May 18, 1971 E. LAND ET AL 3,579,333

MULTICOLOR DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCTS AND PROCESSES WITH A DEVELOPING COMPOSTION COMPRISING A DESENSITIZING AGENT

Filed July 18, 1968 4 Sheets-Sheet 1

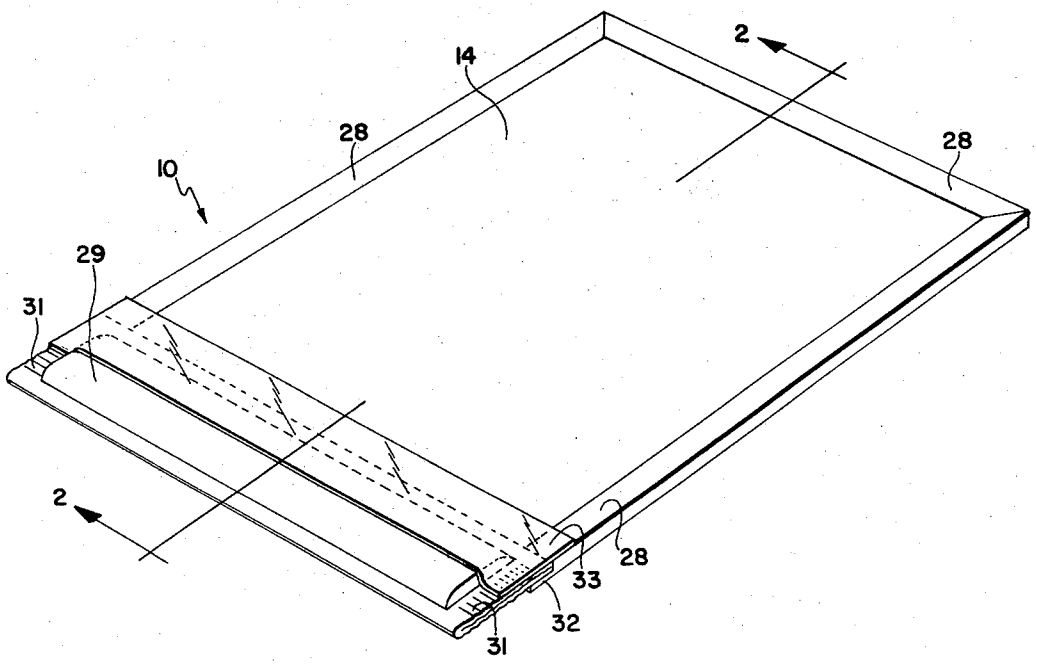


FIG. 1

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Filed July 18, 1968 4 Sheets-Sheet 2

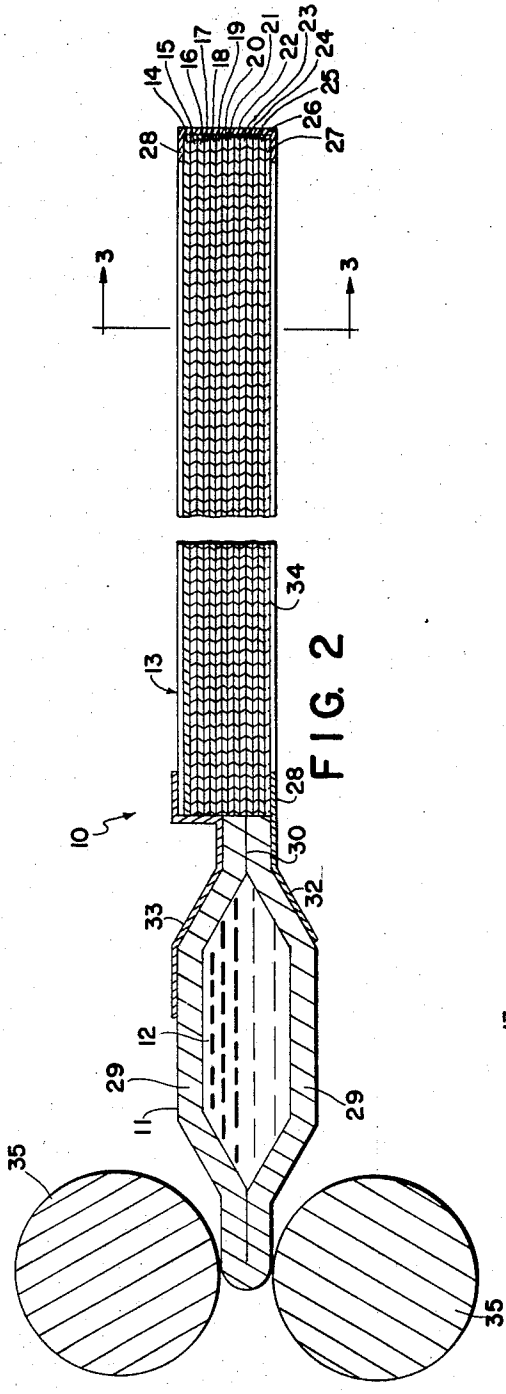


FIG. 2

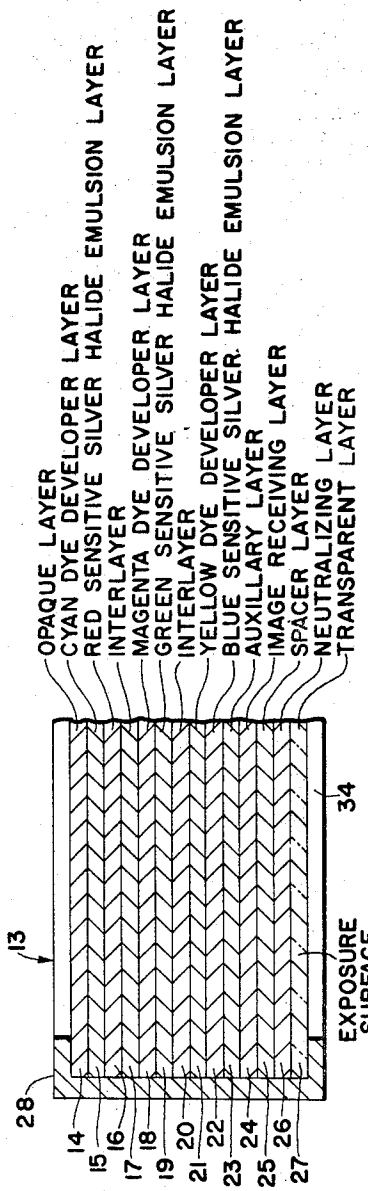


FIG. 3

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Filed July 18, 1968 4 Sheets-Sheet 3

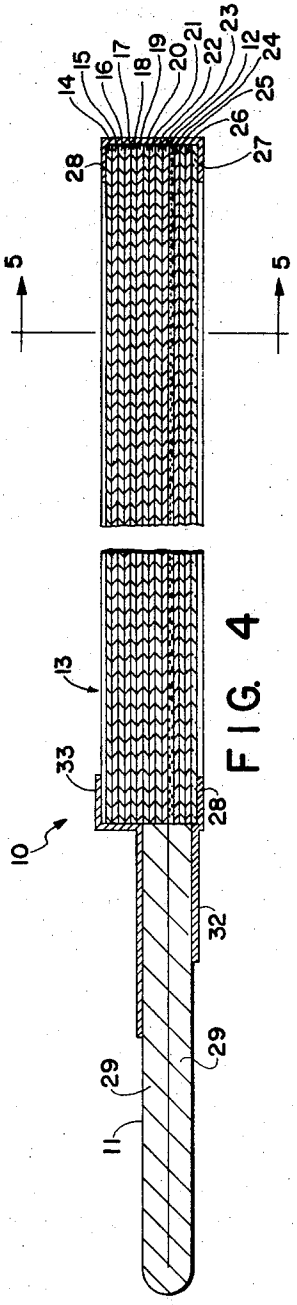


FIG. 4

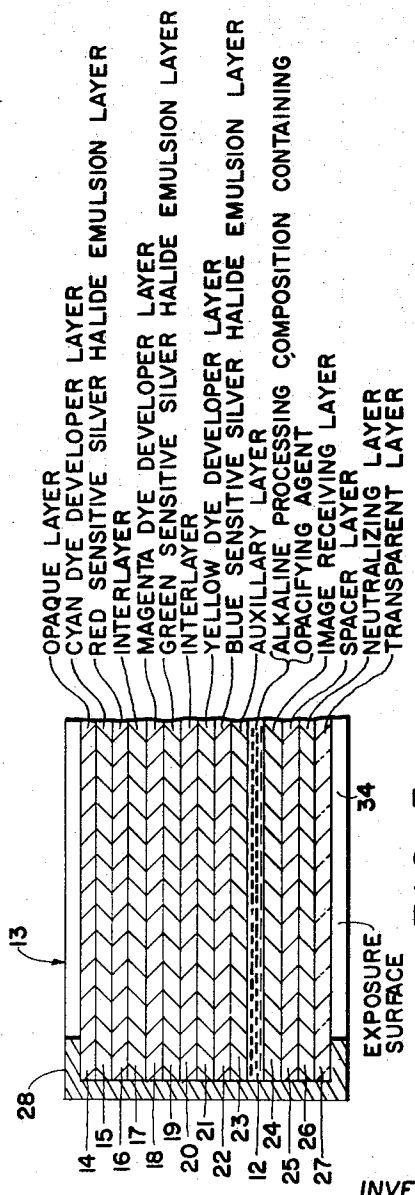


FIG. 5

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Filed July 18, 1968 4 Sheets-Sheet 4

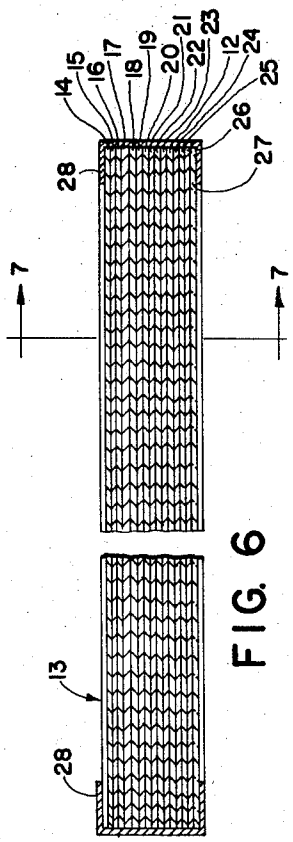


FIG. 6

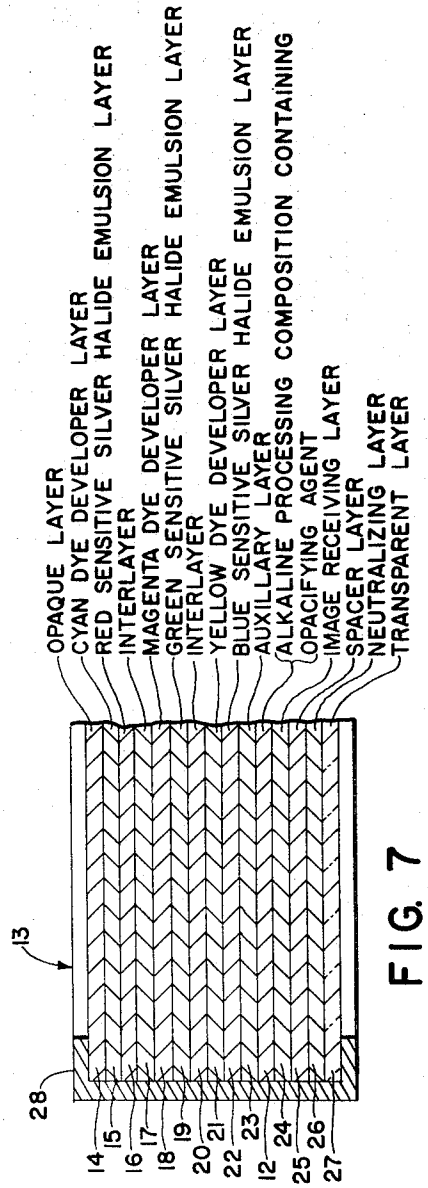


FIG. 7

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3,579,333

MULTICOLOR DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCTS AND PROCESSES WITH A DEVELOPING COMPOSITION COMPRISING A DESENSITIZING AGENT

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Int. Cl. G03c 7/00, 5/54, 5/32
U.S. Cl. 96—3 18 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a composite photosensitive structure containing, as essential layers, in sequence, a dimensionally stable layer; a photosensitive direct negative silver halide emulsion layer having associated therewith a dye which is a silver halide developing agent and is processing composition soluble and diffusible as a function of the photosensitive silver halide emulsion layer's exposure and a silver halide desensitizing agent adapted to effect, subsequent to photoexposure, desensitization of the photosensitive silver halide emulsion layer without substantial detriment to the latent image carried by the emulsion layer; a polymeric layer dyeable by dye diffusing thereto; a dimensionally stable layer transparent to actinic radiation; and to specified photographic diffusion transfer processes employing such composite photosensitive structure.

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

The primary objects of the present invention are to provide photographic products particularly adapted for employment in diffusion transfer photographic color processes; to provide photographic products which comprise a photosensitive composite structure which preferably contains a plurality of 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 alkali, at a first pH, and a silver halide desensitizing agent which is soluble and diffusible in alkali and adapted in the solubilized state to effect desensitization of photosensitive silver halide, a permeable polymeric layer dyeable by the dye image-forming material, a polymeric acid layer containing sufficient acidifying groups to effect reduction of a selected processing solution having the first pH to a second pH at which the dye image-forming material is insoluble and nondiffusible and a dimensionally stable transparent layer; to provide photographic diffusion transfer products comprising a film unit including a photosensitive laminate, of the last-identified type, in combination with a rupturable container retaining an alkaline processing composition having the first pH and containing dispersed therein an opacifying agent, in a quantity sufficient to mask the dye image-forming material; to provide a diffusion transfer film unit, of the last-identified type, having the container fixedly positioned and extending transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the alkaline processing composition intermediate the opposed surfaces of the dyeable polymeric layer and the photosensitive silver halide emulsion 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 perspectivxe 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 composite structure during the three illustrated stages of the transfer process.

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

the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a 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 substractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion, Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

As disclosed in copending U.S. application Ser. No. 234,864, filed Nov. 11, 1962 in the name of Edwin H. Land, now U.S. Pat. No. 3,362,819, issued Jan. 9, 1968, image-receiving elements, particularly adapted for employment in diffusion transfer processes of the type disclosed in aforementioned U.S. Pat. No. 2,983,606, wherein the image-receiving elements are separated from contact with a superposed photosensitive element, subsequent to substantial transfer image formation, preferably comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance, and most preferably include an inert timing or spacer layer intermediate the polymeric acid layer and the image-receiving layer.

As set forth in the last-mentioned application, 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. 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 or cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

The 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 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about 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 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 fur-

ther dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as 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 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 may be employed to help the various polymeric layers adhere to each other during storage and use.

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

As disclosed in last-mentioned 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. application Ser. No. 447,100, filed Apr. 9, 1965 in the names of Leonard C. Farney, Howard G. Rogers and Richard W. Young, abandoned and replaced by Ser. No. 664,503, filed Aug. 30, 1967, 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 stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective within the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer images' color definition.

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

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

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

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

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylons 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 modant 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 ex-

ample, 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 dried 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 equilibruim between oxidized and reduced dye. In that the pH of the dynamic system is such that diffusion of the reduced form of the dye will occur, such reduced dye will, at least in part, transfer to the image-receiving layer and the resultant diffusion will imbalance the equilibrium, in such areas of the photosensitive element, in favor of additional formation of reduced dye. As a function of the efficiency of the image-receiving layer, as a dye sink, such nonimagewise dyeing of the image-carrying layer still further imbalances the equilibrium in favor of the additional formation of dye in reduced, diffusible form. Under such circumstances, the transfer image definition, originally carried by the image-receiving layer, will suffer a continuous decrease in the delta between the image's maximum and minimum densities and may, ultimately, result in the image-receiving element's loss of all semblance of image definition; merely becoming a polymeric stratum carrying a relatively uniform overall dyeing.

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

As previously discussed, U.S. Pat. No. 3,362,819, discloses certain image-receiving elements particularly adapted for employment in diffustion transfer color processes, wherein the image-receiving element is separated from contact with a superposed photosensitive element, subsequent to substantial transfer image formation, and which elements provide particular protection of transfer images from the effects of aerial oxidation of dyes forming the color transfer image.

In copending U.S. application Ser. No. 622,283, filed Mar. 10, 1967 in the name of Edwin H. Land, now U.S. Pat. No. 3,415,644, issued Dec. 10, 1968, it is disclosed that 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 simply and effectively obviated by fabrication of a film unit to include a photosensitive element comprising a composite structure 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; an alkaline solution permeable 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 composite structure, 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.

In the preferred embodiment of that invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, the dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsion strata each having dye image-providing materials of predetermined color associated therewith which are soluble and diffusible, in alkali, at a first pH; the alkaline solution permeable polymeric layer dyeable by the dye image-providing materials; the alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial multicolor transfer dye image formation, of a processing composition having the first pH to a second pH, at which the dye image-providing material is insoluble and nondiffusible; and the dimensionally stable transparent layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing 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 and the dyeable polymeric layer is separated from the polymeric acid layer by an alkaline solution permeable

polymeric spacer layer, most preferably a polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

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

It has now been unexpectedly discovered that a novel integral photographic film unit which is particularly adapted for production of a dye transfer image by a color diffusion transfer process will be constructed to include a photosensitive element containing a photosensitive silver halide emulsion layer having associated therewith a dye image-providing material and a silver halide desensitizing agent both of which are soluble and diffusible in alkali and the desensitizing agent adapted, in the solubilized state, to effect desensitization of photosensitive silver halide, without deleteriously effecting either the composition of and/or the development of a latent image carried by the emulsion; an alkaline solution permeable polymeric layer dyeable by the dye image-providing material; and a dimensionally stable supporting layer.

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

In the preferred embodiment of the present invention, the film unit will comprise a composite structure containing, as essential layers, in sequence, a dimensionally stable layer opaque to actinic radiation; at least one photosensitive silver halide emulsion having associated therewith a dye developer soluble and diffusible in alkali at a first pH and a silver halide desensitizing agent which is soluble and diffusible in alkali and adapted, in the solubilized state, to effect desensitization of photosensitive silver halide; an alkaline solution permeable polymeric layer dyeable by the dye; an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having the first pH to a second pH at which the dye is insoluble and nondiffusible; a dimensionally stable transparent support layer; and means securing the respective layers in fixed relationship.

Such film unit should also include a rupturable container, retaining an alkaline processing solution having the first pH and containing dispersed therein an opacifying agent in a quantity sufficient to mask the dye, fixedly positioned and extending transverse a leading edge of the photosensitive element so as to effect unidirectional discharge of the container's contents between the dyeable polymeric layer and the silver halide emulsion layer next adjacent.

The respective layers comprising the composite structure are secured in fixed relationship which, in whole or in part, may be readily and simply achieved by retaining means such as, for example, a pressure-sensitive tape binding member extending around the edges of the composite structure securing or maintaining the layers of the composite together at their respective edges.

In a preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective plurality of silver halide/dye developer units of the composite structure are predominantly responsive to separate regions of the spectrum and provide a chromatic image possessing an absorption range substantially complementary to the sensitivity range. In general, the composite structure will most preferably be in the form of a tri-pack configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the stable opaque layer, a yellow dye developer/blue-sensitive emulsion unit most distant from the opaque layer and a magenta dye developer/green-sensitive emulsion unit between the preceding units, recognizing that the relative relationship of such units may be varied in accordance with the desires of the operator. 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 copending U.S. application Serial No. 638,817, filed May 16, 1967 in the name of Edwin H. Land, now U.S. Pat. No. 3,415,646, issued Dec. 10, 1968; 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 copending U.S. application Serial No. 622,298, filed Mar. 10, 1967 also in the name of Edwin H. Land, now U.S. Pat. No. 3,415,645, issued Dec. 10, 1968.

Employment of the detailed film unit of the present invention, according to the herein described color diffusion transfer process, specifically facilitates the production of color transfer image formation by diffusion transfer processing of a photoexposed film unit in the presence of radiation actinic to such unit. Desensitization of the photosensitive silver halide, subsequent to latent image formation and without deleterious effect upon the character of or development of such latent image, alleviates the formation of physical fog resultant from actinic radiation incident on photosensitive silver halide during transfer processing. It will be recognized that the question of desensitization required for processing of a selected film unit, in the presence of actinic radiation, will be in part determined by the sensitivity of such silver halide to the incident radiation in question and the efficiency of such opacifying and masking procedures as are adopted to insulate silver halide from response to such radiation.

The silver halide desensitizing agent selected should be conveniently soluble in the processing composition; stable, rapid and complete in destroying sensitivity, but without action on the developer or on the latent image, nonfogging, nonstaining and nonpoisonous. In a preferred embodiment the silver halide desensitizing agent will be disposed in the processing composition as retained in the rupturable container. It will be clearly recognized, however, that alternatively such agent may be conveniently dispersed in a processing composition permeable layer of the composite structure and activated by contact with processing composition permeating such layer and solubilizing the agent.

An extensive compilation of silver halide desensitizing agents adapted for utilization in the practice of the present invention is set forth in both the patent and technical literature relating to silver halide desensitizers. A selection of agents which have been specifically employed in the practice of the present invention are further detailed hereinafter as illustrative examples of desensitizers adapted for employment in accordance with the present invention.

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 composite structure **13**, including, in order, diamensionally 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 **22**; auxiliary layer **23**; which may contain an auxiliary silver halide developing agent; image-receiving layer **24**; spacer layer **25**; neutralizing layer 26; and idemsnionally stable transparent layer **27**, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of the composite structure **13** may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the structure at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer **24** and the silver halide emulsion layer next adjacent thereto, for example, intermediate image-receiving layer **24** and auxiliary layer **23** as illustrated in FIGS. 2 through 7, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the structure, most preferably, in order of substantially no adhesion, 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 composite'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 the composite structure **13**, and maintaining the layers comprising the structure 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 structure **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 processing composition from the film unit's laminate during and subsequent to photographic processing.

Rupturable container **11** may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing solution **12** is retained. The longitudinal marginal seal **30** is made weaker than the end seals **31** so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **29** of the container.

As illustrated in FIGS. 1, 2 and 4, container **11** is fixedly positioned and extends transverse a leading edge of photosensitive composite structure **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 structure **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**, susequent to distribution of processing composition **12**, from the remainder of film unit **10**, flap **32** may be folded over the edge of structure **13**, previously covered by tape **33**, in order to facilitate maintenance of the composite's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer **27**.

