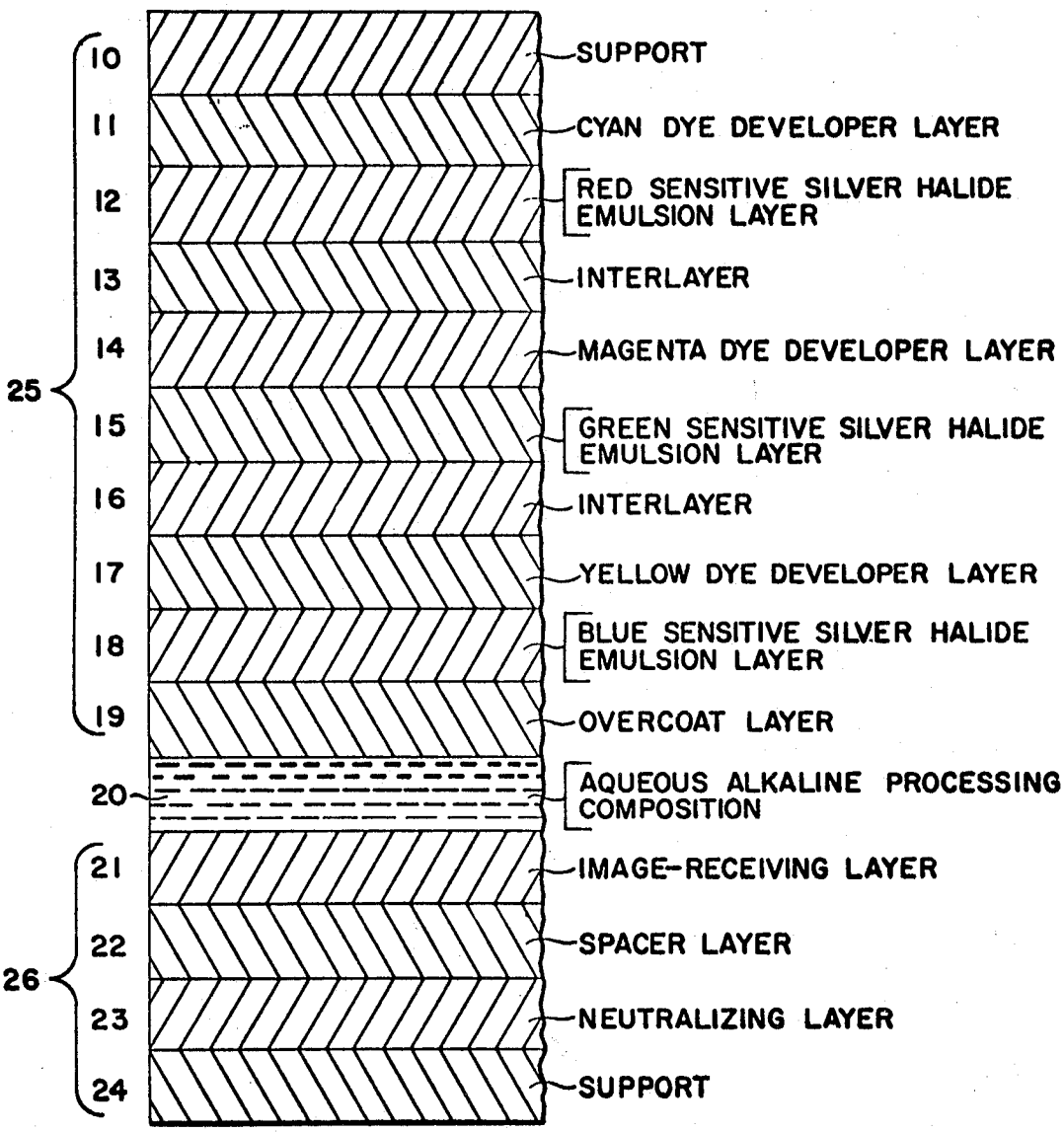
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PHOTOGRAPHIC COLOR DIFFUSION-TRANSFER ELEMENT COMPRISING AQUEOUS FILM-FORMING SYNTHETIC POLYMER SUSPENSION LAYERS INTERMEDIATE ITS SENSITIVE LAYERS AND PROCESSES FOR THEIR USE

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PHOTOGRAPHIC COLOR DIFFUSION-TRANSFER ELEMENT COMPRISING AQUEOUS FILM-FORMING SYNTHETIC POLYMER SUSPENSION LAYERS INTERMEDIATE ITS SENSITIVE LAYERS AND PROCESSES FOR THEIR USE

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ABSTRACT OF THE DISCLOSURE

Diffusion transfer photographic products comprising a support carrying at least two selectively sensitized silver halide emulsion layers, each having a dye which is a silver halide developing agent of predetermined color associated therewith, and a layer intermediate the emulsion layers comprising a dye impermeable coalesced essence of an aqueous film-forming polymer dispersion and a processing composition permeable material associated therewith and adapted to render said layer permeable to solubilized dye image-forming material subsequent to being contacted with processing composition.

This application is a continuation-in-part of U.S. patent application Ser. No. 880,205, filed Nov. 29, 1969 in the names of James A. Avtges, Jerome L. Reid, Herbert N. Schlein and Lloyd D. Taylor.

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

BACKGROUND OF THE INVENTION

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 to actinic radiation 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 disclosed therein, 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 diffusion to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-reeciving element receives a depth-wise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. In one disclosed preferred embodiment, 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 utiilzing 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 stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion status, 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 dye image-forming materials which are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a

coating solution 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.

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 vinyl-phthalimide 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-vinyl-pyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of 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-unsautrated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers or 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 of component layers of photographic film units, reference may be made to U.S. Pats. No. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171; and the like.

U.S. Pat. No. 3,362,819 discloses image-receiving elements, particularly adapted for employment in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, preferably an inert timing or spacer layer, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned patent, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, nondiffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose 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 positive 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, which renders unoxidized dye developer substantially non-diffusible. 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 further dye transfer. This processing technique thus effectively minimizes changes in color balance which might result from a longer than necessary imbibition time for 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 patent 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 patent, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It 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. Other such spacer layers which are suitable for use in the image-receiving element are disclosed and claimed in U.S. Pat. No. 3,421,893.

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

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

For the production of the photoresponsive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or, alternatively, employing any of the various flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pats. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., Photography, Its Materials and Processes, 6th ed., 1962.

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

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

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

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

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as 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 a multiplicity of readily available U.S. patents.

In accordance with U.S. Pat. Nos. 3,415,644, 3,415,645 and 3,415,646, an image-receiving element need not be separated from superposed contact with a photosensitive element comprising a silver halide emulsion subsequent to substantial transfer image formation if the image-receiving element is transparent and a processing composition containing a substance rendering the processing composition layer opaque is spread between the image-receiving layer and the photosensitive element. The use of the interlayers of the present invention is considered applicable to such processes.

Specifically, an integral diffusion transfer photographic film unit particularly adapted for the production of a dye transfer image of improved stability will be constructed, for example, in accordance with aforementioned U.S. Pat. No. 3,415,644 to include a photosensitive element comprising a laminate having in sequence as essential layers, a dimensionally stable opaque support layer, a photosensitive silver halide emulsion layer having as-

sociated therewith dye image-providing material which is soluble and diffusible in alkali at a first pH, an alkaline solution permeable polymeric layer dyeable by the dye image-providing material, a polymeric acid layer containing sufficient acidifying material to effect reduction subsequent to substantial transfer dye image formation of a 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 support layer, said dimensionally stable support layers comprising extremities of the described photographic film unit composite structure. In combination with the laminate a rupturable container retaining an aqueous alkaline processing composition having the first pH and containing an opacifying agent in a quantity sufficient to mask the dye image-providing material, is fixedly positioned and extends transverse the 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.

Employment of such film units according to the described color diffusion transfer photographic process specifically provides for the production of a highly stable color transfer image accomplished at least in part by in process adjustment of the environmental pH of the film unit from a pH at which transfer processing is operative through a pH at which dye transfer is inoperative subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate during exposure, processing, viewing and storage, and such transfer image exhibits the required maximum and minimum dye transfer image densities, dye saturations, hues, definition, etc. It should, however, be recognized that film units fabricated in accordance with the parameters set forth directly above specifically require the presence of the stated neutralizing component disclosed in U.S. Pat. No. 3,362,819 to effect in situ process adjustment of the film units operational pH range thereby terminating the transfer process at such time as the appropriate transfer image has been formed in the image-receiving element.

OBJECTS OF THE INVENTION

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 include a photosensitive element which comprises a plurality of essential layers including, superposed on a common support at least two selectively sensitized photosensitive strata each having associated therewith, as color transfer image-forming components, a dye of predetermined color which is a silver halide developing agent, wherein at least two of said sensitized strata and associated dyes are separated from each other by a layer comprising the coalesced essence of a synthetic polymeric latex and a selective dye permeation-inducing material as specified hereinafter; to provide photographic diffusion transfer products comprising a photosensitive element, of the last-identified type, in combination with a photographic diffusion transfer image-receiving element comprising a plurality of essential layers including a common support carrying a solution dyeable polymeric layer; and to provide photographic diffusion transfer color processes employing photosensitive film units including, in combination, a photosensitive element and a transfer image-receptive element of the last-identified type, and a fluid photographic diffusion transfer processing composition whereupon interimage effects are minimized and color purity is maximized.

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 drawing, wherein the figure detailed is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process, for the production of a multicolor positive transfer print, the thickness of the various materials being exaggerated.

BRIEF SUMMARY OF THE INVENTION

It has been discovered that if one or more of the interlayers of an integral multilayer photosensitive element as described above is specifically selected to comprise the coalesced essence of a latex comprising a synthetic polymer as a continuous phase, and a material which provides predetermined image-forming dye permeation characteristics to said coalesced latex and is compatible therewith as a discontinuous phase, interimage effects are minimized and color purity is maximized.

BRIEF DESCRIPTION OF THE DRAWING

As detailed in the illustrative drawing, a photosensitive element **25** which has been selectively exposed to actinic radiation comprises: a support **10**; a layer **11** containing a cyan die developer; a layer **12** containing a red-sensitive silver halide emulsion layer; an interlayer **13** comprising the coalesced essence of a synthetic polymeric latex and a composition which provides selective dye permeation characteristics thereto; a layer **14** containing a magenta dye developer; a layer **15** comprising a green-sensitive silver halide emulsion; a second interlayer **16** comprising the coalesced essence of a synthetic polymeric latex and a material which provides selective dye permeation characteristics thereto; a layer **17** containing a yellow dye developer; a layer **18** comprising a blue-sensitive silver halide emulsion; and a protective overcoat layer **19**.

As shown in the drawing, the multilayer exposed photosensitive element **25** is in processing relationship with an image-receiving element **26** which, as aforenoted, may be permanently integral therewith, and a layer of processing composition distributed intermediate elements **25** and **26**.

Image-receiving element **26** comprises: a support **24** which may comprise a transparent material an acid reacting neutralizing layer **23**; a spacer layer **22**; and an image-receiving layer **21**. As previously discussed, liquid processing composition **20** is effective to initiate development of latent images in the denoted silver halide emulsion strata and initiate the inherent dye permeation propensities of the denoted interlayers which will ultimately cause the respective dyes associated with the denoted silver halide emulsions to migrate from areas where the dye associated silver halide emulsion has not been subject to exposure, in the direction of the image-receiving element **26** to thereby provide a dye image thereto substantially in relation to the point-to-point degree of actinic radiation stimulus incident on each respective dye associated silver halide emulsion. As has been above noted, after substantial image formation, the image-receptive element may be separated from the photosensitive element or, in certain embodiments, may be permanently integral therewith.

DETAILED DESCRIPTION OF THE INVENTION

It will be appreciated that the essence of the present invention resides in the utilization of a photosensitive diffusion transfer element comprising at least two selec-

tively sensitized silver halide strata separated by an interlayer comprising the coalesced essence of an aqueous film-forming synthetic polymeric dispersion, as a continuous phase, and a material compatible therewith, as a discontinuous phase, characterized in that said compatible material is permeable to, and said coalesced dispersion is either permeable or impermeable to, but preferably permeable to, various photographic-associated materials such as water molecules, hydroxy ions, antifoggant molecules and various other adjuncts generally contained in diffusion transfer photographic processing compositions; and, subsequent to contact of said interlayer with said processing composition, said interlayer is rendered permeable to processing composition solubilized dye image-forming material by reason of said compatible material being rendered image-forming dye permeable. Emphasis is placed upon the compatibility of the permeation-inducing ingredient with the coalesced latex since incompatibility between the two systems will result in a film which is not transparent and is macroscopically not homogeneous. As far as the instant invention is concerned, the coalesced latex film, throughout the requisite period required for the initiation and completion of the photographic functionality of the system, is either permeable to, or provides an impermeable barrier to, hydrophilic species as, for example, hydroxyl ions. It is to be emphasized that the selective image-forming dye permeation properties induced to such a layer are imputed thereto only through the action of a selective dye permeation inducing material, that is, the discontinuous phase. Accordingly it will be appreciated that within the context of the present invention, any interlayer is considered operable therein which comprises a hydrophilic species permeable or impermeable film comprising an image-forming dye impermeable coalesced essence of a synthetic polymeric latex, and a compatible dye permeation-inducing material which is intimately admixed therewith. Various degrees of compatibility, of course, may be achieved and the indicativeness of such compatibility may be appreciated by the clarity of the ultimate film produced—light scatter being a concomitant result of the absence of compatibility between the coalesced latex and the dye permeation-inducing material used therewith, and being further indicative of degree of macromolecular nonhomogeneity. It will therefore be recognized that the discontinuities provided within the coalesced latex film by the dye permeation-inducing material must be sufficiently small so as to obviate the induction of scattering of light incident thereon. From the point of view of the instant invention, an interlayer is considered homogeneous if the coalesced latex contains a dye permeation-inducing component which is distributed compatibly throughout the coalesced latex film so as not to produce scattering of incident light. In absolute terms, that is, on a microscopic level, the layer described herein will generally consist of the predescribed coalesced latex with a multiplicity of small localized areas, comprising the predescribed dye permeation-inducing component, therethrough; such a component will preferably comprise materials disclosed in U.S. patent application Ser. No. 854,491, filed on Sept. 2, 1969 in the name of Richard J. Haberlin, and U.S. Pat. No. 3,421,892, as will be more fully discussed hereinbelow.

Among the various latex materials which have been found to impart the requisite functionality to the herein considered systems are latices of polyvinylidene chloride, lightly carboxylated styrene butadiene copolymers, polyvinyl chloride, vinyl chloride-vinyl acetate copolymers, acrylic polymers and copolymers as, for example, a terpolymer of butylacrylate, methylmethacrylate and small amounts of acrylic acid or methacrylic acid, and innumerable other latices which will readily come to mind to one of ordinary skill in polymer chemistry. An extensive compilation of appropriate latices which may be utilized herein will be found in U.S. Pat. No. 2,795,564.

The latex component of the system comprising the present invention may be chosen so that the coalesced film produced therewith provides a desired hydroxide ion permeability when cast into a film. Preferred latex materials comprise a 60–38–2 copolymer of methylmethacrylate, butylacrylate and acrylic acid, respectively; a 60–30–4–6 copolymer of butylacrylate, diacetone acrylamide, styrene and methacrylic acid, respectively; and a 60–30–4–6–1.5–0.5 copolymer of butylacrylate, diacetone acrylamide, styrene, methacrylic acid, 2-sulfoethyl methacrylate and divinyl benzene, respectively, all proportion designations being on a by weight basis unless otherwise denoted.

The coalesced latex portion of the interlayers comprising the present invention will be denoted as the "continuous phase," while the dye permeation-inducing component will be denoted as the "discontinuous phase." Such terminology is considered to connote an admixture of the two components with the former component being present in greater concentration than the latter—which may be present in the form of continuous channels, etc. throughout the coalesced latex.

The dye permeation-inducing composition utilized in conjunction with the coalesced latex will itself provide a controlled permeability of hydrophilic moieties through the composite barrier layer. Such selective permeability could possibly be provided by, for example, a leaching mechanism wherein the permeation-inducing composition is actually withdrawn from the coalesced latex and leaves in its place channels through which the hydrophilic moieties may migrate or, in a more preferred embodiment, a mechanism wherein the permeation-inducing material is itself hydrated whereupon it swells and allows hydrophilic moieties to pass through its hydrated molecular structure at a predetermined rate. Such materials are disclosed in aforementioned U.S. patent application Ser. No. 854,491 and U.S. Pat. No. 3,421,892, and generally comprise a hydratable synthetic polymer which possesses a hydration rate sufficiently less than the development rate and greater than the fogging rate of the dye associated silver halide emulsion which possesses the slowest development rate and the most rapid fogging rate of the two emulsions intermediate which the barrier material is positioned. As examples of such dye permeation-inducing materials which may be utilized in conjunction with the various latices employed within the context of the present invention, mention may be made of isopropyl cellulose, preferably containing about 1.3 isopropyl groups per cellulosic monomer unit, hydroxypropyl cellulose, acrylonitrile acrylic acid copolymers, methylacrylate acrylic acid copolymers, preferably containing about 3% by weight acrylic acid, poly-N-ethyl acrylamide, polyacrylamide, polyethylene oxide, terpolymers of N-ethylacrylamide, methylacrylamide and acrylamide, copolymers of N-ethylacrylamide and 2-vinyl pyridine, copolymers of N-isopropyl acrylamide and N-vinyl pyrrolidone, copolymers of N-isopropyl acrylamide and dimethylaminoethyl acrylate, etc. As is disclosed in U.S. Pat. No. 3,421,892, many of the above-denoted materials have been found to provide an increase in temperature latitude in various diffusion transfer photographic systems in that the rate at which the permeation induction propensities of such materials are activated after contact with processing composition comprises an inverse function of temperature so that, with increasing temperature, the permeation characteristics of the material diminish, while with decreasing temperature, an increase in permeation propensities is accomplished.

Among other materials which may be utilized as dye permeation-inducing compositions are graft copolymers, particularly on a polyvinyl alcohol backbone, as, for example, those disclosed in U.S. patent application Ser. No. 790,648, filed Jan. 13, 1969. Such materials are generally prepared by ceric ion initiation and may be generically considered as polyvinyl amide graft copolymers. It will, therefore, be appreciated that the dye permeation-

induction material of the present invention is a composition generally permeable to hydrophilic moieties and specifically compatible, according to the above definition, with the coalesced essence of a latex material as described above in detail.

The phenomenon of coalesced latex film healing, that is, the exudation of a discontinuous phase in a coalesced latex film, is a constant problem encountered when one intends to incorporate a material which will produce a microscopically nonhomogeneous coalesced latex system. Within the context of the present invention, it has been found that such a problem may be substantially completely alleviated by incorporating into the latex system a material which will impotentiate healing mechanisms. Succindialdehyde, for example, has been found to prevent healing and provide an additional mechanism for tailoring the permeation characteristics of various coalesced latex interlayers by forming a crosslinked system with certain of the permeation-inducing components as, for example, polyacrylamide.

