latent image contained in each of said red-, green- and blue-sensitive silver halide emulsions;

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

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

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

g. transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline solution to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said solution from said first pH at which said dyes are soluble and diffusible to said second pH at which said dyes are substantially nondiffusible; and

h. maintaining said laminate intact subsequent to said processing;

the improvement which comprises an alkaline solution permeable layer including a light-reflecting agent precursor which comprises, upon contact with said aqueous alkaline processing solution, first ionic species adapted to interact with second ionic species to provide a substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, said rupturable container fixedly positioned extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said processing solution containing said opacifying agent intermediate said blue-sensitive silver halide emulsion layer and said light-reflecting agent precursor containing layer, and effecting thereby interaction between said first and said second ionic species upon contact between said light-reflecting agent precursor layer and said ;istributed processing solution to provide said substantially white, inorganic visible light-reflecting agent intermediate said dyeable polymeric layer and distributed processing composition opacifying agent in a quantity effective to mask said distributed opacifying agent.

38. A process as defined in claim **37** wherein said first pH is above **9** and said second pH is below **9**.

39. A process as defined in claim **37** including the step of separating said container from said laminate subsequent to substantial image formation.

40. A process as defined in claim **37** wherein said opacifying agent is carbon black.

41. A process as defined in claim **37** wherein said reflecting agent precursor is barium ions and said processing solution contains sulfate ions.

42. A process as defined in claim **22** wherein said reflecting agent precursor is present in a quantity sufficient to provide upon contact with said processing composition reflecting agent effective to mask said dye image-forming material associated with said photosensitive silver halide emulsion layer subsequent to processing.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,647,435 Dated March 7, 1972

Inventor(s) Edwin H. Land

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

Column 4, line 34, delete "will".

Column 7, line 24, ";issovered" should be --discovered--;

line 31, ";imensionally" should be --dimensionally--.

Column 12, line 72, ")-nl-" should be --)-1- --.

Column 14, line 58, "state" should be --stated--.

Column 20, line 16, "reflec,ing" should be --reflecting--.

Column 24, line 34, claim 37, "in claim 38" should be changed to read --in claim 36--.

Column 26, line 9, ";istributed" should be --distributed--.

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents