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J. A. AVTGES ET AL  
DYE IMAGE PROVIDING MATERIALS WITHIN DIFFUSION  
TRANSFER BARRIER LAYERS

3,748,129

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2 Sheets-Sheet 1

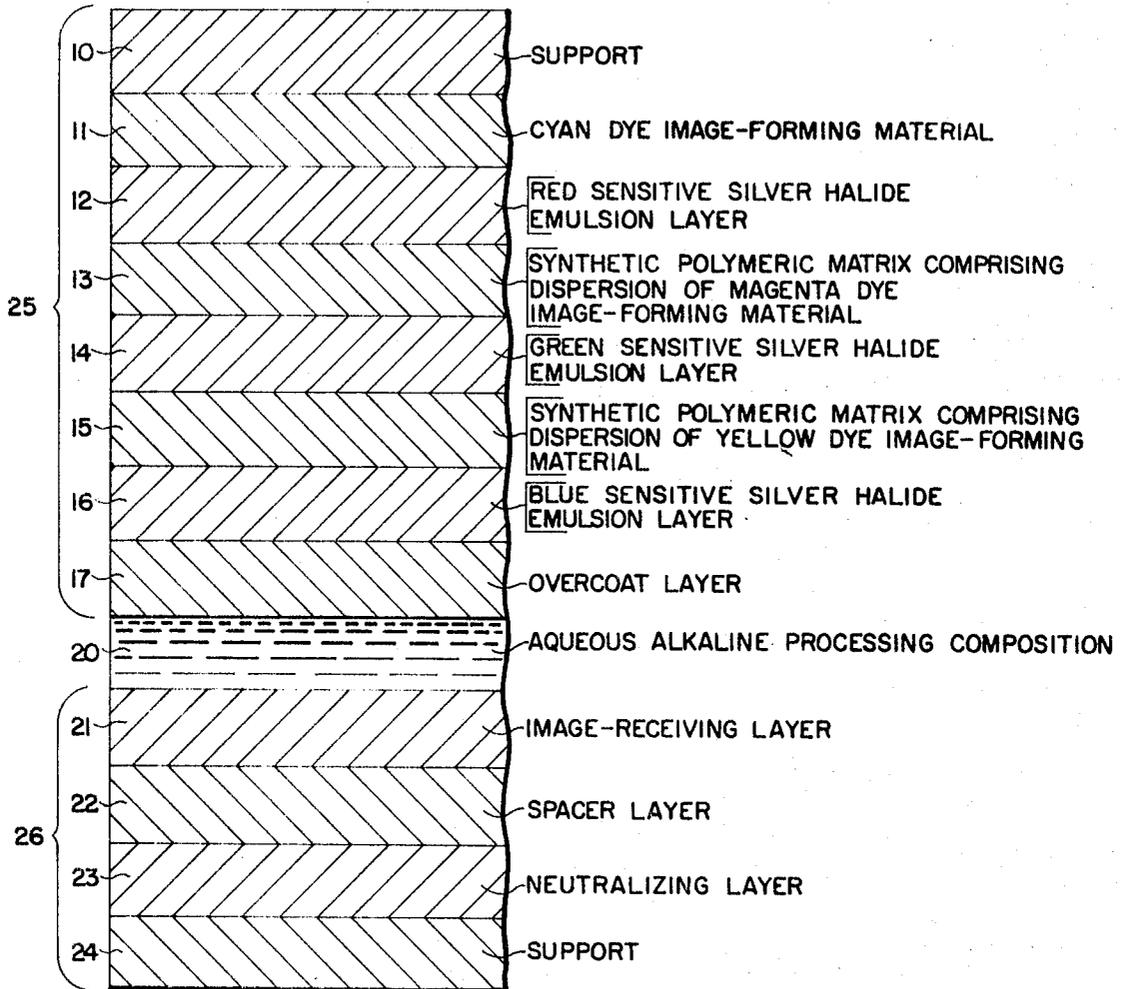


FIG. 1

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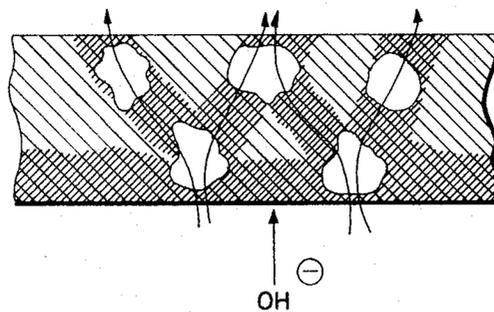
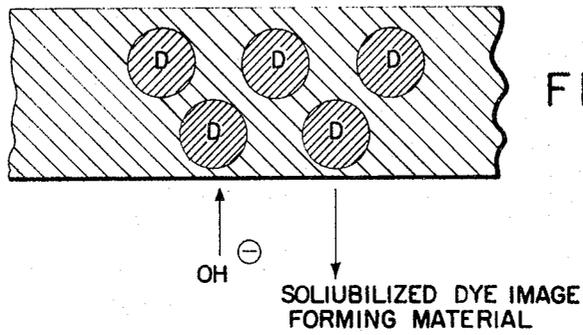
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**DYE IMAGE PROVIDING MATERIALS WITHIN  
DIFFUSION TRANSFER BARRIER LAYERS**

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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 preferably a silver halide developing agent of predetermined color associated therewith, at least one of said dyes being present as a dispersion in a layer immediately adjacent its associated silver halide emulsion layer said dispersion matrix comprising a polymer which is permeable to hydroxyl ion and solubilized dye at a rate which insures substantial development of each dye associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye material.