Further within the context of the present invention, the latex utilized should inherently form a continuous film at, or below casting temperature, since the alternative is an uncoalesced film comprising a multiplicity of ball-like synthetic polymeric particles with an inherent permeation propensity attributable to its porous structure. Dye permeation-inducing compositions within the context of the present invention generally also comprise thickeners for the latex system and provide a desired viscosity in order to facilitate coating of the material in a multilayer film format.

It is, of course, understood that various surfactants, coating aids, etc., may be incorporated in the lattices utilized herein to modulate the coalescense required, etc., to the system. In addition, control of ion concentration and adjustment of other parameters may be routinely carried out according to the desires of the operator. Such materials and techniques are well within the ambit of knowledge possessed by one of ordinary skill in latex chemistry.

Interimage problems in a diffusion transfer color system comprising a multilayer photosensitive negative such as that depicted in the drawing may result from, among other things, the combination of a given silver halide-associated dye with a silver halide emulsion layer other than the silver halide emulsion layer by which its diffusion is intended to be controlled. The combination of a dye with an exposed silver halide emulsion other than its intended controlling silver halide emulsion reduces the number of dye associative sites available in such emulsion to its associated dye material with a concomitant undercontrol of such dye material. It will be accordingly appreciated that color purity is severely affected due to an overcontrol of the migration of certain dye systems and an undercontrol of others. For example, assuming an element such as that depicted in the drawing is exposed to electromagnetic radiation actinic only to the red-sensitive emulsion, in the ideal situation, upon imbibition of processing composition and development of the red-sensitive silver halide emulsion, all of the cyan dye present behind the red-sensitive emulsion should be controlled to the extent that it is prevented from migrating toward the image-receiving element to thereby provide a red image in said element by the total migration of the magenta and yellow dyes. If, however, it is possible for the magenta dye developer to cause development of a portion of the red-sensitive silver halide emulsion by back diffusing through the interlayer, the resultant image will be desaturated by a lack of magenta, which is tied up with the red-sensitive emulsion, and contaminated by the presence of a small amount of cyan dye which has been allowed to migrate since the magenta dye developer has been combined with the cyan dye associated silver halide emulsion. As will be demonstrated by the example hereinbelow, interimage effects due to back migration are substantially obviated by the interlayers of the present invention with the concomitant increase in ultimate color purity in the transferred image.

In order to provide the above-denoted reduction in interimage effects throughout the disclosed exemplary diffusion transfer multicolor system, it has been found that as a practical matter, the interlayer denoted as element **16** in the drawing, that is, the barrier interposed between the green-sensitive silver halide emulsion layer and the yellow dye developer layer, should be "looser" than the barrier denoted in the drawing as reference numeral **13** and positioned between the red-sensitive silver halide emulsion layer and the magenta dye developer layer. By "looseness," it is intended to connote dye permeation characteristics which provide to said layer dye permeability in a time less than that required for the barrier denoted as **16**, to achieve a dye permeable state. The reason for tailoring the barrier layers in this way may be appreciated by referring again to the drawing. As the wave front of processing composition moves from layer **20** toward the support **10**, development of the various emulsion layers is initiated. At this point, interlayer **16** prevents yellow dye developer from migrating into the green-sensitive silver halide emulsion and likewise interlayer **13** prevents magenta dye developer from migrating into and associating with exposed red-sensitive silver halide emulsion. As development progresses, the permeability of interlayers **13** and **16** increases until they reach a point where dye molecules, substantially larger than the processing composition molecular species which initially pass through the barrier materials, are able to migrate therethrough. Ideally, migration of any of the dye materials will be held up until its own associated silver halide emulsion is substantially developed to accurately control the dye throughput in order to assure color purity in the ultimate photographic picture produced in the image-receiving layer. As the development function progresses, the stimulus for dye migration in each of the three dye containing areas of the negative element is increased. There is substantially no impediment to migration of yellow dye in the direction of the image-receiving layer, and it diffuses prior to the magenta or cyan dye, which are not only solubilized at a later time in the process, but are held back by the activity of the interlayers positioned between them and the image-receiving layer. Accordingly, it will be appreciated that even after substantial development of the green-sensitive and red-sensitive silver halide emulsions it would be preferable to cause the interlayer separating the yellow dye developer from the green-sensitive silver halide emulsion layer to become dye permeable at a point in time prior to the instant when the interlayer between the magenta dye developer layer and the red-sensitive silver halide emulsion layer is rendered dye permeable so that the migration stimulus acting on the magenta dye will be toward the image-receiving layer. Such a system will provide for the initial diffusion of yellow dye developer followed by initiation of diffusion of the magenta dye developer and finally, initiation of diffusion of the cyan dye developer through the system toward the image-receiving layer. By providing such barrier functionality to the described diffusion transfer photographic process, only dye material which is intended to be associated with a given spectrally sensitive silver halide emulsion will be coupled therewith so that interimage effects as above described are substantially obviated.

Succinctly, employment of the detailed interlayer during the hereinbefore described diffusion transfer process acts to provide a barrer with respect to retardation of the positional displacement of dye prior to establishment of substantial imagewise emulsion control of the associated dye's diffusion, with the concomitant results of providing significantly higher process speed, greater dye saturation, and improved red, green and blue hues, in addition to, and by reason of, improved photosensitive element interimage effects. These effects result, at least in part, from

prevention of any respective dye's development of silver halide emulsion strata, other than the specific stratum with which the individual dye is directly associated; generally characterized, respectively, as yellow, magenta and cyan "drop-off."

Image-forming dye associated with the silver halide emulsions of the present invention is preferably held immobile by the disclosed barrier material until the silver halide emulsion having the slowest development rate is substantially developed. However, diffusion through said barrier material is not held up so long that the silver halide emulsion having the fastest development rate will fog thereby preventing image-forming dye from reaching the image-receiving element. Under ideal conditions parameters for hydration and/or development of adjacent silver halide emulsion may be determined using conventional techniques. However, it is to be emphasized that in any system utilizing the present invention, the paramount consideration is balancing the relativity of the processing composition permeation rate of the barrier material to the development and fogging rates of the related silver halide emulsions. Absolute numbers may only be used to describe one given system. Broadly speaking one of ordinary skill in the art possessing the present invention would be able to determine the specific parameters which must be utilized in designing the barrier material of the present invention when the fogging and development rates of the associated silver halide emulsions are known.

