

[54] **NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES**

[75] Inventor: **Edwin H. Land**, Cambridge, Mass.

[73] Assignee: **Polaroid Corporation**, Cambridge, Mass.

[22] Filed: **June 13, 1972**

[21] Appl. No.: **262,332**

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 65,084, Aug. 19, 1970, Pat. No. 3,672,890, and Ser. No. 782,075, Dec. 9, 1968, Pat. No. 3,573,043, and Ser. No. 846,442, July 31, 1969, Pat. No. 3,576,625, and Ser. No. 782,056, Dec. 9, 1968, Pat. No. 3,573,043, which is a continuation-in-part of Ser. No. 622,283, March 10, 1967, Pat. No. 3,415,644.

[52] U.S. Cl. **96/3, 96/29 D, 96/77**

[51] Int. Cl. **G03c 7/00**

[58] Field of Search **96/3, 29 D**

References Cited

UNITED STATES PATENTS

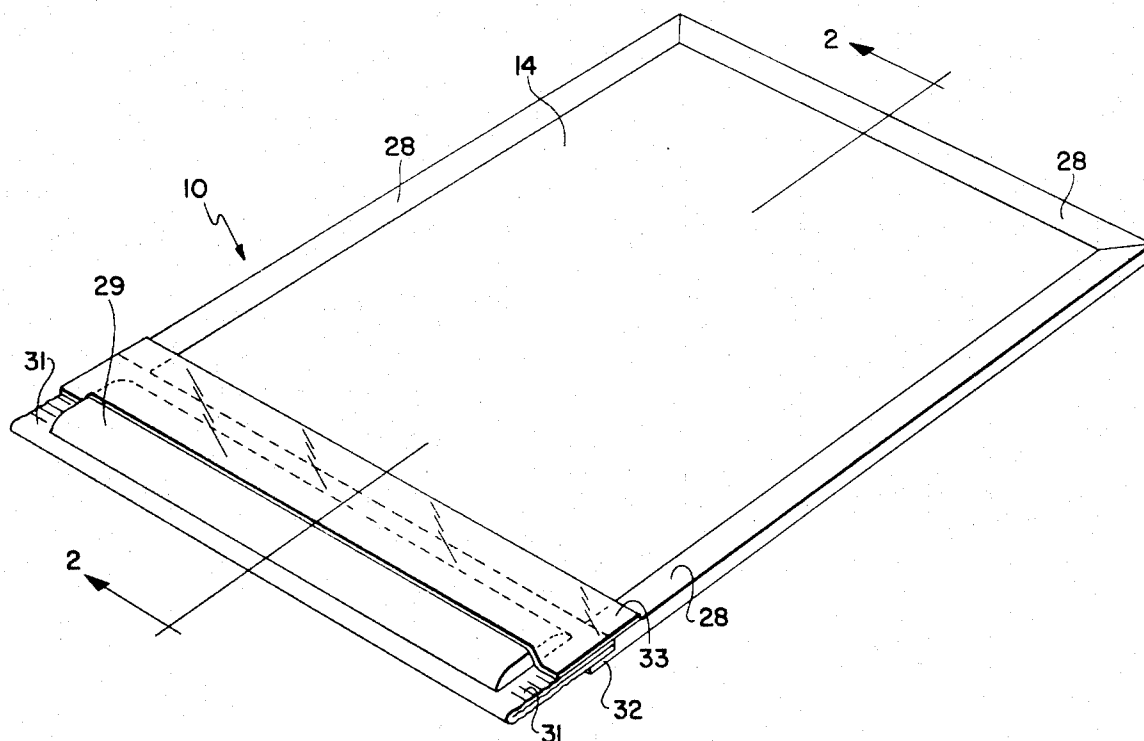
3,415,645	12/1968	Land	96/29 D
3,625,685	12/1971	Avtges et al.	96/29 D

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling
Attorney—Robert M. Ford

[57] **ABSTRACT**

The present invention relates to photography and, more particularly, to diffusion transfer process photographic film units which comprise a photosensitive element adapted to provide, by diffusion transfer photographic processing, selective dye image recording of incident actinic radiation as a function of the point-to-point degree of photosensitive element exposure, which film unit includes a plurality of essential layers including a photosensitive silver halide layer having associated therewith diffusion transfer process dye image-forming material, a layer adapted to receive dye image-forming material diffusing thereto which is a substantially continuous polymeric layer comprising, in essence, a neutral polymer adapted to interact with an aqueous alkaline processing composition in contact with the layer to reduce the alkalinity thereof and to thereby increase the stability of a dye transfer image carried by such layer, and a mordant associated with the layer adapted to mordant dye image-forming material diffusing to the layer; and to specified diffusion transfer processes employing such film units.

45 Claims, 8 Drawing Figures



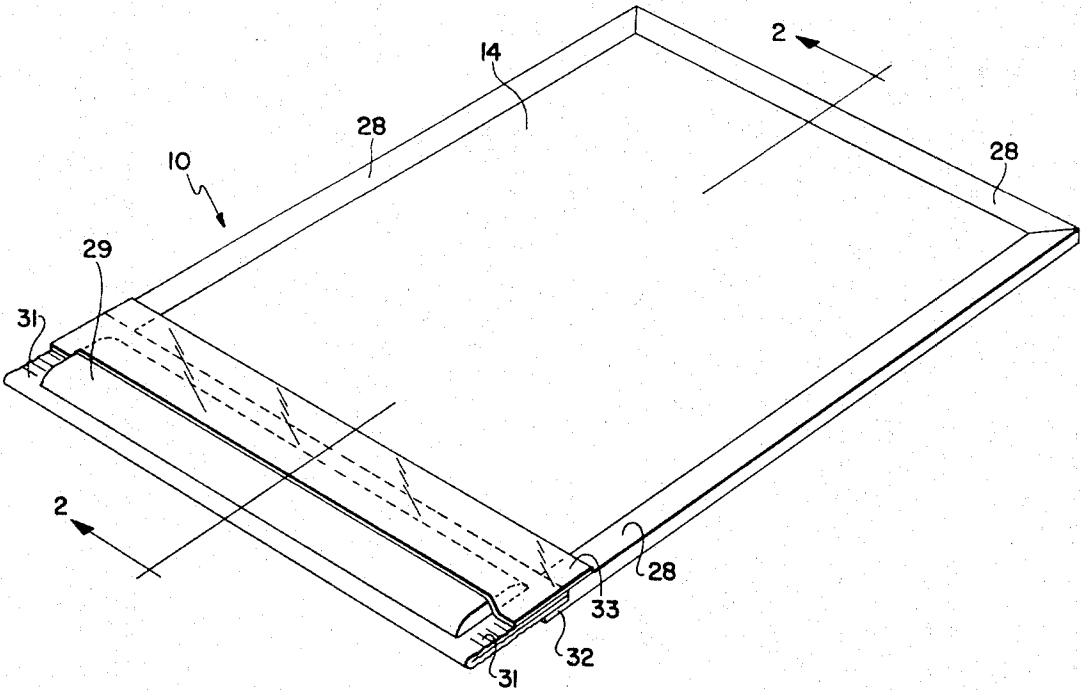
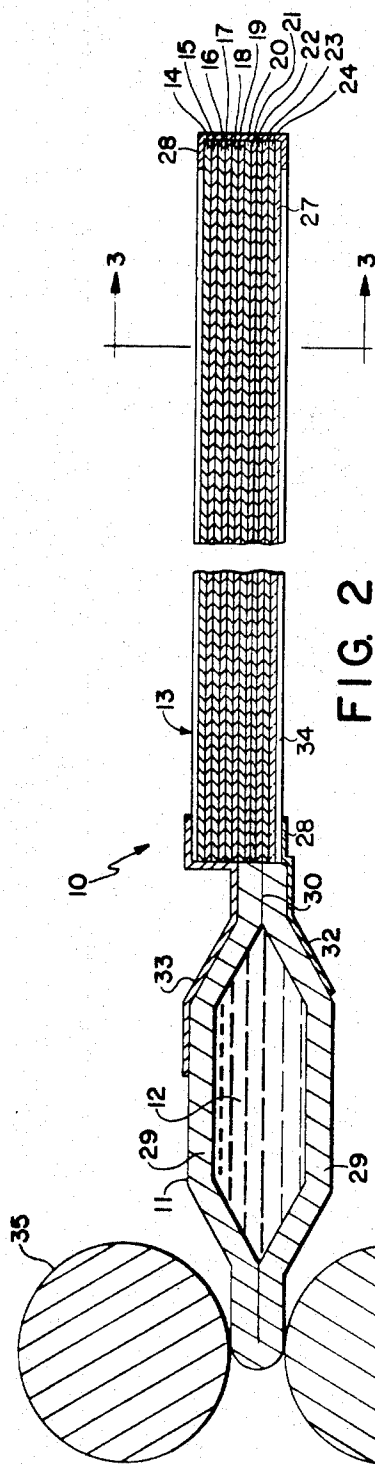