This application is a continuation-in-part of U.S. patent application Ser. No. 119,331, now U.S. Pat. No. 3,625,685, filed Feb. 26, 1971, in the names of James A. Avtges, Jerome L. Reid, Herbert N. Schlein and Lloyd D. Taylor, which in turn is a continuation-in-part of U.S. patent application Ser. No. 880,205, filed Nov. 29, 1969, in the names of the above inventors, now abandoned.

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 sheet-like 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

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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-receiving 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 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 stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion stratum. Each set of silver halide emulsion and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

The dye developers are 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. In many processes they may be incorporated in the respective silver halide emulsion while, in the present invention, at least one such dye developer must be dispersed in a separate layer behind the respective associated silver halide emulsion.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned

U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in Column 27. As examples of additional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Pats. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

Solid dispersions of dye developers adapted for utilization in a diffusion transfer system are disclosed and claimed in U.S. Pat. No. 3,438,775. Specifically, the particulate dye developer is dispersed in an alkali permeable matrix polymer in a ratio of between about 0.1 to 25 mgs. of dye per mg. of polymer, with preferably 75 percent of the dye particles being less than about 1 micron in diameter.

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 or 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. Nos. 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, non-diffusible 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 de-

rivatives 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 polymeric acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry

strength and when necessary or desirable, suitable sub-coats 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. Patent 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 plasticizers; 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. Patent 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 floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Patents 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. Patents 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. No. 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 dye-retaining layer 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 associated therewith dye image-providing material which is soluble and diffusible in alkali at a first pH, an alkaline solution permeable polymeric layer dyeable by the dye image-providing material, a polymeric acid layer containing sufficient acidifying 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 preferably a silver halide developing agent, at least one of said dyes comprising a dispersion in a layer immediately adjacent its associated silver halide emulsion layer, the dispersion matrix comprising a polymer which is permeable to processing composition and solubilized dye developer at a rate which insures substantial development of each dye associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye developer; 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 drawings, wherein:

FIG. 1 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; and

FIGS. 2 and 3 illustrate the migration of processing

composition and solubilized dye image-forming material in the environment of the present invention.

#### BRIEF SUMMARY OF THE INVENTION

It has been discovered that if one or more silver halide emulsion-associated dye image-forming material components of an integral multilayer photosensitive element, as described above, are dispersed in layers immediately adjacent their associated silver halide emulsions wherein said layers comprise, as a matrices for the dye materials, a synthetic polymer which is permeable to processing composition (hydroxyl ion) and solubilized dye material at a rate which insures substantial development of each dye associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye material, the number of layers comprising such photosensitive elements may be reduced with a concomitant improvement in the results obtained with such elements.

#### BRIEF DESCRIPTION OF THE DRAWING

As detailed in FIG. 1 of the drawings, a photosensitive element **25** which has been selectively exposed to actinic radiation comprises: a support **10**; a layer **11** containing a cyan dye developer; a layer **12** containing a red-sensitive silver halide emulsion; a layer **13** comprising a dispersion of a magenta dye developer in a matrix comprising a polymer which is permeable to processing composition and solubilized dye developer at a rate which insures substantial development of the adjacent green-sensitive silver halide emulsion layer **14** prior to contact of such green-sensitive emulsion layer **14** with substantial amounts of solubilized dye developer diffusing from layers **15** or **11**; the aforesaid layer **14** comprising a green-sensitive silver halide emulsion; a layer **15** comprising a dispersion of yellow dye developer in a matrix comprising a synthetic polymer which is permeable to processing composition and solubilized yellow dye developer at a rate which insures substantial development of adjacent blue-sensitive silver halide emulsion layer **16** prior to contact of such blue-sensitive emulsion with substantial amounts of solubilized dye developer from layers **11** or **13**; the aforementioned layer **16** comprising a blue-sensitive silver halide emulsion; and a protective overcoat layer **17**.

As shown in the drawing, the multilayer exposed photosensitive element **25** is in processing relationship with an image-receiving element **26** which, as aforesaid, 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 solubilize the dye developers associated with such strata to 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 subjected 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.