In a preferred embodiment of the present invention, the gelatino silver halide emulsion layers are about 0.6 to 6 microns thick, the dye-retaining layers are about 1 to 7 microns thick, and the polymer interlayers are 0.5 to 3 microns thick. With respect to a preferred image-receiving element, the image-receiving layer is about 0.25 to 0.4 mil. thick, the polymeric acid layer is about 0.3 to 1.5 mils. thick, and the spacer layer is about 0.1 to 0.7 mil. thick. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

The instant invention is thus directly concerned with a photosensitive element which comprises a common support having, positioned on one surface, at least two selectively sensitized photosensitive silver halide emulsion strata, for example, having predominant spectral sensitivity to separate regions of the spectrum, each having a dye of predetermined color associated therewith, for example, a spectral absorption range substantially complementary to the predominant sensitivity range of the associated emulsion, separated by a spacer or interlayer comprising the aforementioned coalesced latex in combination with one or more dye permeation-inducing materials.

Preferably, the selective dye permeation-inducing component is a polymer which is alkaline solution permeable and hydratable; most preferably, substantially instantaneously permeable by solution retained molecules, such as, for example, auxiliary silver halide developing agents, antifoggants, accelerators, arrestors, and the like, having a geometric size less than the geometric size of the transfer image-forming dye, in order that photographic development, and the like, may proceed, with respect to the emulsion next adjacent the support layer, within the earliest time sequence possible.

In a most preferred embodiment, the selected polymer possesses a processing composition hydration rate sufficiently less than the development rate and greater than the fogging rate of the respective dye associated silver halide emulsion possessing the slowest development rate and the most rapid fogging rate of the two emulsions intermediate which the polymer is positioned, in order to, as above denoted, simultaneously retard rearward diffusion of the dye associated with the silver halide emulsion next adjacent the element's surface and forward diffusion of the dye associated with the silver halide emulsion next adjacent the film base, until the respective imagewise emulsion development and control of each dye is substantially established. There is thus provided an effective restriction of each dye's developing function to the specific silver halide emulsion with which it is associated, and thereby color isolation selectively determined by the incident spectral energy distribution per unit area of the respective photoresponsive silver halide emulsion's exposure.

The present invention has been specifically found to possess certain distinct advantages, when compared with certain interlayer systems of the prior art, which teaches the employment of a barrier interlayer to separate an outer emulsion layer and associated dye from an inner emulsion layer and its associated dye, in order that processing may be effected in a stepwise manner. The prior art barrier layer comprises, in general, a polymeric layer which is permeated by the fluid processing composition at a rate sufficiently slow so as to insure that permeation of the fluid composition, from an outer emulsion layer into the next inner emulsion layer, is deferred, until processing of the outer emulsion layer is substantially complete. In general, barrier interlayers of this type comprise two distinct types. The first type comprises impermeable polymeric interlayers which possess a solution rate, upon contact with the fluid processing composition, during photographic processing, such that the interlayer requires a longer time span to be rendered permeable than the time interval necessitated to effect development of the outer emulsion stratum. The second type comprises impermeable polymeric interlayers which possess a hydrolysis rate, upon contact with the fluid processing composition, such that the interlayer requires a time interval for the occurrence of hydrolysis, sufficient as to provide processing composition permeability, in excess of that required to effect development of the outer emulsion layers.

As will be appreciated from the above description of the prior art barrier interlayers, the present invention possesses, when compared with such prior art systems, the specific advantage of providing the previously stated control of dye diffusion during substantially contemporaneous development of all the emulsion strata constituting the integral multilayer photosensitive element. It thus avoids the prior art's necessity of conducting development in relatively insulated steps, with such processes' concomitant increase in the necessary processing time interval and the resultant propensity for image degradation, for example, from fog buildup and the like, in the outer emulsion strata remaining in processing composition contact for an overly extended period, or conducting substantially contemporaneous development of all the emulsion strata, with resultant loss of color isolation, due to undesirable migration of dye preceding effective control; or an empirical system combining the above systems in such a manner as is designed to effect a balance between the undesirable effects of each and to thus minimize the effects to at least some extent.

In accordance with the teachings of the art, the positioning of the respective silver halide emulsion/dye developer units of the tripack configuration detailed above may be varied. However, it is generally preferred to constitute the tripack configuration in accordance with the general scheme set forth in the drawing, that is, the cyan dye developer/red-sensitive emulsion unit next contiguous the support surface and the yellow dye developer/blue-sensitive emulsion unit most distant from the support surface.

The present invention will be illustrated in greater detail in conjunction with the following procedures which set out representative embodiment and photographic utilization of the novel photosensitive elements of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

A photosensitive element (hereinafter control) may be

prepared by coating in succession, on a polyethylene terephthalate base, the following layers:

(1) A layer of cyan dye developer 1,4-bis(β-[hydroquinonyl - α - methyl] - ethylamino) - 5,8-dihydroxyanthraquinone and methyl phenyl hydroquinone dispersed in gelatin, and coated at a coverage of about 75 mgs. 100 mgs. gelatin, and 10 mgs. methyl phenyl hydroquinone/ft.^{2}.

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 200 mgs. of silver and 50 mgs. gelatin/ft.^{2}.

(3) A layer of gelatin coated at a coverage of about 150 mgs./ft.^{2}.

(4) A layer of magenta dye developer 2-(p-[α-hydroquiononyl ethyl] - phenylazo) - 4 - isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of about 75 mgs. dye and 175 mgs. gelatin/ft.^{2}.

(5) A green-sensitive gelatino silver iodo-bromide emulsion coated at a coverage of about 750 mgs. of silver and 50 mgs. gelatin/ft.^{2}.

(6) A layer of gelatin coated at a coverage of 100 mgs./ft.^{2}.

(7) A layer of yellow dye developer, 4-(p-[β-hydroquinonyl ethyl] - phenylazo) - 3 - (N-n-hexyl carboxamido) - 1 - phenyl - 5 - pyrazolone, and methyl phenyl hydroquinone, dispersed in gelatin and coated at a coverage of about 50 mgs. dye, about 75 mgs. gelatin and 15 mgs. methyl phenyl hydroquinone/ft.^{2}.

(8) A blue-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 75 mgs. of silver and 20 mgs. gelatin/ft.^{2}.