FIG. 1



261

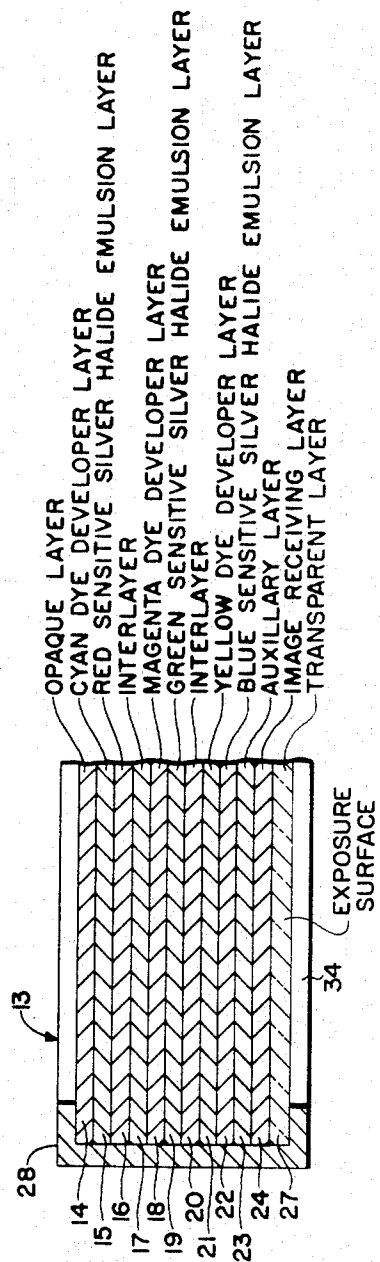
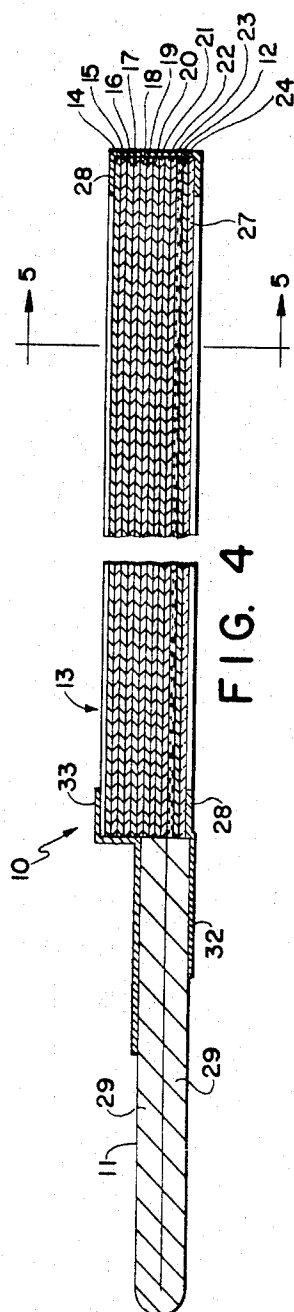
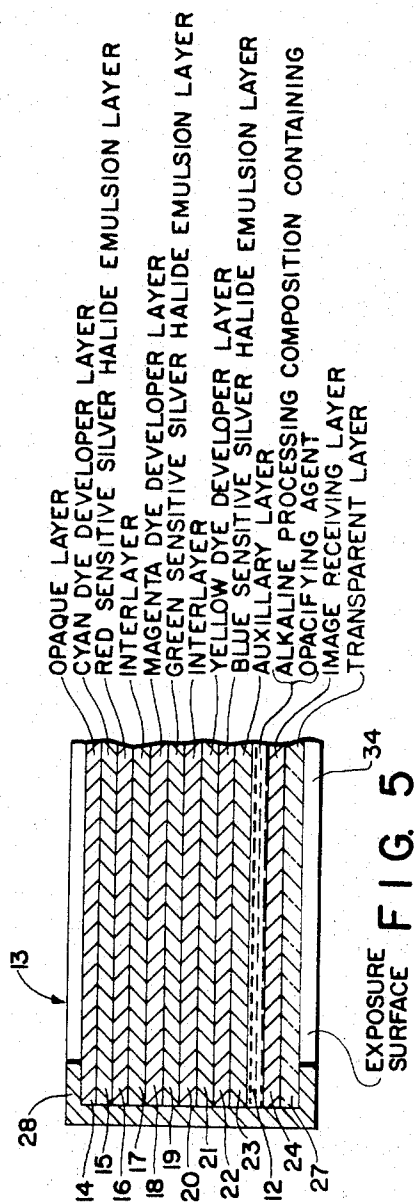