Referring now to FIG. 2 of the drawings, a microscopic slice of thickness through either layers **13** or **15** of element **25** shown in FIG. 1 (from layer interface to interface) is depicted with dye material dispersed in a synthetic polymer matrix which is permeable to hydroxyl ion and solubilized dye developer at a rate which insures substantial development of an associated silver halide

emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye developer. As hydroxyl ion proceeds from the aqueous alkaline processing composition denoted as 20 in FIG. 1 through photosensitive element 25 it meets a substantial impediment when it reaches layer 15. Meanwhile, preferably a booster developer, such as methyl phenyl hydroquinone, contained in overcoat layer 17, is carried by the processing composition to initiate development of latent images in blue-sensitive emulsion layer 16. Since the hydroxyl ion is only slowly permeable through the matrix material in which dye developer is dispersed, it provides a substantial release of dye developer from layer 15 to cause development of silver halide emulsion layer 16 before it proceeds downstream. As processing composition permeates the matrix material, for example, of layer 15, it reaches areas of dye developer which it quickly dissolves, as will be discussed further hereinbelow. The dye developer then migrates toward the image-receiving layer denoted in FIG. 1 as 21. Processing composition proceeds quickly through the area previously occupied by the dye developer until it reaches additional matrix material at which time it is again slowed. As will be appreciated with reference to FIG. 3, as dye developer is solubilized and migrates from its matrix material, it provides an area with substantially no impediment to diffusion of processing composition. Accordingly, channeling through the matrix material favoring areas in which dye material has occupied will, in a predetermined time lag, cause processing composition to completely penetrate the layer comprising dispersed dye material as it proceeds downstream through the photosensitive element. As will be appreciated from FIG. 3, the double cross-hatching generally depicts processing composition penetration through the system wherein it is generally impeded from moving toward the support layer 10, except in areas in the dye dispersion layer wherein channels through areas containing dispersed dye material are formed.

#### DETAILED DESCRIPTION OF THE INVENTION

It will be appreciated that the essence of the present invention resides in deleting from a conventional diffusion transfer photosensitive element one or more layers thereby eliminating one or more areas where problems could be introduced into the photosensitive element fabrication procedure and providing a simplified structure. This is accomplished by associating with at least one photosensitive silver halide emulsion layer in a diffusion transfer environment a dispersion of a dye image-forming material, and preferably a dye developer, in a matrix material which comprises a polymer which is permeable to aqueous processing composition and solubilized dye image-forming material at a rate which insures substantial development of its associated silver halide emulsion prior to contact of that emulsion layer with substantial amounts of solubilized unassociated dye material.

In a typical multicolor diffusion transfer photographic process, a positive image is generally formed within about sixty seconds, that is, it takes approximately sixty seconds for sufficient image-forming dye material to be fixed in the image-receiving layer, or image-receiving element, to provide a finished multicolor photograph.

Since the permeability of a polymeric material to a given liquid material will be a function of the thickness of the polymer utilized, it may be seen that in certain thicknesses polymeric layers will be impermeable to given liquid materials in a predetermined time while thicknesses of a smaller magnitude may be permeated by such liquid material within such given time. This is basically the mode by which the instant invention is considered to provide the extraordinarily fine photographic results achieved therewith; that is, by tailoring certain areas of a substantially processing composition impermeable layer based upon the absolute thickness of that layer, to provide that various portions of the layer may be rendered permeable to proc-

essing composition within such given time due to the presence within that layer of dye image-forming materials which are soluble in processing composition thereby providing a shorter path length through the dispersion matrix in area containing dispersed dye image-forming material. Distinct and unexpected advantages are imparted to diffusion transfer systems comprising photosensitive elements of such constituency.

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 effected due to an overcontrol of the migration of certain dye systems and an undercontrol of others. For example, assume 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, 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 areas of 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 addition to the advantages provided by the present system related to enhanced economics, simplicity over the prior art and ease of manufacturing, the primary advantage provided thereby over other systems is that substantial reductions in interimage effects are achieved with concomitant improvements in color isolation and purity. By incorporating the dye image-forming material associated with a given emulsion into a diffusion transfer photosensitive element by dispersing such dye image-forming material in a layer adjacent its associated silver halide emulsion in a matrix of a thickness which, by itself, would be impermeable to processing composition during the period generally required to complete development and diffusion procedures, such layer may be permeated through areas containing dye image-forming material within such period due to the fact that dye image-forming material is dissolved therefrom by processing composition and is caused to migrate from the matrix material toward the image-receiving element thereby selectively providing processing composition migratory paths through the matrix. Looking at FIG. 1, for example, as aqueous alkaline processing composition diffuses from position 20 toward support 10, it first passes through layer 17 into blue-sensitive emulsion layer 16 where, for example, latent image development may be initiated by a booster developer. As the aqueous alkaline processing composition wavefront progresses through the photosensitive element, it next confronts layer 15 which comprises a polymeric material of a thickness which would be impermeable to the aqueous

alkaline processing composition during the time normally employed to complete the diffusion transfer image formation in the image-receiving layer. However, dispersed through this layer are dye image-forming materials which are soluble in the aqueous alkaline processing composition and are dissolved and diffused from the matrix material, thus leaving between areas in which such dye image-forming material was located thin segments of matrix which may be permeated in a small fraction of the time required to complete the entire image-forming process. Accordingly, after a finite time, channels will be formed within layer 15 as denoted, for example, in FIG. 3 through which processing composition ultimately passes into green-sensitive silver halide emulsion layer 14. As the wavefront passes layer 14 and confronts layer 13, the same phenomenon as discussed with regard to layer 15 governs its passage through layer 13 and into layers 12 and 11.