(9) A layer of gelation coated at a coverage of about 50 mgs. gelatin/ft.^{2}.

Similar photosensitive elements to those prepared according to the procedure denoted in the paragraph next above were fabricated with the sole exceptions that layers **3** and **6**, instead of comprising gelatin, respectively, comprised, in the first instance (hereinafter Test 1) layers comprising the coalesced essence of an aqueous polymeric dispersion comprising a 60–38–2 terpolymer of methylmethacrylate, butylacrylate and acrylic acid, coated in layer **3** at a coverage of about 150 mgs./ft.^{2} of terpolymer, and in layer **6** at a coverage of about 100 mgs. of terpolymer/ft.^{2}, layer **3** additionally containing approximately 5 mgs./ft.^{2} of polyacrylamide having a molecular weight of about three million, and layer **6** containing such polyacrylamide at a level of approximately 12 mgs./ft.^{2}.

In the second instance (hereinafter Test 2) a photosensitive film unit was fabricated similar to Test 1 with the exception that about 5 mgs./ft.^{2} of succindialdehyde was included in the coating material of layer **6**. It should be noted at this point that the succindialdehyde, or other anti-healing agents, may be incorporated in the system of the present invention by being placed in any layer of the photosensitive element not deleteriously effected thereby.

A multiplicity of diffusion transfer image-receiving elements may be prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polyethylene/malec anhydrde 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 polymerc acid layer approximately 0.75 mil. thick. The external surface of the acid layer may be coated with a 4% solution of polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.3 mil. thick. The external surface of the spacer layer may then be coated by a 2:1 mixture by weight of polyvinyl alcohol and poly-4-vinyl pyridine at a coverage of approximately 600 mgs./ft.^{2} to provide a polymeric image-receiving layer approximately 0.40 mil. thick. The thus-prepared image-receiving elements may then be baked at 180° F. for 30 minutes and then allowed to cool.

The control and test photosensitive elements **1** and **2** may be next exposed through a sensitometer to light in columns of yellow, red and green ranges of the visible spectrum, by interposing between the elements and a xenon light source, respectively, Wratten Filters Nos. 2B and 15; 29; and 99; all such exposures being made through a step wedge (Eastman Kodak standard colloidal carbon in glass wedge with a slope of 1.18 density units per inch with a cutoff at 340 nms.) and adjusted to provide an exposure in the maximum exposure area of two meter candle seconds; the minimum exposure area, of course, representing zero exposure. The photosensitive elements may then be processed by spreading an aqueous liquid processing composition comprising:

Water—100 cc.
Potassium hydroxide—11.2 gms.
Hydroxyethyl cellulose (high molecular weight)—3.9 gms.
Potassium thiosulfate—0.5 gms.
Benzotriazole—3.5 gms.
N-benzyl-*a*-picolinium bromide—2.0 gms.

between an individual image-receiving element and each of the exposed multicolor photosensitive elements as they are brought into superposed relationship. After an imbibition period of 60 seconds the image-receiving element may be separated from the remainder of the film assembly and analytical dye densities, calculated from measurements made on a continuously reading densitometer (including corrections for multiple internal reflections and dye tail absorptions) may be tabulated and illustrative results appear in tabular form below. With respect to film units fabricated in the general manner set forth above. Table 1 describes, for the red column (i.e., the image resultant from exposure through the Wratten Filter No. 29) magenta dye density at no exposure and at maximum exposure; magenta dye drop-off, that is, the difference in magenta dye detected when the element has received no exposure versus that detected at maximum exposure; yellow dye density at maximum exposure; and the ratio of yellow dye density to magenta dye density at maximum exposure. The second table, which relates to the green column (i.e., the image resultant from exposure through the Wratten Filter No. 99) shows, respectively, yellow dye density at no exposure and maximum exposure; yellow dye drop-off; magenta dye density at maximum exposure; cyan dye density at maximum exposure; and the ratio of yellow dye density to cyan dye density at maximum exposure. Table 3 denotes the dye density of yellow dye in the yellow column (i.e., the image resultant from exposure through the Wratten Filters Nos. 2B and 15) at maximum exposure.

TABLE 1.—ANALYTICAL DYE DENSITIES—RED COLUMN

(Area exposed through Wratten Filter No. 29)

	Control	Test 1	Test 2
1. Magenta density—no exposure	1.30	1.25	1.18
2. Magenta density—maximum exposure	0.80	0.90	0.88
3. Magenta drop-off (1. minus 2.)	0.50	0.35	0.30
4. Yellow density—maximum exposure	0.71	0.87	0.97
5. Yellow density—maximum exposure/ magenta density—maximum exposure	0.88	1.10	0.97

TABLE 2.—ANALYTICAL DYE DENSITIES—GREEN COLUMN

(Area exposed through Wratten Filter No. 99)

	Control	Test 1	Test 2
1. Yellow density—no exposure	0.85	1.03	1.10
2. Yellow density—maximum exposure	0.35	0.75	0.85
3. Yellow drop-off (1. minus 2.)	0.50	0.28	0.25
4. Cyan density—maximum exposure	0.80	0.38	0.45
5. Magenta density—maximum exposure	0.23	0.11	0.10
6. Yellow density—maximum exposure/ cyan density—maximum exposure	0.44	1.97	1.89

TABLE 3.—ANALYTICAL DYE DENSITIES—YELLOW COLUMN

(Area exposed through Wratten Filters 2B and 15)

	Control	Test 1	Test 2
Yellow density—maximum exposure	0.33	0.66	0.74

The unusually outstanding results produced by the instant invention are quite evident from the tabulations reproduced above. Note, for example, with reference to Table 1, that the magenta drop off in the red column in the photosensitive units prepared according to the present invention is substantially less than that produced utilizing a conventional gelatin interlayer of the same coverage while producing comparable dye densities.

In addition, it will be noted that the red color produced is richer in the yellow component giving brighter, more natural reds as evidenced by the yellow/magenta dye densities at maximum exposure. In effect, the denoted magenta drop-off in the red column measures the amount of magenta being held back in the system—mostly by being controlled by the red-sensitive emulsion due to back diffusion of the magenta dye material through the interlayer between it and the red-sensitive emulsion. The fact that a much lower magenta drop-off is found in the photosensitive elements produced by the present invention than the gelatin control indicates that less magenta is diffusing back through the interlayer to be caught up by the red-sensitive silver halide emulsion whose sole purpose in the system is to control only cyan dye—the color red being produced by a mixture of yellow and magenta dyes and the absence of the cyan constituent of the photosensitive element.