The fluid contents of the container comprise an aqueous alkaline solution having a pH at which the dye developers are soluble and diffusible, contains an opacifying agent in a quantity sufficient to mask the dye developers associated with the silver halide emulsions subsequent to processing, and contains a silver halide desensitizing agent. In general, a concentration of opacifying agent and desensitizing agent is desired for employment which will be at least sufficient to prevent further exposure of the film unit's selected silver halide emulsion or emulsions subsequent to desensitization, by actinic radiation traversing through the dimensionally stable transparent layer, subsequent to distribution of the processing solution intermediate the dyeable polymeric layer and the stated layer next adjacent thereto. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of the laminate are appropriately desensitized and additionally protected from incident radiation, at one major surface by the opaque processing composition and at the remaining major surface by the dimensionally stable opaque layer. If the illustrated binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The selected opacifying agent, however, should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric layer. In general, while substantially any opacifying agent may be employed, it is preferred that an opacifying agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable opacifying agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially, those agents possessing the optical properties desired for reflection of incident radiation.

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

A particularly preferred agent comprises titanium dioxide due to its highly effective reflection properties. In general, based upon percent titanium dioxide ("weight volume"), a processing composition containing about 40-

50 grams of titanium dioxide dissolved in 100 cc. of water will provide a percent reflectance of about 85–90%. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of above 85%.

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

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

Alkaline processing solution **12** permeates emulsion layers **16**, **19** and **22** to effect desensitization thereof and to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **15**, **18** and **21**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer **24** to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline solution **12** transfers, by diffusion, through permeable polymeric layer **24**, permeable spacer layer **25** and to permeable polymeric acid layer **26** whereby alkaline solution **12** decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers in the reduced form, are insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image.

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

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

Film units similar to that shown in the drawing may be prepared, for example, by coating, in succession, on a gelatin subbed, opaque cellulose triacetate film base, the following layers:

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

(7) a layer of the yellow dye developer 4-(p-[β-hydroquinonylethyl] - phenylazo)-3-(N-n-hexylcarboxamido)-1-phenyl-5-pyrazolone dispersed in gelatin and coated at a coverage of about 40 mgs./ft.² of dye and 50 mgs./ft.² of gelatin;

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

(9) a layer containing 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 10 mgs./ft.² of 4'-methylphenyl hydroquinone and about 30 mgs./ft.² of gelatin.

Then a transparent cellulose triacetate film base may be coated, in succession, with the following illustrative layers:

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

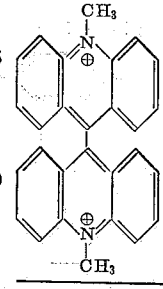
(2) a solution of hydroxypropyl cellulose in water to provide a polymeric spacer layer approximately 0.075 mil thick;

(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) then baking the element at 180° F. for 30 minutes and cooling.

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 retaining an aqueous alkaline processing solution comprising:

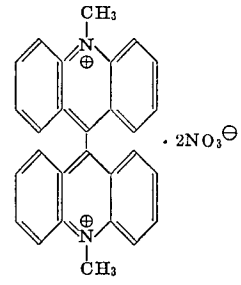
	Grams
Water	(1)
Potassium hydroxide	11.2
Hydroxyethyl cellulose (high viscosity [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4
N-benzyl-α-picolinium bromide	1.5
Benzotriazole	1.0
Titanium dioxide	40.0
	0.2

[1] 100 cc.

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 the 4'-methylphenyl hydroquinone containing layer and the polymeric image-receiving layer.

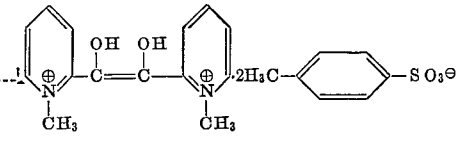
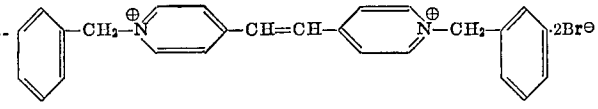
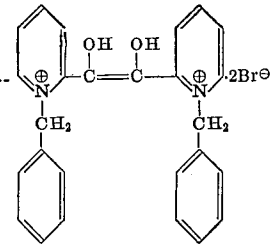
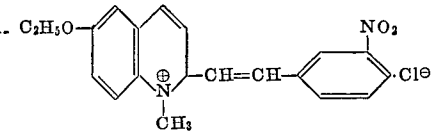
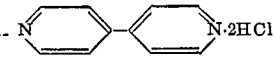
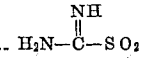
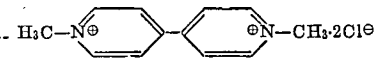
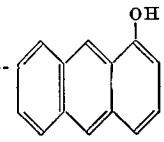
The photosensitive laminates may then be exposed through step wedges to selectively filtered radiation incident on the transparent cellulose triacetate layer and initially processed, in the absence of actinic radiation, by passage of the exposed film unit through suitably gapped opposed rolls, to effect rupture of the container and distribution of its contents. Subsequent thereto, for example, in the order of less than twenty seconds the film unit's processing may be continued in the presence of actinic radiation. During such further processing, the multicolor dye transfer image formation may be viewed through the transparent cellulose triacetate film base and such image formation is found to be substantially completed and exhibiting the required color brilliance, hues, saturation, and isolation, within a period of approximately 1–2 minutes.

Examination of test multicolor dye transfer images formulated in the general manner detailed above, in direct comparison with control transfer images, formulated with the exception that the silver halide desensitizing agent

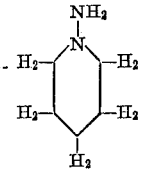
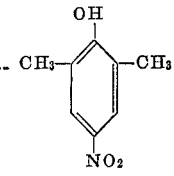


was absent from the processing composition, revealed decreased physical fog formation resultant from sensitivity of the film unit's photosensitive silver halide emulsions to actinic radiation present during processing.