It will be appreciated that at such time as solubilized dye image-forming material begins migrating, for example, from layer 13 toward image-receiving layer 21, emulsion layer 16 will have been developed to a substantial degree by contact with solubilized yellow dye developer. Accordingly, with regard, for example, to solubilized dye image-forming material diffusing from layer 15 toward image-receiving layer 21, layer 16, the blue-sensitive silver halide emulsion layer, will be developed as a function of its point-to-point degree of exposure by solubilized yellow dye developer which will only be permitted to pass therethrough in unexposed areas. All exposed areas of emulsion layer 16 will be "tied up" with yellow dye developer and will not be available to control cyan or magenta. Likewise, it will be appreciated that a finite time is required for aqueous alkaline processing composition to solubilize yellow dye developer, for example, from layer 15, in order to provide sufficient channels, as depicted, for example, in FIG. 3, to continue its progress through the photosensitive element. The yellow dye image-forming material will migrate, for reasons which will be discussed hereinbelow, toward the image-receiving layer 21 and will not back diffuse into the green-sensitive silver halide emulsion layer, which obviates the possibility of its combining therewith to provide undercontrol of magenta dye image-forming material with concomitant overcontrol of yellow dye image-forming material. Specifically, then, the instant invention provides a degree of color purity not before achieved in the diffusion transfer photographic art, while concomitantly reducing the complexity of the system used to provide such purity.

Succinctly, employment of the detailed dye dispersion layers during the hereinbefore described diffusion transfer process acts to provide a barrier 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."

The particular dye image-forming material dispersion utilized in the context of the present invention is preferably a solid dispersion, that is, a dispersion as hereinbefore described comprising solid particles of dye image-forming material dispersed in a matrix which provides the permeability parametric considerations defined hereinabove. As also stated hereinabove, other than a solid dispersion of dye image-forming material may be used as, for example, a dispersion comprising microdroplets, that is, microscopic droplets of a solution of dye image-form-

ing material, which droplets are immiscible with the matrix.

Regardless, however, of whether a solid or liquid dye dispersion is employed in the present invention, it should be employed for optimum results at a volume of approximately thirty to forty percent of the volume of the matrix material employed. The thirty to forty percent volume is based upon the fact that if the matrix comprised hard-packed spheres as, for example, a latex before coalescence, the spheres would fill about sixty-seven percent of the volume, theoretically. Accordingly, it will be appreciated that the ideal theoretical volume for the dye image-forming material dispersed in the matrix will be about one-third, or about thirty-three percent, of the volume of the matrix. However, it has been found that in order to assure good processing composition channeling through the matrix, the dispersion should comprise perhaps slightly more than one third of the volume of the matrix for optimum effects. As will be appreciated, too much dye loading in the matrix will cause processing composition to permeate the layer too quickly while too little dye in the matrix will deleteriously impede the transfer of processing composition through the system.

Diffusion studies on the system of the present invention have demonstrated that migrating dye image-forming materials follow a natural propensity to diffuse toward the image-receiving element. Referring, for example, to FIG. 1, at such time as yellow dye image-forming material is solubilized in layer 15, it diffuses upstream with respect to the aqueous alkaline processing composition imbibed from area 20. Naturally, diffusion in this direction is aided by the fact that as yellow image-forming material is solubilized, the point just downstream from such material still is impermeable to processing composition and dye image-forming material while little impediment to diffusion can be "seen" by solubilized dye image-forming material on its upstream side.

In the event that the dye image-forming material dispersion utilized in the present invention is not a solid dispersion, which is the preferred embodiment, then, as hereinbefore noted, the liquid microdroplets of dissolved dye image-forming material should comprise approximately one-third the volume of the matrix. Specific compositions which are recommended for dissolving dye image-forming material for ultimate dispersion into the matrix are recited in the U.S. patents listed hereinabove and are well known in the art.

The matrix materials into which the dye image-forming materials of the present invention are dispersed comprise coalesced lattices. The matrix will be a continuous phase containing a dye material as a discontinuous phase. Among the various latex materials which have been found to impart the requisite permeation characteristics to the herein considered systems, are lattices of: polyvinylidene chloride; lightly carboxylated styrene-butadiene copolymers; polyvinyl chloride; vinylchloride-vinylacetate copolymers; acrylic copolymers and copolymers as, for example, a terpolymer of butylacrylate, methylmethacrylate and small amounts of acrylic or methacrylic acid; and enumerable other lattices which will readily come to mind of one of ordinary skill in polymer chemistry. An extensive compilation of such lattices will be found in U.S. Pat. No. 2,795,564. Preferred latex materials for utilization in the present invention comprise a 60-38-2 copolymer of methylmethacrylate, butyl acrylate and acrylic acid; a 60-30-4-6 copolymer of butyl acrylate, diacetone acrylamide, styrene and methacrylic acid; a 60-30-4-6-1.5-0.5 copolymer of butyl acrylate, diacetone acrylamide, styrene, methacrylic acid, 2-sulfoethylmethacrylate, and divinylbenzene; and a 99-1 copolymer of ethyl acrylate and methacrylic acid which contains 1.5 parts of 2-sulfoethylmethacrylate; all proportion designations being on a weight basis unless otherwise denoted.