FIG. 3



६७४



565

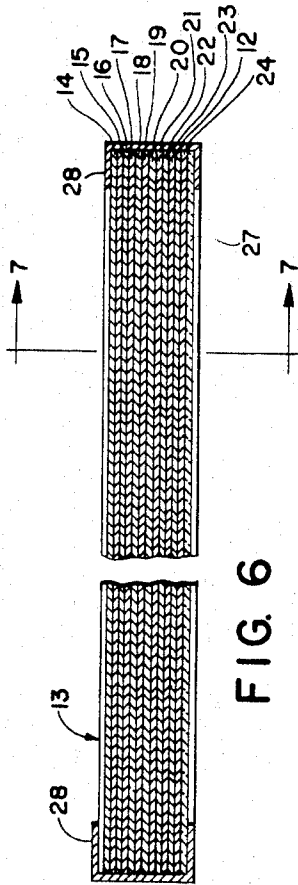


FIG. 6

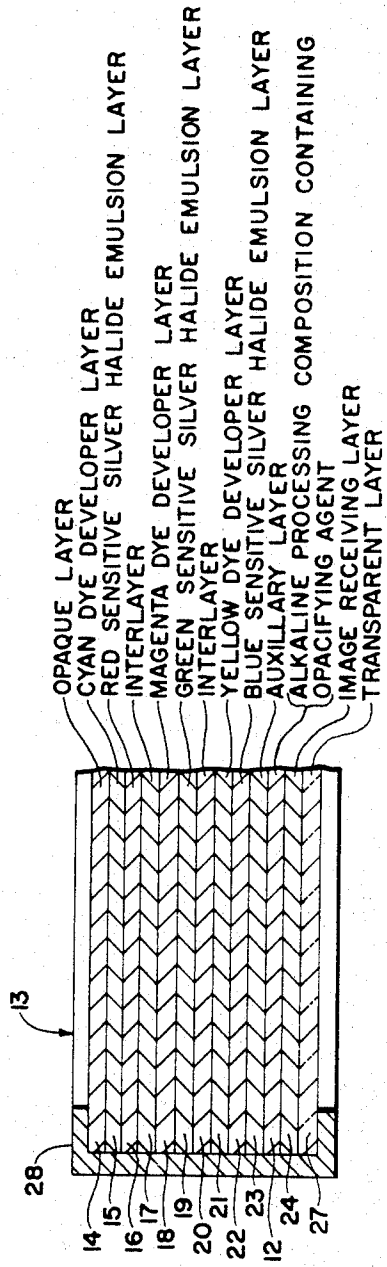


FIG. 7

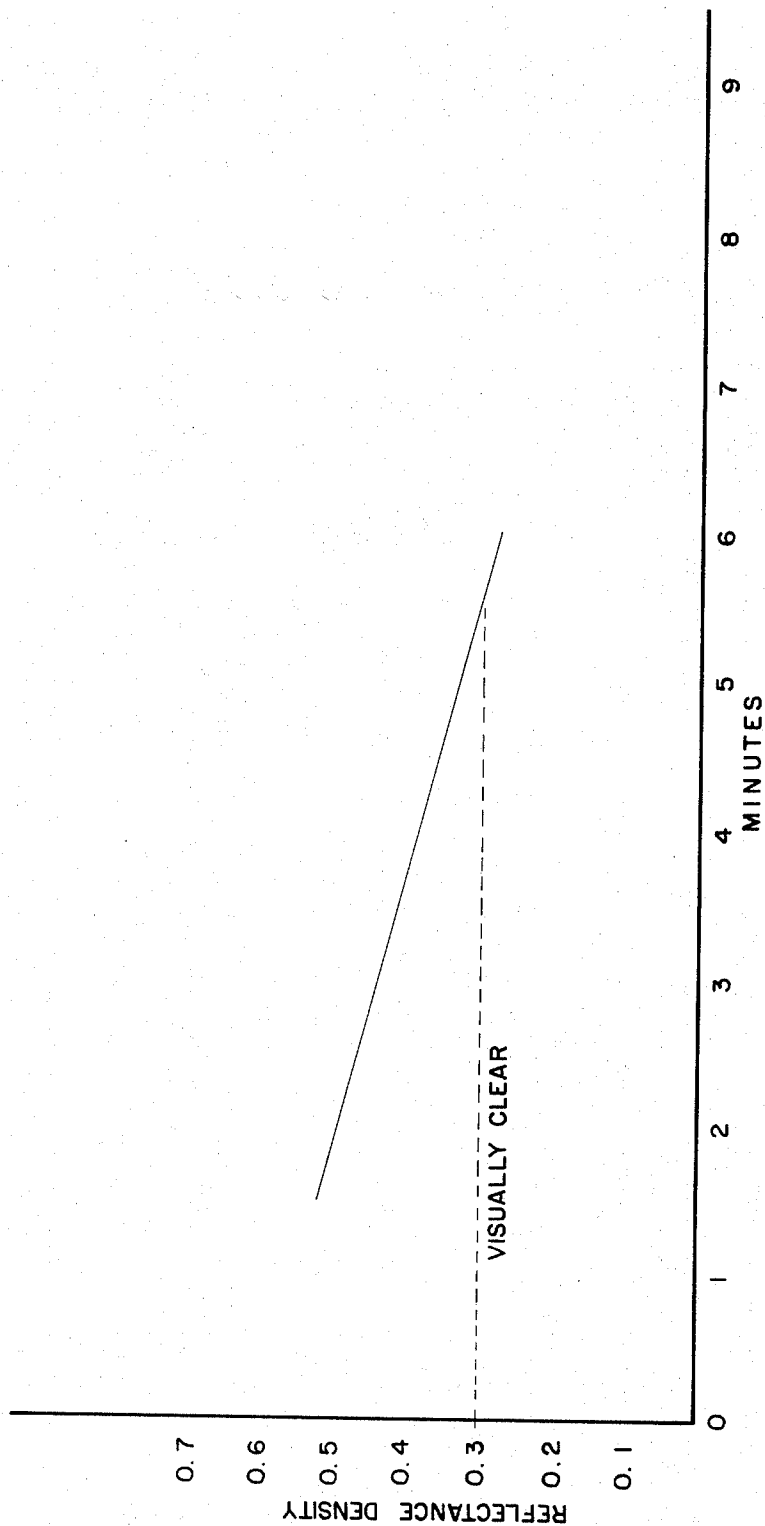


FIG. 8

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

This application is a continuation-in-part of application Ser. No. 65,084, filed Aug. 19, 1970, now U.S. Pat. No. 3,672,890, a continuation-in-part of application Ser. No. 782,075, filed Dec. 9, 1968, now U.S. Pat. No. 3,573,043, application Ser. No. 846,442, filed July 31, 1969, now U.S. Pat. No. 3,576,625, and application Ser. No. 782,056, filed Dec. 9, 1968, now U.S. Pat. No. 3,573,043, the latter in turn a continuation-in-part of application Ser. No. 622,283, filed Mar. 10, 1967, now U.S. Pat. No. 3,415,644.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to providing new and improved diffusion transfer process photographic film units adapted to provide, as a function of the point-to-point degree of photoexposure, by diffusion transfer processing a dye transfer image.

2. Description of Prior Art

As disclosed in U. S. Pat. No. 3,415,644, a composite photosensitive structure, particularly adapted for reflection type photographic diffusion transfer color process employment, which comprises a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first processing pH, as a function of the point-to-point degree of its associated silver halide emulsion's exposure to incident actinic radiation; a polymeric layer adapted to receive solubilized dye image-providing material diffusing thereto; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition from the first pH to a second pH at which the dye image-providing material is substantially nondiffusible; and a dimensionally stable transparent layer, may be exposed to incident actinic radiation and processed by interposing, intermediate the silver halide emulsion layer and the reception layer, an alkaline processing composition possessing the first pH and containing opacifying agent, which may reflect incident radiation, in a quantity sufficient to mask dye image-providing material associated with the silver halide emulsion.

In a preferred embodiment, the composite photosensitive structure includes a rupturable container, retaining the alkaline processing composition having the first pH and opacifying agent, fixedly positioned extending transverse a leading edge of the composite structure in order to effect, upon application of compressive pressure to the container, discharge of the processing composition intermediate the opposed surfaces of the reception layer and the next adjacent silver halide emulsion.

The liquid processing composition, distributed intermediate the reception layer and the silver halide emulsion, permeates the silver halide emulsion layers of the composite photosensitive structure to initiate development of the latent images contained therein resultant from photoexposure. As a consequence of the development of the latent images, dye image-providing material associated with each of the respective silver halide emulsion layers is individually mobilized as a function of the point-to-point degree of the respective silver hal-

ide emulsion layer's photoexposure, resulting in image-wise distributions of mobile dye image-providing materials adapted to transfer, by diffusion, to the reception layer to provide the desired transfer dye image. Subsequent to substantial dye image formation in the reception layer, a sufficient portion of the ions of the alkaline processing composition transfer, by diffusion, to the polymeric neutralizing layer to effect reduction in the alkalinity of the composite film unit to the second pH at which dye image-providing material is substantially nondiffusible, and further dye image-providing material transfer is thereby substantially obviated.

The transfer dye image is viewed, as a reflection image, through the dimensionally stable transparent layer against the background provided by the opacifying agent, distributed as a component of the processing composition, intermediate the reception layer and next adjacent silver halide emulsion layer. The thus-formed opacifying stratum effectively masks residual dye image-providing material retained in association with the silver halide emulsion layer subsequent to processing.

In U. S. Pat. No. 3,415,646, the dimensionally stable layer of the film unit next adjacent the photosensitive silver halide layer or layers is disclosed to be transparent to incident actinic radiation and as disclosed in U. S. Pat. No. 3,415,645, in such instance the opacifying agent may be initially disposed in the film unit intermediate the reception layer and next adjacent silver halide layer.

As disclosed in U. S. Pat. No. 3,615,421 and in the copending U. S. Pat. application Ser. No. 3646 of Sheldon A. Buckler, filed Jan. 19, 1970, the opacifying component of the film unit may optionally be initially disposed as a preformed processing composition permeable layer, intermediate the reception layer and next adjacent silver halide layer, in a concentration which prior to photoexposure is insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the film unit's silver halide emulsion layers, and in U. S. Pat. No. 3,647,435, the opacifying component of the film unit may optionally be initially formed in situ, intermediate the reception layer and next adjacent silver halide layer, during photographic processing of the film unit.

In U. S. Pat. No. 3,647,437, the opacifying component is disclosed to optionally comprise a light-absorbing reagent such as a dye which is present as an absorbing species at the first pH and which may be converted to a substantially non-absorbing species at the second pH, and in U. S. Pat. Nos. 3,473,925; 3,573,042 and 3,576,626, opacifying and reflecting component, respectively, may be individually interposed intermediate the silver halide layer and reception layer by selective distribution from a composite or a plurality of rupturable containers.

In U. S. Pat. No. 3,573,043, the polymeric neutralizing layer is disclosed to be optionally disposed intermediate the dimensionally stable opaque layer and next adjacent essential layer, i.e., next adjacent silver halide/dye image-providing material component, to effect the designated modulation of film unit's environmental pH; U. S. Pat. No. 3,576,625 discloses the employment of particulate acid distributed within the film unit to effect the modulation of the environmental pH, and U.S. Pat. No. 3,573,044 discloses the employment of pro-

cessing composition solvent vapor transmissive dimensionally stable layers to effect process modulation of dye transfer as a function of solvent concentration.