Looking now at the results obtained in the green column, it will be apparent that substantially higher yellow densities are achieved in exposed areas and a much smaller yellow dye drop-off is produced by the units fabricated in accordance with the instant invention. It is further worthy of note that the magenta dye densities denoted in the green column are far smaller in the units produced by the instant invention than in the control unit. Since the green color is produced by a mixture of yellow and cyan dyes and, ideally, a total absence of magenta dye, it will be appreciated that the lower magenta dye densities produced with the units of the present invention represent a cleaner green color. Furthermore, the yellow to cyan dye ratios in exposed areas indicate a substantially higher yellow dye level in the green color produced, thereby providing greens which are more pleasing to the eye.

Finally, the outstanding performance of the systems produced by the present invention may be further appreciated with reference to Table 3 which indicated more than double the yellow dye densities in the yellow column produced by the instant invention as compared with the control in exposed areas. This, of course, can also be appreciated from the yellow dye density figures denoted for the red column and indicates that more yellow is allowed to come across in the format of the instant invention than in the control due to the prevention of back diffusion of yellow dye with subsequent control of the back diffused dye by the green-sensitive emulsion.

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-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethyleneimino 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.

Although the invention has been discussed in detail throughout employing dye developers, the preferred dye image-forming 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, 2,661,293, 2,698,244, 2,698,798, and 2,802,735, 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, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer.

In products employed in the diffusion transfer processes of this invention, it may be preferable to expose from the emulsion side. In such instances, it is, therefore, desirable to hold the photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera apparatus suitable for processing film of the type just mentioned is provided by the Polaroid Land Camera, sold by Polaroid Corporation, Cambridge, Mass., or similar camera structure such, for example, as the roll film type camera forming the subject matter of U.S. Pat. No. 2,435,717 or the film pack type camera forming the subject matter of U.S. Pat. No. 2,991,702. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure members which rupture a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

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, silver halide solvents, etc., other than those specifically mentioned, provided that the pH of the composition is preferably in excess of at least 10 initially. 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 ex-

posure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminum; 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.

The nature and construction of rupturable containers is well understood in the art; see, for example, U.S. Pat. No. 2,543,181, issued Feb. 27, 1951, and U.S. Pat. No. 2,634,886, issued Apr. 14, 1953.

It will be further apparent that, by appropriate selection of the image-receiving element materials from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency.

While a rupturable container provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition, as by coating the composition on said photosensitive element or otherwise wetting said element with the composition, following which the permeated, exposed photosensitive element, still, without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

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

Throughout the specification and claims, the expression "superposed" has been used. This expression is intended to cover the arrangement of two layers in overlaying relation to each other either in face-to-face contact or in separated condition and including between them at least a layer of fluid processing composition.

In addition, throughout the specification reference has been made to the "coalesced essence" of an aqueous polymeric dispersion. By such it is intended to connote a coalesced film ultimately produced by the removal of the aqueous component of a latex within the parameters set forth hereinabove.

Further throughout the specification a material which provides selective barrier properties to the coalesced latex has been defined as having "permeation-inducing" characteristics. By such it is intended to connote that barrier permeability, at least in part to processing composition components, and substantially totally to dye molecules, is provided to the system primarily by such material.

It also will be recognized that, where desired, the film unit structure may also comprise an integral positive/negative construction carried on a single support.

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, etc.

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 photosensitive element which comprises, in combination:
   (a) a support layer;
   (b) at least two selectively sensitized silver halide layers each having associated therewith a dye image-forming material of predetermined color; and
   (c) a layer intermediate said silver halide layers comprising, as a continuous phase, the coalesced essence of an aqueous film-forming synthetic polymer dispersion adapted to provide a dye image-forming material impermeable polymeric layer upon coalescence and, as a discontinuous phase, a processing composition permeable material adapted to render said intermediate layer permeable to processing composition solubilized dye image-forming material subsequent to contact of said layer with said processing composition.

2. The invention of claim 1 wherein at least one of said dye image-forming materials comprises a dye which is a silver halide developing agent and said processing composition comprises an aqueous alkaline processing composition.

3. The invention of claim 2 wherein said dye is disposed in a separate layer contiguous its associated silver halide layer.

4. The invention of claim 3 wherein said separate layer contiguous said associated silver halide layer comprises gelatin.

5. The invention of claim 1 wherein said film-forming synthetic polymer continuous phase comprises a 60–38–2 terpolymer of methylmethacrylate, butylacrylate and acrylic acid, respectively.

6. The invention of claim 1 wherein said processing composition permeable material comprises polyacrylamide.

7. The invention of claim 1 wherein said processing composition permeable material is a polymer which is processing composition hydratable, upon contact with said processing composition, at a rate which renders said intermediate layer permeable to said solubilized dye image-forming material subsequent to development of the dye image-forming material associated silver halide layer possessing the slowest development rate and preceding substantial fogging of the dye image-forming material associated silver halide layer possessing the most rapid fogging rate.

8. The invention of claim 1 wherein said intermediate layer additionally contains a material adapted to prevent exudation of said processing composition permeable material from said layer.

9. The invention of claim 8 wherein said exudation-preventing material comprises succindialdehyde.

10. The invention of claim 1 wherein said processing composition permeable material is adapted to render said intermediate layer permeable to said processing composition solubilized dye image-forming material, subsequent to contact of said layer with said processing composition, as an inverse function of temperature.

11. The invention of claim 1 which comprises, in combination, a photosensitive element having a diffusion transfer image-receiving element affixed at least one edge thereof, said photosensitive element comprising, as essential layers:
   (a) a support layer;
   (b) at least two selectively sensitized silver halide emulsion layers each having a dye which is a silver halide developing agent of predetermined color associated therewith; and
   (c) a layer intermediate said silver halide emulsion layers comprising, as a continuous phase, the coalesced essence of an aqueous film-forming synthetic polymer dispersion adapted to provide dye

image-forming material impermeable polymeric layer upon coalescence and, as a discontinuous phase, an alkaline processing composition permeable material adapted to render said intermediate layer permeable to alkaline processing composition solubilized dye subsequent to contact of said layer with said alkaline processing composition;

said diffusion transfer image-receiving element comprising, as essential layers:

(1) a support layer; and

(2) an alkaline processing composition permeable and dyeable layer, wherein said photosensitive and said image-receiving elements are adapted to be superposed, the support layers of each element comprising the extremities of the superposed structure.