In general, the thickness of the dye dispersion-comprising layers will be on the order of about one and

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One-half to five microns. Preferably, the dye image-forming material component particles or microdroplets should be on the order of between about 0.3 to 1.6 microns, and preferably on the order of about 0.5 micron, while the latex material should comprise particles from about 0.1 to about 1.0 microns.

As has been described, the present invention produces a diffusion transfer photographic system in which various photosensitive emulsions associated with given dye image-forming material components are developed in relatively insulated steps, that is, the blue-sensitive silver halide emulsion would "see" the processing composition wavefront, and be substantially fully developed by its associated dye image-forming material, amounts of which diffuse toward the image-receiving element before the next exposed photosensitive emulsion "sees" the processing composition wavefront. It must be emphasized that in any system utilizing the present invention, the paramount consideration is balancing the processing composition and solubilized dye image-forming material permeation characteristics of the various dye dispersion matrices to the dynamics desired of the entire system; that is, providing permeability characteristics which will satisfy performance considerations in a predetermined time span. 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 in terms of layer thicknesses, particle sizes and volumetric ratios in order to provide appropriate development and diffusion rates to facilitate formation of a finished multicolor photographic image in a predetermined time span.

In a preferred embodiment of the present invention, gelatino silver halide emulsion layers will be about 0.6 to 6 microns thick and the dye dispersion layers will be from about 1.5 to 5 microns thick. With respect to the preferred image-receiving portion of the structure, the image-receiving layer will be about 0.25 to 0.4 mil. thick, the polymeric acid layer will be about 0.3 to 1.5 mils. thick and the spacer layer will be about 0.1 to 0.7 mil. thick. It will be specifically recognized that the relative dimensions recited may be appropriately modified in accordance with the desires of the operator with respect to the specific product to be ultimately prepared.

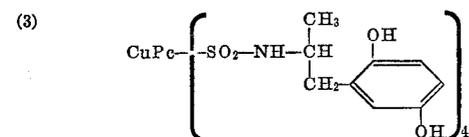
In accordance with the teachings of the art, the positioning of the respective silver halide emulsion/dye developer units of the configuration detailed in FIG. 1 may be varied. However, it is generally preferred to constitute the configuration of the photosensitive units of the present invention according to that depicted herein, that is, the cyan dye image-forming material/red-sensitive emulsion unit next contiguous the support surface and the yellow dye image-forming material/blue-sensitive emulsion unit most distal from the support surface.

The present invention will be illustrated in greater detail in conjunction with the following example which sets out a representative embodiment and photographic utilization of the novel photosensitive elements of this invention and illustrates the particular advantages achieved thereby.

The following example should not be limited to the details therein set forth and is 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 the copper phthalocyanine cyan dye developer



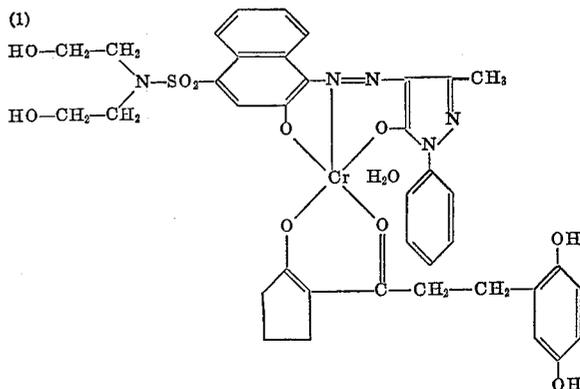
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dispersed in gelatin, and coated at a coverage of about 100 mgs. dye and 150 mgs. gelatin/ft.<sup>2</sup>.

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 140 mgs. silver and 91 mgs. gelatin/ft.<sup>2</sup>.

(3) A layer of a 60-38-2 terpolymer of methyl methacrylate, butyl acrylate and acrylic acid coated at a coverage of about 75 mgs./ft.<sup>2</sup> containing Kelcosol (sodium alginate) coated at a coverage of 4.0 mgs./ft.<sup>2</sup>.

(4) A layer of magenta dye developer of the formula:

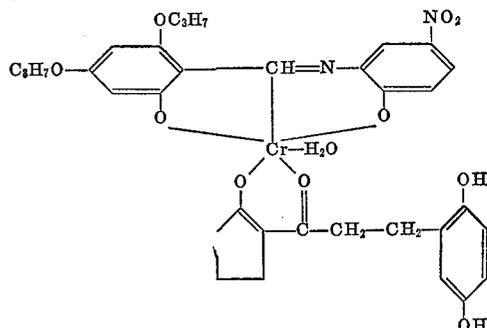


dispersed in gelatin and coated at a coverage of about 65 mgs. dye and 45 mgs. gelatin/ft.<sup>2</sup>.

(5) A green-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 80 mgs. of silver and 56 mgs. gelatin/ft.<sup>2</sup>.

(6) A layer of a 60-38-2 terpolymer of methyl methacrylate, butyl acrylate and acrylic acid coated at a coverage of about 40 mgs./ft.<sup>2</sup> containing Kelcosol (sodium alginate) coated at a coverage of about 2.5 mgs./ft.<sup>2</sup>.