Where desired, the film unit may also be constructed in accordance with the disclosure of U. S. Pat. Nos. 3,594,164 and 3,594,165 to comprise a composite photosensitive structure including a transparent dimensionally stable layer carrying a reception layer, a processing composition permeable opaque layer and a photosensitive silver halide layer and the film unit may include a separate dimensionally stable sheet element adapted to be superposed on the surface of the photosensitive structure opposite the dimensionally stable layer and may further include means such as a rupturable container retaining processing composition for distribution of a processing composition intermediate the sheet and photosensitive structure to effect processing. As further disclosed in the last-cited applications, in structures wherein the receptor is positioned next adjacent the transparent layer or the processing composition and/or the sheet is to be separated from the remainder of the film unit subsequent to processing, the latter elements may optionally include opacifying component.

As disclosed in U. S. Pat. No. 3,620,724, the dimensionally stable layer last referred to may be opaque and in which instance the photosensitive silver halide layer is positioned next adjacent the opaque support layer and the opacifying component of the film unit's processing composition permeable opaque layer will be disposed in the unit in a concentration insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the silver halide layer, and as disclosed in U. S. Pat. No. 3,647,434, the opacifying agent may be optionally formed in such film unit, in situ, during processing of the unit.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved, preferably integral negative/positive, diffusion transfer process photographic film unit adapted to provide, by diffusion transfer processing, photographic color image reproduction as a function of exposure of such film unit to incident actinic radiation.

The film unit assemblage construction to be employed in the practice of the present invention preferably comprises a film unit of the general type set forth in aforementioned U. S. Pat. Nos. 2,983,606; 3,345,163; 3,415,644; 3,415,645; 3,415,646; 3,473,925; 3,573,042; 3,573,043; 3,573,044; 3,576,625; 3,576,626; 3,594,164; 3,594,165; 3,615,421; 3,620,724; 3,647,434; 3,647,435; and 3,647,437; and will specifically include a dye image-receptor layer which is a substantially continuous polymeric layer essentially comprising neutral polymer adapted to interact with aqueous alkaline processing composition contacted with the layer during processing to reduce the alkalinity thereof to increase the stability of a dye transfer image retained in the layer, and a mordant associated with the layer adapted to mordant dye image-forming material diffusing to the layer. Specifically, such film unit construction will comprise a plurality of layers including, in relative order, a dimensionally stable layer preferably opaque to incident actinic radiation;

one or more photosensitive silver halide layers having associated therewith diffusion transfer process dye image-forming material; a substantially transparent layer adapted to receive dye image-forming material diffusing thereto and, optionally, a dimensionally stable layer transparent to incident actinic radiation; means for providing, intermediate the silver halide layers and the reception layer, opacifying agent; and means for providing an aqueous alkaline processing composition possessing an alkaline pH at which dye image-forming material is diffusible during processing as a function of the film unit's photoexposure, in contact with the photosensitive and image-receptive layers of the unit.

In accordance with a specifically preferred embodiment of the present invention, a film unit assemblage of the aforementioned generalized structural parameters will be adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation and may be fabricated to employ, as means to provide opacifying agent intermediate the reception layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment dispersion containing reflecting pigment and, most preferably, at least one optical filter agent, at a pH above the pKa of the optical filter agent and at which pH the dye image-forming material is diffusible during processing as a function of silver halide layer photoexposure, in a concentration in admixture effective to provide a barrier to transmission of actinic radiation therethrough, and the means of interposing the opacifying agent and the processing composition may comprise a rupturable container, retaining the opacifying agent disposed in the processing composition selected, fixedly positioned extending transverse a leading edge of the film unit and adapted, upon application of compressive pressure, to distribute its contents intermediate the reception layer and next adjacent silver halide layer.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIGS. 2, 4 and 6 are diagrammatic enlarged cross-sectional views of the film unit of FIG. 1, along section line 2—2, illustrating the association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a multicolor transfer image according to the invention, the thickness of the various materials being exaggerated, and wherein FIG. 2 represents an exposure stage, FIG. 4 represents a processing stage and FIG. 6 represents a product of the process;

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

FIG. 8 is a graphic representation of the time/pH modulation characteristic curve of a preferred multicolor dye transfer process of the present invention detailed hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

As previously characterized, diffusion transfer photographic processing may be employed to provide a positive dye image, as a direct function of actinic radiation incident on a film unit assemblage which unit is prefer-

ably constructed to comprise a plurality of sequential layers including a dimensionally stable layer most preferably opaque to incident radiation; a photosensitive silver halide layer having associated therewith dye image-forming material which is processing composition diffusible at a selected first pH as a function of the point-to-point degree of silver halide layer photoexposure; a layer adapted to receive dye image-forming material diffusing thereto; a dimensionally stable layer transparent to incident radiation; means for interposing, intermediate the silver halide layer and the reception layer, opacifying agent preferably including an inorganic reflecting pigment dispersion; means for providing a processing composition possessing an alkaline pH and a solvent concentration at which the dye image-forming material is diffusible as a function of the film unit's exposure to incident actinic radiation; and means for converting the pH of the film unit from the first pH to a second pH at which the dye image-forming material is substantially nondiffusible subsequent to substantial dye image-forming material diffusion to the reception layer.

It now has been discovered, however, that improved photographic reproduction in color by diffusion transfer processing may be accomplished by employment of a diffusion transfer process film unit which comprises a plurality of layers including the layer adapted to receive dye image-forming material diffusing thereto, i.e., the receptor layer, constructed to specifically comprise a substantially continuous polymeric layer essentially comprising neutral polymer adapted to interact with aqueous alkaline processing composition in contact with the layer to reduce the alkalinity thereof and to thereby increase the stability of a dye transfer image carried by the layer, and a mordant associated with the layer adapted to mordant dye image-forming material diffusing to the layer.

Employment of diffusion transfer color process film units possessing the defined image-receptive element components have been discovered to provide markedly more efficient, economical and effective utilization of film unit components and fabrication methods.

Specifically, in the practice of the present invention, the image-receptive layer of the diffusion transfer color process film unit comprises a neutral polymer adapted to provide, upon contact of the layer with an aqueous alkaline processing composition, acid equivalents sufficient to effectively reduce the pH of the aqueous alkaline processing composition from a first processing pH to a second pH lower than the first pH, generally in excess of one pH unit less than the first processing pH, providing increased stability to a diffusion process dye transfer image carried by the receptor layer, at a rate effective to allow maintenance of the first processing pH until substantial completion of transfer dye image formation in the receptor layer. The pH reduction referred to thus must be modulated to provide a reduction time scale compatible with effective transfer image formation in the receptor element. This modulated pH reduction may be obtained, in accordance with this invention, by the employment of an aqueous alkaline processing composition hydrolyzable neutral polymer adapted to neutralize alkali as a function of hydrolysis wherein the rate of the hydrolysis of the polymer is balanced to effect the required pH reduction within the time sequence determined by the transfer process's operative environmental pH range. In a particularly pre-

ferred embodiment of the present invention, the neutral polymer will comprise a polycarboxylic acid ester polymer adapted to hydrolyze upon aqueous alkaline processing composition contact with a receptor comprising the polymer at a rate commensurate with generating free carboxylic acid reduction of the pH subsequent to substantial dye transfer image formation in the receptor layer. Specifically, preferred carboxylic acid ester polymers have been found to comprise the acetate ester of cellulose and particularly cellulose acetates which possess an acetate D.S. (degree of substitution) within the range of about 1.5 to about 2.8 acetate groups per anhydroglucose unit of the cellulosic polymer backbone and in particular cellulose acetate possessing a D.S. of about 2.3. As examples of additional polycarboxylic acid ester polymers contemplated for employment in the practice of the present invention mention may also be made of polymethylacrylate methyl, ethyl, etc., esters; styrene carboxylic acid methyl, ethyl, etc., esters; and the like.

Although polysulfonic acid ester polymers are technically feasible for employment in the practice of the present invention as, for example, sulfonic acid ester analogues of the last-identified carboxylic acid esters, it is preferred that the carboxylic esters be so employed.

Where desired, the neutral polymer may also comprise an alkaline processing composition hydrolyzable polymeric salt of an acid and a base and preferably an acid and a polymeric base.