12. The invention of claim **11** including a rupturable container retaining an aqueous alkaline processing composition affixed one edge of said photosensitive and said image-receiving elements and adapted upon rupture to distribute its contents intermediate said superposed photosensitive and said image-receiving elements.

13. The invention of claim **12** wherein said image-receiving element includes a polymeric acid layer adapted to reduce the alkalinity of said aqueous alkaline processing composition upon contact therewith positioned intermediate said dyeable polymeric layer and said support layer next adjacent thereto.

14. The invention of claim **12** wherein said aqueous alkaline processing composition possesses a pH of not less than about **12.**

15. The invention of claim **11** wherein said image-receiving element support layer is transparent.

16. The invention of claim **15** wherein said photographic film unit comprises a composite structure containing said photosensitive element and said image-receiving element permanently affixed each to the other in superposed relationship, the support layers of each of said elements comprising the extremities of said composite structure, and including a rupturable container retaining an aqueous alkaline processing composition affixed transverse a leading edge of said composite structure and adapted upon application of compressive pressure to distribute its contents intermediate said photosensitive element and said image-receiving element.

17. The invention of claim **11** wherein said photosensitive element contains a plurality of essential layers, including, in sequence:

(a) a support layer;

(b) a red-sensitive silver halide emulsion layer having associated therewith a cyan dye;

(c) an interlayer;

(d) a green-sensitive silver halide emulsion layer having associated therewith a magenta dye;

(e) an interlayer; and

(f) a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye, each of said cyan, magenta and yellow dyes being silver halide developing agents and at least one of said interlayers comprising, as a continuous phase, the coalesced essence of an aqueous film-forming synthetic polymer dispersion adapted to provide a dye image-forming material impermeable polymeric layer upon coalescence and, as a discontinuous phase, an alkaline processing composition permeable material adapted to render the said interlayer permeable to alkaline processing composition solubilized cyan, magenta and yellow dye subsequent to contact of said layer with said alkaline processing composition.

18. The invention of claim **17** wherein said film-forming synthetic polymer continuous phase comprises a 60–38–2 terpolymer of methylmethacrylate, butylacrylate and acrylic acid, respectively.

19. The invention of claim **18** wherein said alkaline processing composition permeable material comprises polyacrylamide.

20. The invention of claim **19** wherein said interlayer comprising said coalesced polymer contains succindialdehyde.

21. A process for forming transfer images in color which comprises the steps of:

exposing a photosensitive element comprising at least two selectively sensitized silver halide emulsion layers each having associated therewith a dye image-forming material and a layer intermediate at least two of said silver halide layers comprising, as a continuous phase, the coalesced essence of an aqueous film-forming synthetic polymer dispersion adapted to provide a dye image-forming material impermeable polymeric layer upon coalescense, and as a discontinuous phase, a processing composition permeable material adapted to render said intermediate layer permeable to processing composition solubilized dye image-forming material subsequent to contact of said layer with said processing composition;

contacting said exposed photosensitive element with said processing composition effecting thereby development of said silver halide emulsions and including dye image-forming material permeability to said intermediate layer whereby imagewise distributions of mobile dye are formed as a function of the point-to-point degree of exposure thereof; and

transferring by diffusion at least a portion of each of said imagewise distribution of mobile dye to a superposed image-receiving layer to provide thereto a multicolored dye image.

22. The invention of claim **21** wherein said film-forming synthetic polymer continuous phase comprises a 60–38–2 terpolymer of methylmethacrylate, butylacrylate and acrylic acid, respectively.

23. The invention of claim **21** wherein said processing composition permeable material is a polymer which is processing composition hydratable at a rate which renders said intermediate layer permeable to said solubilized dye image-forming material subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate.

24. The invention of claim **21** wherein said processing composition permeable material is polyacrylamide.

25. The invention of claim **21** wherein said intermediate layer additionally contains a material adapted to prevent exudation of said processing composition permeable material from said layer.

26. The invention of claim **25** wherein said material comprises succindialdehyde.

27. The invention of claim **21** wherein said processing composition permeable material is adapted to render said intermediate layer permeable to said processing composition solubilized dye image-forming material, subsequent to contact of said layer with said processing composition, as an inverse function of temperature.

28. The invention of claim **21** which comprises the steps of:

exposing a photosensitive element which comprises blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers mounted on a common support layer, said blue-sensitive, green-sensitive and red-sensitive silver halide layers having associated therewith, respectively, yellow, magenta and cyan dyes, each of said dyes being a silver halide developing agent, and a layer intermediate at least two of said silver halide layers comprising, as a continuous phase, the coalesced essence of an aqueous film-forming synthetic polymer dispersion adapted to provide a dye image-forming material impermeable layer upon coalescense, and, as a discontinuous phase, a processing composition permeable material

adapted to render said intermediate layer permeable to processing composition solubilized dye image-forming material subsequent to contact of said layer with said processing composition;

contacting said exposed photosensitive element with said processing composition effecting thereby development of said silver halide emulsions; and

inducing dye image-forming material permeability to said intermediate layer thereby immobilizing said yellow, magenta and cyan dyes as a result of the development of the exposed areas of their associated silver halide emulsions forming thereby an imagewise distribution of mobile yellow, magenta and cyan dyes in unexposed areas of their associated emulsions as a function of the point-to-point degree of exposure and transferring, by diffusion, at least a portion of said imagewise distribution of dye to a superposed image-receiving layer to provide thereto a multicolor dye image.

29. The invention of claim **28** wherein said film-forming synthetic polymer continuous phase comprises a 60–38–2 terpolymer of methylmethacrylate, butylacrylate and acrylic acid, respectively.

30. The invention of claim **28** wherein said processing composition permeable material is a polymer which is processing composition hydratable at a rate which renders said intermediate layer permeable to said solubilized dye image-forming material subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate.

31. The invention of claim **28** wherein said processing composition permeable material is polyacrylamide.

32. The invention of claim **28** wherein said intermediate layer additionally contains a material adapted to prevent exudation of said processing composition permeable material from said layer.

33. The invention of claim **32** wherein said material comprises succindialdehyde.

34. The invention of claim **28** wherein said processing composition permeable material is adapted to render said intermediate layer permeable to said processing composition solubilized dye image-forming material, subsequent to contact of said layer with said processing composition as an inverse function of temperature.

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