(7) A layer of yellow dye developer of the formula:



dispersed in gelatin and coated at a coverage of about 70 mgs. dye and 51 mgs. gelatin/ft.<sup>2</sup>.

(8) A blue-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 65 mgs. of silver and 45 mgs. gelatin/ft.<sup>2</sup>.

(9) A layer of gelatin coated at a coverage of about 30 mgs. gelatin/ft.<sup>2</sup> containing about 15 mgs./ft.<sup>2</sup> of methyl phenyl hydroquinone.

Similar photosensitive elements to those prepared according to the procedure denoted in the paragraph next above were fabricated and two test series were composed which are illustrative of the results achieved by the practice of the present invention; in the first instance by illustrating control of yellow dye image-forming material, and in the second instance by illustrating control of magenta dye image-forming material.

The first series of test negatives was fabricated according to the formula denoted above with the following changes. The gelatin denoted in layer 1 was moved into layer 2 providing thereby about 140 mgs. of silver and 241 mgs. of gelatin/ft.<sup>2</sup>. 50 mgs./ft.<sup>2</sup> of a composition comprising 100 parts of a 99/1 copolymer of ethylacrylate/methacrylic acid, 1.5 parts 2-sulfoethylmethacrylate

and 0.2 parts of a surfactant (Dowfax 2AL) were utilized as a matrix for the dye material in layer 1 to provide a suitable binder therefor. Layer 3 was eliminated and layer 4 comprised 65 mgs./ft.<sup>2</sup> of the denoted dye to 65 mgs./ft.<sup>2</sup> of the ethylacrylate/methacrylic acid composition denoted with reference to layer 1 in lieu of the gelatin. The gelatin was removed from layer 4 and was incorporated in layer 5 to provide a coverage of 80 mgs./ft.<sup>2</sup> silver and 101 mgs./ft.<sup>2</sup> gelatin. Layer 6 was eliminated and layer 7 had the gelatin removed and incorporated in layer 8 with varying ratios of latex material substituted for the gelatin in layer 7, as well be discussed hereinbelow. Layer 8 then comprised 65 mgs. of silver/ft.<sup>2</sup> and 75 mgs. of gelatin/ft.<sup>2</sup>. Layer 9 was unchanged. Three test negatives formulated as disclosed immediately above were prepared with layer 7 comprising, respectively, 35, 70, and 140 mgs./ft.<sup>2</sup> of the latex material described with respect to layer 1 along with the recited 70 mgs./ft.<sup>2</sup> of yellow dye developer.

A multiplicity of diffusion transfer image-receiving elements may be prepared by coating a cellulose nitrate sub-coated baryta paper with 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. 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.<sup>2</sup> 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.

Next the three test negatives having the varying ratios of yellow dye developer to polymer were exposed through a sensitometer to light in columns of blue, red and green ranges of the visible spectrum, by interposing between the negatives and a xenon light source appropriate Wratten Filters, 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. Reflection readings of integral densities were then taken on a MacBeth densitometer, Model RD-400, using Wratten Filters Nos. 72B, 93 and 94, respectively, each of which was used in conjunction with a Wratten Filter No. 301. The exposed photosensitive elements may then be processed by spreading an aqueous liquid processing composition comprising:

Water	-----cc---	100
Potassium hydroxide (anhydrous)	-----grams---	7.5
Cesium hydroxide (anhydrous)	-----do-----	4.5
Carboxymethyl cellulose (Hercules 7H4)	___do___	3.5
Titanium dioxide (rutile)	-----do-----	50.0
Phenylethyl- $\alpha$ -picolinium bromide	-----do-----	1.72
5-hydroxyl-4-azabenzimidazole	-----gram---	0.115
2-methyl imidazole	-----do-----	0.35
6-bromo-5-methyl-4-azabenzimidazole	___do___	0.05
Benzotriazole	-----grams---	1.15

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.

Table 1 below lists various resultant photographic properties attributed to the photosensitive elements of the present invention compared to the control described here-

inabove. All experiments and measurements were carried out at room temperature, i.e., 75° F.

TABLE 1

	Control	Neg. 1	Neg. 2	Neg. 3
1. D <sub>max.</sub> Red (neutral column).....	1.95	1.91	1.83	1.94
2. D <sub>min.</sub> Red (neutral column).....	0.17	0.18	0.17	0.15
3. D <sub>max.</sub> Green (neutral column).....	2.10	2.45	2.46	2.46
4. D <sub>min.</sub> Green (neutral column).....	0.21	0.25	0.22	0.17
5. D <sub>max.</sub> Blue (neutral column).....	2.16	2.26	2.25	2.27
6. D <sub>min.</sub> Blue (neutral column).....	0.27	0.25	0.24	0.26
7. Blue Density (yellow column <sup>1</sup> ).....	1.43	0.60	1.50	1.56
8. Green Density (yellow column <sup>1</sup> ).....	0.33	0.35	0.31	0.27
9. Red Density (yellow column <sup>1</sup> ).....	0.18	0.18	0.12	0.13

<sup>1</sup> Exposure to red and green—no exposure to blue.