In particular, the receptor layer may comprise a polymeric salt of a strong acid and a weak base adapted to effect the required pH modulation. In general, the stated salt hydrolyzes to provide an acid reaction and, as a function thereof, the subsequent pH modulation forms a polymeric base, in contradistinction to neutralization reactions wherein an acid derived from a precursor such as the aforementioned polycarboxylic acid esters reacts with alkali to form a salt.

The present invention, accordingly, contemplates color diffusion transfer process film units which include a receptor layer, adapted to modulate the pH of an alkaline processing composition contacted therewith, comprising an acid salt of a polymeric base, e.g., the polymeric salt of a strong acid and a weak base which will hydrolyze to provide an acid reaction within the time sequence required by the elected transfer process parameters.

The bases employed to form the salts generally are the amines, primary, secondary or tertiary, including aliphatic, aromatic or heterocyclic amines. As examples of useful amines of this description, mention may be made of polymers, copolymers and graft copolymers of 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, N-vinylimidazole, t-butylaminoethyl methacrylate, aminoethylvinyl ether, etc. Also of interest are aminated polysaccharides such as deacetylated chitin, aminoethyl ether derivatives of cellulose, and the like.

The acids employed to form the salts generally have a pKa less than 4, preferably less than 3, and include the strong mineral acids such as nitric, hydrochloric, phosphoric and sulfuric, as well as strong organic acids such as lactic, chloroacetic, trifluoroacetic, p-toluene sulfonic, etc. Most preferred is nitric acid, since the ni-

trate salts are non-tacky and are not hygroscopic, as compared, for example, to the chlorides or sulfates.

The hydrolyzable polymeric salts may be formed by reacting an amine monomer with the desired amount of acid and then polymerizing to form the polymeric salt; or by reacting the polyamine with the acid. Both reactions are well known and per se comprise no part of this invention; and the salts obtained thereby are generally also old. In either of the above procedures for forming the salts, the amount of acid employed will depend upon the degree of neutralization or protonation desired. For example, if fully neutralized salts are contemplated, stoichiometric amounts of acid will be employed.

It will be thus appreciated that the amount or degree of neutralization of the hydrolyzable salts will be at least in part dependent upon the degree of pH reduction contemplated in the particular film unit and system in which these salts are employed. The lesser the amount of neutralization, the fewer the acidic ions which will be present for a given coverage of the salt. In a typical receptor layer, which is desirably thin and may contain on the order of 3000 mgs./ft.² or less of solids, the salt employed in this layer should preferably be at least 50% neutralized, i.e., at least 50% of the basic groups should be neutralized, and most preferably at least 75% neutralized. However, salts having a lesser degree of neutralization may be completely adequate and hence are also contemplated. In any event, it will be appreciated that the absence of sufficient acid ions at a given coverage of the salt may be compensated for by other means, including the use of higher coverages in the hydrolyzable salt receptor layer. It is to be expressly understood that hydrolyzable polymeric salts for employment in the practice of this invention may include those bases which are not fully neutralized or protonated.

As specific examples of polymeric salts contemplated for employment in the practice of the present invention, mention may be made of deacetylated chitin hydronitrate, dimethylaminoethyl methacrylate hydronitrate, graft copolymer of 4-vinyl pyridinium nitrate on cellulose, etc.

Specifically, in the context of the present invention and throughout the specification and claims of this application, the term "neutral polymer" is intended to encompass polymeric materials which do not detrimentally modulate photographically the pH of the film unit's processing composition upon initial contact therebetween during diffusion transfer processing of the unit and thus are substantially neutral polymeric materials with respect to transfer image generation, irrespective of whether or not a selected polymeric material is or would be classified as an acidic, basic or neutral material in a different context.

The rate of hydrolysis of a selected alkaline processing composition hydrolyzable neutral polymeric stratum may be readily controlled, in accordance with the present invention, by controlling the rate of alkaline solution penetration of the stratum to thus selectively determine the concentration of acid neutralizing component made available for interaction with processing composition per unit processing time. By timed control of the neutral polymer stratum penetration, the reactive site availability of hydrolyzable groups for hydrolytic contact with the alkaline processing composition may be modulated in accordance with the stringent re-

quirements of the dye transfer process for production of optimum dye transfer image formation.

In the practice of the present invention, the acid equivalents generated during processing will be predetermined commensurate with the concentration of alkali to be neutralized and, accordingly, may be readily calculated by the operator for a selected transfer process system and expeditiously confirmed empirically.

In a particularly preferred embodiment of the present invention employing dyes which are silver halide developing agents as the diffusion transfer process dye image-providing material selected, the neutral polymer layer employed will contain at least sufficient alkali neutralizing 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 dye diffusion period, and preferably to a pH of about 5 to 8 within a short time after substantial completion of dye transfer image formation in the receptor layer.

As previously stated, it is, of course, necessary that the action of the polymer be so controlled as not to interfere with either development of the negative or image transfer of dye. For this reason, in the last-mentioned preferred embodiment the pH of the image layer is kept at a level of pH 12 to 14 until the dye image has been formed in the receptor, 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 substantially nondiffusible. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is thus 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 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.

As previously described, in order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the hydrolyzable groups may be so distributed in the neutral polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of penetration or swelling of the polymer layer which rate in turn has a direct relationship to the rate of alkali neutralization.

The desired availability of the required component groups in the polymer for reaction with the aqueous alkaline processing composition may be readily effected by either the employment of a polymeric layer possessing the desired penetration rate parameters or the employment of a neutral polymer substantially impermeable to processing composition in continuous layer form having appropriate permeator material disposed in the polymeric layer. In general, the permeator material means will comprise a discontinuous phase distribution in a continuous phase neutral polymer system of the class designated and may comprise, in essence, physical disruption of the receptor layer as, for example, appropriate tunnelling, etc., and/or a selectively permeable dispersed material, polymeric or otherwise, associated with the receptor layer as the discontinuous phase, rendering the receptor layer permeable in ac-

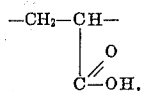
cordance with a predetermined time sequence. The permeation control mechanism utilized may thus itself provide, in substance, the desired control of the permeability of and processing composition interaction with the receptor layer.

As examples of permeator materials preferred for employment in the practice of the present invention in conjunction with neutral polymeric substrate materials of the class set forth above, mention may be made of polyacrylamide, polyvinyl alcohol and the derivatives thereof.

In accordance with the present invention, the receptor layer will possess associated therewith a mordant adapted to effect mordanting of diffusion transfer process dye image-forming material diffusing to the layer during transfer processing of the film unit.

A wide variety of mordants for photographic dyes can be utilized in the present invention. Such materials are well known to those skilled in the art. Mordants that are opposite in charge to the dye being mordanted being generally utilized in accordance with usual practice. As most of the useful photographic image dyes have acidic properties, generally cationic mordants are utilized. Typical mordants are organic quaternary phosphonium salts, organic ternary sulfonium salts and organic quaternary ammonium salts. Suitable mordants include polymers of amino guanidine derivatives of vinyl methyl ketone described in U. S. Pat. No. 2,882,156. Other suitable mordants include the polymers of 2-vinylpyridine quaternized with toluene sulfonate and similar compounds described in U. S. Pat. No. 2,484,430.

U. S. Pat. No. 3,271,147 discloses mordanting compositions comprising a finely-divided uniform dispersion particles of a salt of an organic acidic composition containing free acid moieties and a cationic, nonpolymeric, organic dye mordant for acid dyes. Generally, the salts in such dispersions are in particles less than about 30 microns in diameter. In preparing the mordanting compositions containing such salts or coacervates, any of the conventional cationic mordant compounds, either water-soluble or water-insoluble, are combined with an organic acidic composition (e.g., having free acid groups such as carboxy and sulfonic acid groups) including gelatin that has been reacted with an α -haloacetic acid or acylated with a dicarboxylic acid such as phthalic, malonic, succinic, maleic, glutaric, suberic, and the like acids. Other organic acid compositions include polymers containing such moieties as



long-chain fatty acids such as stearic acid, and other ballasted compounds containing a carboxylic acid moiety such as di-n-amy-phenoxylbutyric acid, long-chain alkyl sulfates and sulfonates and the like organic acidic compounds.

The organic acid composition is sufficiently ballasted to render the resulting salt non-wandering in the polymeric continuous phase in which it is dispersed.