The preceding test embodiment may be reproduced, in concert with a corresponding control, employing, respectively, in substitution for the preferred desensitizing agent of the test, at the concentration detailed:

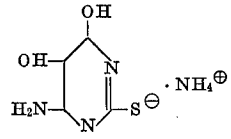
Desensitizing agent	Concentration, gram
(1) 	~0.42
(2) 	~0.2
(3) 	~0.2
(4) 	~0.1-0.2
(5) 	~0.2
(6) 	~0.02
(7) 	~0.2
(8) 	~0.2-0.4
(9) 	~0.2

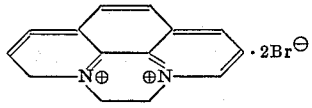
TABLE—Continued

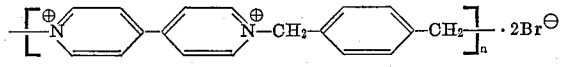
Desensitizing agent	Concentration, gram
(10) 	~0.2
(11) 	~0.59

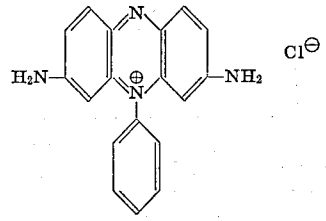
Each such test embodiment, as compared with its respective control, will exhibit decreased physical fog formation resultant from sensitivity to actinic radiation present during processing.

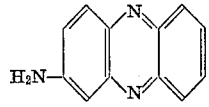
As examples of additional silver halide desensitizing agents specifically found to be adapted to effect desensitization of a photoexposed silver halide emulsion without deleterious effect to the emulsion's latent image, mention may be made of:

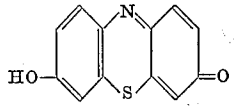
(12) 

(13) 

(14) 

(15) 

(16) 

(17) 

and the like.

In such instances where it is particularly desired to employ one or more desensitizing agents of a type or in a concentration which induces chemical fog formation of emulsion strata, in addition to the desired desensitization, such chemical fog formation may be obviated, to the extent required, by the presence of one or more conventional antifoggants employed in a concentration effective to provide the desired chemical fog inhibition. Embodiments of the present invention employing a plurality of superpositioned emulsion strata and disposition of one or more of the desensitizing agents in the processing composition or compositions utilized may advantageously employ one or more antifoggants possessing a sufficiently low mobility as to be effective for inhibition of chemical fog formation in the emulsion stratum in most direct contact with the processing composition, substantially without photographic effect on emulsion strata positioned more distant from initial processing composition contact, in instances where the selected concentration of desensitizing agent desired to effect desensitization of the emulsion strata is such as to provide chemical fog formation of the emulsion stratum in initial contact with the processing composition. Thus, for example, in the tripack film unit configuration described above, a low mobility antifoggant may be employed to alleviate chemical fogging of the blue-sensitive silver halide emulsion stratum, without substantial effect on the green- and red-sensitive silver halide emulsion strata, where it is specifically desired to employ a processing composition containing desensitizing agent in a concentration which induces chemical fogging of the blue-sensitive emulsion stratum, contacted initially by such composition during the described diffusion transfer processing.

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

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, 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 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 exposures, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

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

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

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of 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 terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,264; and the like.

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

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

Although the invention has been discussed in detail throughout employing dye developers, the preferred dye image-providing materials, it will be readily recognized that other, less preferred, dye image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; and 2,802,735, issued Aug. 13, 1957, wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. No. 2,774,668, issued Dec. 18, 1956, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a continuous image-receiving layer.

For the production of the photosensitive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing

agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pats. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., Photography—Its Materials and Processes, 6th ed., 1962.

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

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

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

The emulsions may include the various adjuncts, or addenda, according to the techniques disclosed in the art, such as speed-increasing compounds of the quaternary ammonium type, as described in U.S. Pats. Nos. 2,271,-623; 2,288,226; and 2,334,864; or of the polyethyleneglycol type, as described in U.S. Pat. No. 2,708,162; or of the preceding combination, as described in U.S. Pat. No. 2,886,437; or the thiopolymers, as described in U.S. Pats. Nos. 3,046,129 and 3,046,134.

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

Hardening agents such as inorganic agents providing polyvalent metallic atoms, specifically polyvalent aluminum or chromium ions, for example, potash alum

$$[K_2Al_2(SO_4)_4 \cdot 24H_2O]$$

and chrome alum $[K_2Cr_2(SO_4)_4 \cdot 24H_2O]$ and inorganic agents of the aldehyde type, such as formaldehyde, glyoxal, mucochloric, etc.; the ketone type such as diacetyl; the quinone type; and the specific agents described in U.S. Pats. Nos. 2,080,019; 2,725,294; 2,725,295; 2,725,305; 2,-726,162; 2,732,316; 2,950,197; and 2,870,013, may be incorporated, where desired and compatible, in the selected coating solution compositions.

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

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,327,-808; polyacrylamides, as described in U.S. Pat No. 2,-541,474; vinyl polymers such as described in U.S. Pats. Nos. 2,253,078; 2,276,322; 2,276,323; 2,281,703; 2,310,-223; 2,311,058; 2,311,059; 2,414,208; 2,461,023; 2,484,-456; 2,538,257; 2,579,016; 2,614,931; 2,624,674; 2,632,-704; 2,642,420; 2,678,884; 2,691,582; 2,725,296; 2,753,-264; and the like.

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

It will be recognized that, by reason of the 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 the film unit should be accomplished through an image reversing optical system such a camera possessing such 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 drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

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

a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable layer opaque to actinic radiation; a photosensitive direct negative silver halide emulsion layer adapted to provide a silver image in terms of the exposed areas of the emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of the photosensitive emulsion layer to incident actinic radiation, having associated therewith a dye which is a silver halide developing agent processing composition soluble and diffusible as a function of exposure of the photosensitive silver halide emulsion; a substantially transparent polymeric layer dyeable by dye diffusing thereto; a dimensionally stable layer transparent to actinic radiation; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining a processing composition containing dispersed therein opacifying agent in a quantity sufficient to mask said dye associated with said photosensitive silver halide emulsion layer and a diffusible silver halide desensitizing agent adapted to effect desensitization of said photosensitive silver halide emulsion, fixedly positioned and extending transverse a leading edge of said photosensitive element adapted to effect discharge of said container's contents intermediate said dyeable polymeric layer and next adjacent photosensitive silver halide emulsion layer.