The maximum and minimum dye densities as read in the neutral column of the control and test negatives are comparable as would be expected since all contain the same levels of gelatin and dye image-forming materials. It is worthy of note, however, that less red and green contamination appears in negative 3 compared to the control and it displays higher blue saturation. It is further worthy of note that the blue saturation and red and green contaminations improved as the ratio of polymer to dye image-forming material increases from a 1 latex:2 dye situation in negative 1 as compared with a 2 latex:1 dye situation in negative 3.

The following table contains similar experimental data as read from the magenta column in a test negative where the ratio of magenta dye developer to matrix material is varied as compared to the control. For this comparison, negatives like that denoted as Neg. 1 in Table 1, wherein the layer containing the magenta dye developer (layer 4) comprised, respectively, in Neg. 4, 65 mgs./ft.<sup>2</sup> magenta dye developer and 65 mgs./ft.<sup>2</sup> polymeric material as denoted with respect to Neg. 1, layer 4; in Neg. 5, 65 mgs./ft.<sup>2</sup> of magenta dye developer and 97.5 mgs./ft.<sup>2</sup> of polymer composition as denoted above; and in Neg. 6, 65 mgs./ft.<sup>2</sup> of magenta dye developer and 130 mgs./ft.<sup>2</sup> of polymer as denoted above; were used. In each case the yellow dye developer (layer 7) was coated at 70 mgs./ft.<sup>2</sup> in a polymer matrix as described above at 100 mgs./ft.<sup>2</sup>.

Table 2 below tabulates the experimental observations with Negs. 4, 5 and 6 compared to the control.

TABLE 2

	Control	Neg. 4	Neg. 5	Neg. 6
1. D <sub>max.</sub> Red (neutral column).....	1.95	1.80	1.76	1.72
2. D <sub>min.</sub> Red (neutral column).....	0.17	0.20	0.20	0.22
3. D <sub>max.</sub> Green (neutral column).....	2.10	2.04	2.01	2.12
4. D <sub>min.</sub> Green (neutral column).....	0.21	0.24	0.24	0.25
5. D <sub>max.</sub> Blue (neutral column).....	2.16	1.60	1.58	1.65
6. D <sub>min.</sub> Blue (neutral column).....	0.27	0.34	0.36	0.35
7. Blue Density (magenta column <sup>1</sup> ).....	0.53	0.72	0.78	0.80
8. Green Density (magenta column <sup>1</sup> ).....	0.73	0.94	1.07	1.21
9. Red Density (magenta column <sup>1</sup> ).....	0.34	0.27	0.28	0.34

<sup>1</sup> Exposure to red and blue—no exposure to green.

Note particularly that the blue density does not change appreciably while the green density is significantly elevated. In the main, much of the blue and red contamination denoted is reflected by blue and red "tails" of the magenta dye image-forming material which, when considered, enhances the experimental data.

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-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 described 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., U.S.A., 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, alkalis, 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 exposure, 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 overlying 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 "associated" and "unassociated" dye image-forming materials relative to silver halide emulsions. Such terms connote dye image-forming materials, the diffusion of which is either to be controlled by a given silver halide emulsion, or by other than that given silver halide emulsion, respectively.

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 drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photosensitive element which comprises a support layer carrying, in order, from the support layer, at least first and second selectively sensitized silver halide emulsion layers, each emulsion layer having associated therewith a processing composition soluble dye image-forming material, at least the dye image-forming material associated with said second silver halide emulsion layer being dispersed in a matrix layer comprising a coalesced latex intermediate said second silver halide emulsion layer and said first silver halide emulsion layer, said matrix layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer on the side opposed to said support layer at a rate which insures substantial development of said second silver halide emulsion layer prior to contact of said second silver halide emulsion layer with substantial amounts of processing composition solubilized dye image-forming material initially associated with said first silver halide emulsion layer.

2. The invention of claim 1 wherein said dye image-forming materials are silver halide developing agents and said processing composition comprises an aqueous alkaline composition.

3. The invention of claim 2 wherein said latex comprises about a 99-1 copolymer of ethylacrylate and methacrylic acid, respectively, and additionally contains about 1.5 parts 2-sulfoethylmethacrylate per 100 parts of copolymer.

4. The invention of claim 2 wherein said dispersion of dye developer is a solid dispersion.

5. The invention of claim 4 wherein said solid dispersion of dye developer comprises particles between about 0.3 to 1.6 microns in diameter.

6. The invention of claim 5 wherein the thickness of said matrix layer comprising said solid dispersion of dye developer is from 1.5 to 5.0 microns.

7. A photographic diffusion transfer unit which comprises, in combination, a photosensitive element having a diffusion transfer image-receiving element affixed to at least one edge thereof, such photosensitive element comprising, as essential layers, a support layer carrying, in order, from the support layer, at least first and second selectively sensitized silver halide emulsion layers, each emulsion layer having associated therewith a processing composition soluble dye image-forming material, at least the dye image-forming material associated with said second silver halide emulsion layer being dispersed in a matrix layer comprising a coalesced latex intermediate said second silver halide emulsion layer and said first silver halide emulsion layer, said matrix layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer on the side opposed to said support layer at a rate which insures substantial development of said second silver halide emulsion layer prior to contact of said second silver halide emulsion layer with substantial amounts of processing composition solubilized dye image-forming material initially associated with said first silver halide emulsion layer; said diffusion transfer image-receiving element comprising, as essential layers,

(1) a support layer; and

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

8. The invention of claim 7 wherein said dye image-forming materials are silver halide developing agents and said processing composition comprises an aqueous alkaline composition.