Basic or cationic, nonpolymeric mordant compounds useful in preparing the dye mordanting compositions include quaternary ammonium, phosphonium, and ter-

nary sulfonium compositions in which there is linked to the N, P or S onium atom at least one hydrophobic ballast group, such as long-chain alkyl or substituted alkyl groups. The onium atom can be part of an open-chain or of a heterocyclic ring and there can be more than one onium ring in the molecule. When referring to the nonpolymeric nature of the mordant compounds of such mordanting compositions, it is intended that the cationic or the basic mordant does not have regularly occurring units containing cationic groups beyond dimer structures. However, the ballast group attached to the quaternary or ternary atom of the cation group can contain repeating groups such as tetraethoxy, polymethylene, etc.

Another useful class of mordanting compositions comprises a finely divided uniform dispersion of droplets or globules of a high-boiling water-immiscible organic solvent in which is dissolved a high concentration of a cationic nonpolymeric organic dye-mordanting compound for acid dyes. The droplets of the water-immiscible solvent are typically prepared to be less than 5 microns in size, and more generally in the range of 0.5 to 5 microns in size. Such mordanting compositions are disclosed in U. S. Pat. No. 3,271,148.

The cationic, nonpolymeric organic mordant compounds useful in the mordanting compositions last described are of the type that are capable of entering into salt-forming reactions, e.g., quaternary ammonium group, and at least one ballast group which prevents wandering, such as a long-chain aliphatic group, e.g., those disclosed in U. S. Pat. No. 3,271,147 described above.

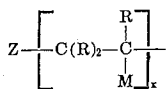
The solvent or carrier for the ionic nonpolymeric mordant compound in the dispersed phase of the mordanting compositions is a high-boiling water-immiscible organic liquid having a boiling point above about 175° C. The high-boiling solvent can be used alone in forming the dispersion, or it can be admixed with some low-boiling organic solvent (e.g., boiling at least 25° C. below the boiling point of the high-boiling solvent), or a water-soluble organic solvent as an auxiliary solvent to facilitate the solution of the mordant material. Preferred ranges of proportions of high-boiling solvent to auxiliary solvent are 1/0 to 1/10 on a weight basis. Any of the high-boiling, water-immiscible solvents described on page 2, Column 2 and page 3, Column 1 of U. S. Pat. No. 2,322,027 can be utilized. Particularly useful solvents are organic carboxylic acid esters and organic phosphate esters.

Also, of course, any of the conventional particulate mordanting materials can be dispersed directly in the receptor in accordance with usual practice to form suitable mordanting compositions. As examples of such mordanting materials for employment in the practice of the present invention, mention may be made of poly-4-vinyl pyridine, trimethyl benzyl tosylate of the acetal of polyvinyl alcohol, 2-methyl-5-vinyl pyridine, and the like.

Where desired, the mordant may also be grafted onto the polymer comprising the receptor layer in accordance with the procedures disclosed in the copending U. S. Pat. application of Stanley F. Bedell, Ser. No. 156,035, filed June 23, 1971.

Specifically, the graft polymers and/or copolymers used in the dyeable stratum or layer of the color diffusion transfer film units may conform to the following formula:

11



wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state; said catalyst having an oxidation potential, in acidic solution, of a least about 1 volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; M is a moiety which can provide a mordant capability; each R is the same or different substituent which will not hinder grafting of the mordant through the vinyl group such as hydrogen, hydroxy, alkyl radicals, alkanol radicals, alkoxy radicals and aryl radicals with hydrogen, hydroxy, lower alkyl or alkoxy, e.g., from one to four carbon atoms, being the preferred substituents; and X is a positive integer.

With regards to the backbone polymer or copolymer of the graft polymer, in general, any organic polymer or copolymer comprising repeating units comprising structural units containing the



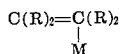
grouping; wherein Y is selected from the group consisting of hydroxyl, amino, mercapto, acyl and aryl, amido are capable of being oxidized by a transition metal ion catalyst as stated above, and are therefore useful in the present invention. The terms hydroxyl, acyl and aryl as used above are intended to encompass partial acetals of these particular functional group terms. Preferred backbones are substituted cellulosic or polyvinyl polymers, and most preferably, a backbone selected from the group consisting of carboxylic acid esters of cellulose and substituted celluloses such as methyl cellulose, etc.

It is believed that upon oxidation of the



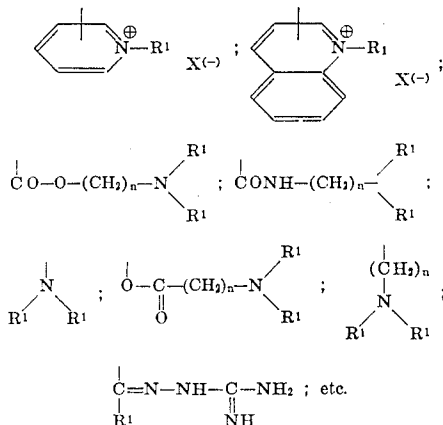
grouping, a free radical is formed, which attacks the graftable site of the compound providing the mordant capability thus providing the graft polymer and/or copolymer.

Graftable compounds which can provide the mordant capability are those which in their monomeric form, conform to the following formula



where, as described before, $(\text{CR})_2=\text{C}(\text{R})_2$ represents a graftable vinyl site and M is a moiety providing a mordant capability. Compounds of this type are known to the art and include, among others, those wherein the M moiety can conform to the following formulae:

12



wherein n is an integer from 1 to 8; each R^1 can be hydrogen, an alkyl radical an alicyclic radical, an alkoxy radical, a saturated heterocyclic ring, and an aryl radical or substituted derivative thereof and each R^1 can be the same or different; X represents an anion such as an aryl sulfonate anion, e.g., benzenesulfonate, p-toluenesulfonate, etc., an alkylsulfonate anion, e.g., methyl sulfate, ethyl sulfate, n-propyl sulfate, n-butyl sulfate, etc.; or X can be a halide ion, e.g., iodide, chloride bromide or other acid anion radical.

Particular compounds conforming to the above generic formulae include the vinyl pyridines and salts thereof such as 4-vinylpyridine, 2-vinylpyridine, 5-vinyl-2-methylpyridine, etc.

Additional compounds include 2-methyl-N-vinylimidazole B-(trimethyl amino) ethyl methacrylate nitrate, B-(trimethyl amino) ethyl methacrylate methyl sulfate, dimethyl amino ethyl methacrylate nitrate, 5-vinyl-2-methyl-N-benzyl pyridinium bromide, 4-vinyl pyridinium tosylate, p-vinyl benzyl triethylammonium chloride, 4-vinylpyridine methyl tosylate, 5-vinyl-2-methyl-pyridine methyl tosylate, vinyl benzyl trimethyl ammonium chloride, vinyl benzyl triethyl ammonium chloride, vinyl benzyl pyridinium chloride, vinyl benzyl-N-methyl morpholinium chloride, and the like.

Further details relating to compounds that can provide a mordant capability may be readily ascertained from U. S. Pat. Nos. 2,537,924; 2,548,575; 2,564,726; 2,583,076; 2,635,535; 2,635,536; 2,753,263; 3,048,487; 3,075,841; etc.

The graft copolymers may be prepared, in general, by oxidizing an organic polymeric backbone containing hydroxyl, amino, mercapto, amido, acyl, or aryl groups with a transition metal ion catalyst, in the presence of the mordant monomer. Generally, a one to 10%, by weight, aqueous solution of the backbone polymer is deaerated for about 30 minutes with stirring. The monomer may then be added and nitrogen bubbled through the solution for about 1 hour. At this point, the nitrogen may be passed over the stirred solution and the pH adjusted to around 1.5 with concentrated acid. The selected catalyst, dissolved in a minimum amount of water, is quickly added to the polymerization mixture and stirring continued under the nitrogen atmo-

sphere for at least 2 more hours with stirring times up to 24 hours, giving no adverse effect to the graft copolymer. The resulting graft copolymers are generally obtained from the reaction vessel in the form of aqueous solutions and may then be coated directly from solution to provide novel image-receiving layers. However, in preferred embodiments, the pH may be raised, e.g., with NH_3 , to a point at which an aqueous emulsion is formed, generally a pH of around 7, depending at least in part upon the ratio of catalyst to backbone polymer and backbone polymer to mordant monomer.