2. A photographic film unit as defined in claim 1 including an alkaline processing composition permeable polymeric layer containing sufficient acidifying capacity to effect reduction subsequent to substantial dye transfer image formation of a processing composition having a first pH at which said dye image-providing material is soluble and diffusible to a second pH at which said dye image-providing material is substantially nondiffusible positioned intermediate said dimensionally stable transparent layer and said dyeable polymeric layer.

3. A photographic film unit as defined in claim 1 wherein said opacifying agent and said desensitizing agent are present in said film unit in a quantity effective, subsequent to distribution intermediate said dyeable polymeric layer and next adjacent photosensitive silver halide emulsion layer, to prevent exposure of said emulsion layer during processing in the presence of radiation actinic to said emulsion layer incident on said dimensionally stable transparent layer.

4. A photographic film unit as defined in claim 1 wherein said silver halide desensitizing agent is initially dispersed in a processing composition permeable layer of said composite structure and said agent is soluble and diffusible in said processing composition and adapted in the solubilized state to effect desensitization of the photosensitive silver halide of said emulsion layer upon contact therebetween.

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

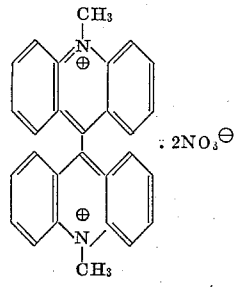
6. A photographic film unit as defined in claim 1 wherein said photosensitive element includes at least two selectively sensitized direct negative silver halide emulsion layers possessing predominant spectral sensitivity to separate regions of the visible spectrum, each emulsion layer comprising a direct negative silver halide emulsion layer adapted to provide a silver image in terms of the exposed areas of such emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of the photosensitive emulsion layer to incident actinic radiation, and having a dye image-providing material associated therewith which possesses subsequent to substantial dye transfer image formation a spectral absorption range substantially complementary to the predominant sensitivity range of its associated silver halide emulsion layer.

7. A photographic film unit as defined in claim 6 which is adapted to be processed by passing said unit between a pair of juxtaposed, pressure-applying members which comprises, in combination:

a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable processing composition impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of said red-, green- and blue-sensitive silver halide emulsion layers comprising a direct negative silver halide emulsion layer adapted to provide a silver image in terms of the exposed areas of such emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of the emulsion layer to incident actinic radiation and each of said cyan, magenta and yellow dyes being a silver halide developing agent and being soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of exposure of its associated silver halide emulsion layer; an alkaline processing composition permeable polymeric layer dyeabel by said dyes; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition having said first pH to a second pH at which said dyes are substantially nondiffusible; a dimensionally stable processing composition impermeable transparent layer; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition having said first pH and containing dispersed therein opacifying agent in a quantity sufficient to mask said cyan, magenta and yellow dyes associated with said red-, green- and blue-sensitive silver halide emulsion layers and a diffusible silver halide desensitizing agent adapted to effect desensitization of said silver halide emulsion layers, said container fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition contents intermediate said dyeable polymeric layer and said photosensitive silver halide emulsion layer upon application of compressive pressure to said container.

8. A photographic film unit as defined in claim 7 wherein said desensitizing agent is



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

(a) exposing a photographic film unit which is adapted to be processed by passage of said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination, a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable layer opaque to actinic radiation; a photosensitive direct negative silver halide emulsion layer adapted to provide a silver image in terms of the exposed areas of said silver halide emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of said photosensitive silver halide emulsion layer to incident actinic radiation, having associated therewith a dye which is a silver halide developing agent processing composition soluble and diffusible as a function of exposure of said photosensitive silver halide emulsion layer; a substantially transparent polymeric layer dyeable by dye diffusing thereto; a dimensionally stable layer transparent to actinic radiation; and means securing said layers in substantialy fixed relationship; and a rupturable container retaining a processing composition containing dispersed therein opacifying agent in a quantity sufficient to mask said dye associated with said photosensitive silver halide emulsion layer and a diffusible silver halide desensitizing agent adapted to effect desensitization of said photosensitive silver halide emulsion, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's contents, intermediate said dyeable polymeric layer and next adjacent photosensitive silver halide emulsion layer, upon application of compressive pressure to said container, to provide to said photosensitive silver halide emulsion layer a latent image in terms of the exposed areas of said photosensitive silver halide emulsion layer as a function of the point-to-point degree of exposure thereof;

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

(c) effecting thereby development of said latent image in said exposed areas of said photosensitive silver halide emulsion layer as a function of the point-to-point degree of exposure thereof and desensitization of the photosensitive silver halide of said photosensitive silver halide emulsion;

(d) immobilizing said dye associated with said silver halide emulsion layer as a result of said development;

(e) forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of photosensitive silver halide emulsion layer photoexposure;

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

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

10. A process of forming transfer images in color as defined in claim 9 including the step of separating said rupturable container from said composite structure subsequent to substantial dye transfer image formation.

11. A process of forming transfer images in color as defined in claim 9 wherein said composite photosensitive structure includes a processing composition permeable polymeric layer containing sufficient acidifying capacity to effect reduction, subsequent to substantial dye transfer image formation, of a processing composition having a first pH at which said dye image-providing material is soluble and diffusible to a second pH at which said dye image-providing material is substantially non-diffusible, positioned intermediate said dimensionally stable transparent layer and said dyeable polymeric layer, and including the step of transferring, by diffusion, subsequent to substantial dye transfer image formation, a sufficient portion of the ions of said processing composition to said polymeric layer to thereby reduce the alkalinity of said processing composition from said first pH to said second pH.