9. The invention of claim 8 wherein latex comprises about a 99-1 copolymer of ethylacrylate and methacrylic acid, respectively, and additionally contains about

1.5 parts 2-sulfoethylmethacrylate per 100 parts of copolymer.

10. The invention of claim 8 including a rupturable container retaining said aqueous alkaline processing composition affixed one edge of said photosensitive and said image-receiving element and adapted upon rupture to distribute its contents intermediate said superposed photosensitive and image-receiving elements.

11. The invention of claim 10 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 adjacent thereto.

12. The invention of claim 11 wherein said aqueous alkaline processing composition possesses a pH of not less than about 12.

13. The invention of claim 12 wherein said image-receiving element support layer is transparent.

14. The invention of claim 13 wherein said diffusion transfer unit comprises a composite structure including 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.

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

(a) a support layer;

(b) a cyan dye image-forming material which is a silver halide developing agent;

(c) a red-sensitive silver halide emulsion layer;

(d) a magenta dye image-forming material which is a silver halide developing agent dispersed in a matrix layer comprising a coalesced latex, said layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer at a rate which insures substantial development of its associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye image-forming material;

(e) a green-sensitive silver halide emulsion layer;

(f) a yellow dye image-forming material which is a silver halide developing agent dispersed in a matrix layer comprising a coalesced latex, said layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer at a rate which insures substantial development of its associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye image-forming material; and

(g) a blue-sensitive silver halide emulsion layer.

16. The invention of claim 15 wherein at least one of said matrix materials comprises a coalesced latex comprising about a 99-1 copolymer of ethylacrylate and methacrylic acid, respectively, and additionally contains about 1.5 parts 2-sulfoethylmethacrylate per 100 parts of copolymer.

17. A process for forming diffusion transfer photographic images in color, which comprises the steps of:

exposing a photosensitive element comprising a support layer carrying, in order, from the support layer, at least first and second selectively sensitized silver halide emulsion layers, each emulsion layer having associated therewith a processing composition soluble dye image-forming material, at least the dye image-forming material associated with said second silver halide emulsion layer being dispersed in a matrix layer comprising a coalesced latex intermediate said second silver halide emulsion layer and said first silver halide emulsion layer, said matrix layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer on the side opposed to said support layer at a rate

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which insures substantial development of said second silver halide emulsion layer prior to contact of said second silver halide emulsion layer with substantial amounts of processing composition solubilized dye image-forming material initially associated with said first silver halide emulsion layer; 5

contacting the surface of said exposed photosensitive element opposed to its support layer with processing composition effecting thereby sequential development of said silver halide emulsion layers whereby dye image-forming materials associated with each of said emulsions is immobilized as a result of development forming thereby a distribution of mobile dye image-forming material as a function of the point-to-point degree of exposure of said photosensitive element; 15 and

transferring, by diffusion, at least a portion of said distribution of mobile dye image-forming material to a superposed image-receiving layer to provide thereto a multicolor dye image. 20

18. The invention of claim 17 wherein said dye image-forming materials are silver halide developing agents.

19. The invention of claim 18 wherein said latex comprises about a 99-1 copolymer of ethylacrylate and methacrylic acid, respectively, and additionally contains about 1.5 parts 2-sulfoethylmethacrylate per 100 parts copolymer. 25

20. A process for forming diffusion transfer photographic images in color which comprises the steps of: exposing a photosensitive element which comprises, in sequence 30

- (a) a support layer;
- (b) a cyan dye image-forming material which is a silver halide developing agent;
- (c) a red-sensitive silver halide emulsion layer; 35
- (d) a magenta dye image-forming material which is a silver halide developing agent dispersed in a matrix layer comprising a coalesced latex, said layer being permeable to processing composition applied to the surface of its associated silver 40 halide emulsion layer at a rate which insures sub-

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stantial development of its associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye image-forming materials;

(e) a green-sensitive silver halide emulsion layer;

(f) a yellow dye image-forming material which is a silver halide developing agent dispersed in a matrix layer comprising a coalesced latex, said layer being permeable to processing composition applied to the surface of its associated silver halide emulsion layer at a rate which insures substantial development of its associated silver halide emulsion layer prior to contact of such layer with substantial amounts of solubilized unassociated dye image-forming material; and

(g) a blue-sensitive silver halide emulsion layer;

contacting the surface of said exposed photosensitive element opposed to its support layer with processing composition effecting thereby sequential development of said silver halide emulsion layers and providing a distribution of mobile yellow, magenta and cyan dye image-forming materials as a function of the point-to-point degree of exposure of their associated silver halide emulsions;

transferring, by diffusion, at least a portion of said imagewise distributions of dyes to a superposed image-receiving layer to provide thereto a multicolor dye image.

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