The choice of catalyst is wide ranging, with particularly good results being obtained when catalysts containing Ce^{+4} , V^{+5} and Cr^{+6} are employed in providing the graft copolymers.

Although as mentioned the pH is generally adjusted to around 1.5 with concentrated nitric acid for providing the graft copolymeric material, pH's of up to about 7 have proven operative in instances, depending at least in part on the ratio of catalyst to backbone polymer.

As examples of graft polymers which are contemplated for employment in the practice of the present invention, mention may be made of 4-vinylpyridine graft on cellulose acetate; 5-vinyl-2-methylpyridine graft on cellulose acetate; 4-vinylpyridine, vinyl benzyl trimethyl ammonium chloride graft on cellulose acetate; vinyl benzyl trimethyl ammonium chloride graft on cellulose acetate; etc.

It has been generally found that for any given graft polymer system, the penetration characteristics of the layer prepared therefrom can be manipulated by the judicious choice of (1) backbone/monomer species selection and (2) backbone/catalyst ratio. With respect to the latter, in general, any two polymers having the same backbone, comprised of the same monomers, and having the same monomer to backbone polymer ratio, will result in layers having different diffusion characteristics if they are prepared in the presence of different backbone/catalyst ratios. In general, decreasing the amount of catalyst (and hence increasing the backbone/catalyst ratio) results in increased impermeability.

As was stated hereinbefore, any transition metal ion catalyst of a first oxidation state having an oxidation potential, in acidic solution of at least about 1 volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state, is operable in the present invention. As preferred catalysts, mention may be made of transition metal ion catalysts comprised of a member selected from the group consisting of V^{+5} , Ce^{+4} and Cr^{+6} .

In general, a backbone/catalyst ratio of from about 10 to about 130 is the most useful range, irrespective of the monomers used.

Where desired, the receptor layer may also contain ultraviolet absorbing materials to protect the mordanted dye transfer image from fading due to ultraviolet light such as those selected from the general class of benzotriazoles and benzophenones as, for example, the substituted 2-phenyl-benzotriazole agents disclosed in U. S. Pat. Nos. 3,004,896; 3,189,615; etc. the 2-hydroxybenzophenones such as 2-hydroxy-4-methoxybenzophenone; 2,2'-dihydroxy-4-methoxybenzophenone; 2-hydroxy-4-octyloxybenzophenone; etc., both water and organic solvent soluble agents being contemplated, and/or brightening

agents such as those selected from the general class of triazinestilbenes, coumarins, anthracenes, terphenyls, tetraphenylbutadienes, quinoxalines, conventional for use as fluorescent agents and as optical brightening agents. Suitable triazine-stilbene optical brightening agents are disclosed in U.S. Pat. No. 2,933,390; coumarins are disclosed in British Pat. No. 786,234; and various agents are disclosed in U. S. Pat. Nos. 2,171,427; 2,473,475; 2,595,030; 2,660,578; and British Pat. Nos. 595,065; 623,849; 624,051; 624,052; 678,291; 681,642; 705,406; etc. Commercially available brightening agents are distributed under the trade designation Tinopal (SP, WR, SFG, BV277, 2B, GS, NG) Leucophor B, Calcofluor White MR, Blaneofor SC, Hitamine (BSP, N, SOL., 6T6), and the like, and commercially available ultraviolet absorbing agents are distributed under the trade designation Tinuvin and the like.

In general, ultraviolet absorbing and optical brightening agents may be employed in concentrations varying over an extended range. Suitable concentrations include those within the range of about 0.2 to 10 mgs./ft.² of receptor layer surface area and, preferably, between about 1 to 5 mgs./ft.².

The agents may be incorporated in the receptor layer in any suitable manner as, for example, a constituent component of the casting and/or coating solution or formulation employed to provide the layer employing an organic solvent or water carrier or as a latex dispersion.

In the circumstances wherein the receptor layer does not possess the dimensional stability to provide a self-sustaining layer conformation, the layer may optionally be coated on or carried by an appropriate dimensionally stable support layer of the various types and classes specifically designated hereinafter.

Ordinarily, when the image receptor stratum comprises a layer carried on a separate dimensionally stable support layer, the receptor stratum will comprise in the order of about 0.1 to 0.4 mils. in thickness whereas such stratum employed as a self-sustaining layer will comprise in the order of about 3 to 6 mils. in thickness.

The latter stratum may be provided by the casting of the polymeric composition in accordance with any one or more of the casting procedures conventional in the packaging and/or photographic art for the production of dimensionally stable polymeric layer or sheet materials. Specifically, a preferred cellulose acetate receptor element may be prepared by doctor blade casting, at room temperature, of a 20% solution of cellulose acetate (D.S. $\approx$ 2.3), in 3:1 ethyl acetate/methanol, and 20% poly-4-vinyl pyridine, by weight of cellulose acetate, on a glass plate support to provide an approximately 5 mil. (dry thickness) sheet dried at about 100° F.

In a preferred embodiment of the present invention, the means for interposing the processing composition selected intermediate the reception layer and the silver halide layer comprises a rupturable container retaining a processing composition including the solvent and pH concentrations required fixedly positioned and extending transverse a leading edge of the film unit to effect, upon application of compressive pressure, discharge of the processing composition intermediate the reception layer and the photosensitive silver halide layer next adjacent. In such embodiment the opacifying agent is preferably disposed within the processing composition,

as retained in the rupturable container, for distribution as a component of such composition intermediate the reception and silver halide layers, subsequent to selective exposure of the film unit.

Multicolor images may be obtained using color image-forming components in the diffusion transfer process of the present invention by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing, for example, dye developers as dye image-providing materials by employment of an integral multilayer photosensitive element such as is disclosed in aforementioned U. S. Pat. No. 3,415,644 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 the opaque support carrying a red-sensitive silver iodochlorobromide stratum, a green-sensitive silver iodochlorobromide stratum and a blue-sensitive silver iodochlorobromide 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 stratum, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide strata. Each set of silver halide strata 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.

In a preferred embodiment of the present invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, the dimensionally stable opaque layer; at least two selectively sensitized silver halide strata each having dye image-providing material of predetermined color associated therewith, for example, dye developers as detailed above, which are soluble and diffusible in processing composition as a function of the point-to-point degree of exposure of the respective associated silver halide stratum; a polymeric layer dyeable by the dye image-providing materials; and a dimensionally stable transparent layer.

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

The 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.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide stratum. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide stratum and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

The silver halide strata comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at a first pH possessing, subsequent to processing, a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

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

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

Although in one embodiment of the present invention the dimensionally stable layers employed in the practice of the invention may possess a vapor transmission rate of 1 or less gms./24 hrs./100 in.²/mil., in a preferred embodiment of the invention, the layers employed will possess a vapor transmission rate for the selected processing composition solvent averaging not less than about 100 gms./24 hrs./100 in.²/mil., most preferably in terms of the preferred solvent, water, a vapor transmission rate averaging in excess of about 300 gms. of water/24 hrs./100 in.²/mil., and may advance

tageously comprise a microporous polymeric film possessing a pore distribution which does not unduly interfere with the dimensional stability of the layers or, where required, the optical characteristics of such layers. Such pore distribution may comprise, for example, an average pore diameter of from < about 20 microns to > about 100 microns and a pore volume of < about 3 percent to > about 7 percent.

The preferred dimensionally stable layers are designed so that there is no liquid flow through the layers while allowing the vapor of the processing composition solvent to pass by diffusion from the evaporating liquid body and the operational efficiency of the film unit is directly dependent upon the nature and quality of the vapor permeable membrane characteristics of the layers selected. The vapor transmission characteristics desired are directed to maximization of the rate at which the required quantity of processing solvent is effectively evacuated from the film unit subsequent to substantial dye transfer image formation by diffusion transfer processing, commensurate with maintaining the liquid impermeability and dimensional stability characteristics of the layers. Thus, the layers should possess the maximum vapor transmission capacity which permits the passage of processing composition solvent vapor, and any gas dissolved therein, at its vapor pressure, without allowing passage of fluid processing composition. The layers employed in accordance with the present invention therefor should be as thin as possible for solvent vapor transmission efficiency yet retain sufficient strength to provide stability to and resist chemical and physical degradation of the film unit under conditions of use.