12. A process of forming transfer images in color as defined in claim 9 wherein said silver halide desensitizing agent is initially disposed in a processing composition permeable layer of said composite photosensitive structure and adapted to diffuse into functional contact with the photosensitive silver halide of said photosensitive silver halide emulsion layer upon contact of said agent with said processing composition, and including the step of contacting said silver halide desensitizing agent, subsequent to photoexposure of said film unit, with said processing composition and transferring, by diffusion, said silver halide desensitizing agent into functional contact with the photosensitive silver halide of said photosensitive silver halide emulsion layer.

13. A process of forming transfer images in color as defined in claim 9 wherein said opacifying agent and said desensitizing agent are present in said film unit in a quantity effective, subsequent to distribution intermediate said dyeable polymeric layer and said next adjacent photosensitive halide emulsion layer, to prevent exposure of said emulsion layer during processing in the presence of radiation actinic thereon incident on said dimensionally stable transparent layer.

14. A process of forming transfer images in color as defined in claim 10 which comprises, in combination, the steps of:

(a) exposing a photosensitive film unit which is adapted to be processed by passage of said unit between a pair of juxtaposed pressure-applying members and which includes, in combination, a photosensitive element comprising a composite structure including, as essential layers, in sequence, a dimensionally stable layer opaque to actinic radiation; at least two selectively sensitized direct negative silver halide emulsion layers possessing predominant spec-

tral sensitivity to separate regions of the visible spectrum, each adapted to provide a silver image in terms of exposed areas of said selectively sensitized silver halide emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of the respective selectively sensitized silver halide emulsion layer to incident actinic radiation, and each having a dye associated therewith which is a silver halide developing agent and which possesses, subsequent to substantial dye transfer image formation, a spectral absorption range substantially complementary to the predominant sensitivty range of its associated selectively sensitized silver halide emulsion layer and is processing composition soluble and diffusible as a function of exposure of its associated selectively sensitized silver halide emulsion layer; a substantially transparent polymeric layer dyeable by dye diffusing thereto; a dimensionally stable layer transparent to actinic radiation, and means securing said layers in substantially fixed relationship; and a rupturable container, retaining a processing composition containing dispersed therein opacifying agent in a quantity sufficient to mask said dye associated with each of said selectively sensitized silver halide emulsion layers and a diffusible silver halide desensitizing agent adapted to effect desensitization of said selectively sensitized silver halide emulsion layers, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition contents intermediate said dyeable polymeric layer and next adjacent selectively sensitized silver halide emulsion layer upon application of compressive pressure thereto, to thereby provide to each of said selectively sensitized silver halide emulsion layers a latent image in terms of the exposed areas of said selectively sensitized silver halide emulsion layers as a function of the point-to-point degree of exposure thereof;

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

(c) effecting thereby development of the latent image in the exposed areas of each of said selectively sensitized silver halide emulsion layers as a function of the point-to-point degree of exposure thereof and desensitization of the photosensitive silver halide of said selectively sensitized silver halide emulsion layers;

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

(e) forming thereby an imagewise distribution of mobile dye associated with each of said silver halide emulsion layers as a function of the point-to-point degree of the respective emulsion's photoexposure;

(f) transferring, by diffusion, at least a portion of each of said imagewise distributions of mobile dye to said dyeable polymeric layer to provide thereto a dye image in terms of each of said imagewise distributions; and

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

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

(a) exposing a photosensitive element which comprises a composite structure including, as essential layers, in sequence, a dimensionally stable processing composition impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of said red-, green- and blue-sensitive silver halide emulsion layers comprising direct negative silver halide emulsion layers adapted to provide a silver image in terms of the exposed areas of the respective silver halide emulsion layer, upon development with a silver halide developing agent, as a function of the point-to-point degree of exposure of the respective silver halide emulsion layer to incident actinic radiation, and each of said cyan, magenta and yellow dyes being a silver halide developing agent and being soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of exposure of its associated silver halide emulsion layer; an alkaline solution permeable polymeric layer dyeable by said dyes; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition having said first pH to a second pH at which said dyes are substantially nondiffusible; a dimensionally stable processing composition impermeable transparent layer; and means securing said layers in substantially fixed relationship; and a rupturable container, retaining an aqueous alkaline processing composition having said first pH and containing dispersed therein opacifying agent in a quantity sufficient to mask said cyan, magenta and yellow dyes associated with said red-, green- and blue-sensitive silver halide emulsion layers and a diffusible silver halide desensitizing agent adapted to effect desensitization of said silver halide emulsion layers, fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition contents intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, to provide to each of said red-, green- and blue-sensitive silver halide emulsion layers a latent image in terms of the exposed areas of each of said red-, green- and blue-sensitive silver halide emulsion layers as a function of the point-to-point degree of exposure thereof;

(b) applying compressive pressure to said rupturable container to effect unidirectional discharge of said container's aqueous alkaline processing composition contents intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer;

(c) effecting thereby development of the latent image contained in the exposed areas of said red-, green- and blue-sensitive silver halide emulsion layers as a function of the point-to-point degree of exposure thereof and desensitization of said red-, green- and blue-sensitive silver halide emulsion layers;

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

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

(f) transferring, by diffusion, at least a portion of each of the imagewise distributions of cyan, magenta and yellow dye to said dyeable polymeric layer to provide thereto a multicolor dye image;

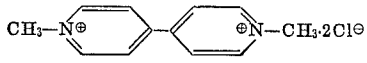
(g) transferring, by diffusion, subsequent to substantial dye transfer, a sufficient portion of the ions of the aqueous alkaline processing composition to the polymeric acid layer to thereby reduce the alkalinity of said film unit from said first pH at which said cyan, magenta and yellow dyes are diffusible to said second pH at which said dyes are substantially nondiffusible; and

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

16. A process of forming transfer images in color as defined in claim **15** wherein said opacifying agent is actinic radiation reflective.

17. A process of forming transfer images in color as defined in claim **16** wherein said opacifying agent is titanium dioxide.

18. A process of forming transfer images in color as defined in claim **17** wherein said desensitizing agent is



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