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

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

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

Film unit 10 comprises rupturable container 11, retaining, prior to processing, aqueous processing composition 12, and photosensitive laminate 13 including, in order, dimensionally stable opaque layer 14, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer 15; red-sensitive silver halide emulsion layer 16; interlayer 17; magenta dye developer layer 18; green-sensitive silver halide emulsion layer 19; interlayer 20; yellow dye developer layer 21;

blue-sensitive silver halide emulsion layer 22; auxiliary layer 23, which may contain an auxiliary silver halide developing agent; image-receiving layer 24; and dimensionally stable transparent layer 27, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of laminate 13 may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the laminate at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer 24 and the silver halide emulsion layer next adjacent thereto, for example, image-receiving layer 24 and auxiliary layer 23 as illustrated in FIGS. 2 through 7, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the laminate, in order to facilitate distribution of processing solution 12 intermediate the stated image-receiving layer 24 and the silver halide emulsion layer next adjacent thereto. The laminate's structural integrity may also be enhanced or provided, in whole or in part, by providing a binding member extending around, for example, the edges of laminate 13, and maintaining the layers comprising the laminate intact, except at the interface between layers 23 and 24 during distribution of processing composition 12 intermediate those layers. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape 28 securing and/or maintaining the layers of laminate 13 together at its respective edges. Tape 28 will also act to maintain processing solution 12 intermediate image-receiving layer 24 and the silver halide emulsion layer next adjacent thereto, upon application of compressive pressure to pod 11 and distribution of its contents intermediate the stated layers. Under such circumstances, binder tape 28 will act to prevent leakage of fluid processing composition from the film unit's laminate during and subsequent to photographic processing.

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

As illustrated in FIGS. 1, 2 and 3, container 11 is fixedly positioned and extends transverse a leading edge of photosensitive laminate 13 whereby to effect unidirectional discharge of the container's contents 12 between image-receiving layer 24 and the stated layer next adjacent thereto, upon application of compressive force to container 11. Thus, container 11, as illustrated in FIG. 2, is fixedly positioned and extends transverse a leading edge of laminate 13 with its longitudinal marginal seal 30 directed toward the interface between image-receiving layer 24 and auxiliary layer 23. As shown in FIGS. 1, 2 and 4, container 11 is fixedly secured to laminate 13 by extension 32 of tape 28 extending over a portion of one wall 29 of the container, in combination with a separate retaining member such as illus-

trated retaining tape 33 extending over a portion of laminate 13's surface generally equal in area to about that covered by tape 28.

As illustrated in FIGS. 1, 2 and 4, extension flap 32 of tape 28 is preferably of such area and dimensions that upon, for example, manual separation of container 11 and tape 33, subsequent to distribution of processing composition 12, from the remainder of film unit 10, flap 32 may be folded over and secured to the edge of laminate 13, previously covered by tape 33, in order to facilitate maintenance of the laminate's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer 27.

The fluid contents of the container preferably comprise an aqueous alkaline solution having a pH and solvent concentration at which the dye developers are soluble and diffusible and contains inorganic light-reflecting pigment and at least one optical filter agent at a pH above the pKa of such agent in a quantity sufficient, upon distribution, effective to provide a layer exhibiting optical transmission density $>$ about 6.0 and optical reflection density $<$ about 1.0 to prevent exposure of photosensitive silver halide emulsion layers 16, 19 and 22 by actinic radiation incident on dimensionally stable transparent layer 27 during processing in the presence of such radiation and to afford immediate viewing of dye image formation in image-receiving layer 24 during and subsequent to dye transfer image formation. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of laminate are appropriately protected by incident radiation, at one major surface of the opaque processing composition and at the remaining major surface by the dimensionally stable opaque layer. If the illustrated binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented.

The selected reflecting pigment should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric layer. In general, while substantially any reflecting agent may be employed, it is preferred that a reflecting agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable reflecting agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially those agents possessing the optical properties desired for reflection of incident radiation.

As examples of reflecting pigments adapted for employment in the practice of the present invention, mention may be made of barium sulfate, zinc sulfide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

A particularly preferred reflecting agent comprises titanium dioxide due to its highly effective reflection

properties. In general, in such preferred embodiment, based upon percent titanium dioxide (weight/volume) a processing composition containing about 1500 to 4000 mgs./ft.² titanium dioxide dispersed in 100 cc. of water will provide a percent reflectance of about 85 to 90 percent. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of $>$ about 85 percent.

In embodiments wherein the dispersion comprises a preformed layer positioned intermediate the reception layer and next adjacent silver halide layer, the pigment layer will be sufficiently transparent to allow transit of exposing radiation through the pigment layer and may comprise titanium dioxide reflecting agent possessing a particle size distribution averaging $<$ about 0.2 micron in diameter and preferably $<$ about 0.05 micron in diameter as initially present preceding exposure of the film unit, which preferred materials, upon contact with aqueous alkaline processing composition, preferably aggregate to provide particles possessing a diameter $>$ about 0.2 micron in diameter and will be coated at a coverage of about 200 to 1000 mgs./ft.². Specifically, the reflecting agent will be present in a quantity insufficient to prevent exposure of the emulsion layers by actinic radiation incident on the dimensionally stable transparent layer of the film unit but in a concentration sufficient, subsequent to processing, to mask dye developer associated with the silver halide emulsion strata from the dye transfer image. In the preferred construction of such embodiment, the pigment such as titanium dioxide will be initially present in a relatively small particle size to provide unexpectedly efficient transit of radiation through the reflecting layer during exposure which upon contact with an alkaline processing composition and aggregation of the pigment particles provides efficient light reflectivity and masking capacity subsequent to such aggregation.

In general, the reflecting agents to be employed are those which remain substantially immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible inorganic pigment dispersions within the layer in which they are disposed.

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

The optical filter agent selected should be one exhibiting, at a pH above its pKa, maximum spectral absorption of radiation at the wavelengths to which the film unit's photosensitive silver halide layer or layers are sensitive and should be substantially immobile or nondiffusible within the pigment dispersion, during performance of its radiation filtration function, in order to maintain and enhance the optical integrity of the dis-

person as a radiation filter unit functioning in accordance with the present invention, and to prevent its diffusion into and localized concentration within the image-receiving layer thereby decreasing the efficiency of the reflecting pigment dispersion as a background against which image formation may be immediately viewed, during the initial stages in the diffusion transfer processing of the film unit, by filter agent absorption of dispersion reflected visible radiation prior to reduction in the environmental pH below the pKa of the agent. Commensurate with the spectral sensitivity range of the associated silver halide layer or layers, the optical filter agent selected may comprise one or more filter dyes possessing absorption complementary to such silver halide layers in order to provide effective protection against physical fog providing radiation during processing. Recognizing that the filter agent absorption will derogate from image-viewing characteristics by contaminating reflecting pigment background, the selected agents should be those exhibiting major spectral absorption at the pH at which processing is effected and minimal absorption at a pH below that which obtains during transfer image formation. Accordingly, the selected optical filter agent or agents should possess a pKa below that of the processing pH and above that of the environmental pH subsequent to transfer image formation, and will be preferably selected for employment in the minimum concentration necessary to provide an optical transmission density $>$ about 6.0, at wavelengths at which the silver halide layer is maximally responsive, and an optical reflection density $<$ about 1.0 at such wavelengths.

As specific examples of such pH-sensitive optical filter agents adapted for employment in the practice of the present invention, reference is directed to the agents set forth in U. S. Pat. No. 3,647,437, incorporated herein by reference.

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

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

In the performance of a diffusion transfer multicolor process employing film unit 10, the unit is exposed to radiation, actinic to photosensitive laminate 13, incident on the laminate's exposure surface, as illustrated in FIG. 3.

Subsequent to exposure, as illustrated by FIGS. 2 and 4, film unit 10 is processed by being passed through opposed suitably gapped rolls 35 in order to apply compressive pressure to frangible container 11 and to effect rupture of longitudinal seal 30 and distribution of alkaline processing composition 12, possessing inorganic light-reflecting pigment and optical filter agent at a pH above the pKa of the filter agent and a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible as a function of the point-to-point degree of exposure of red-sensitive silver halide emulsion layer 16, green-sensitive silver halide emulsion layer 19 and blue-sensitive silver halide emulsion layer 22, respectively, intermediate image-receiving layer 24 and auxiliary layer 23.

Alkaline processing composition 12 permeates emulsion layers 16, 19 and 22 to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers 15, 18 and 21, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to dyeable polymeric layer 24 to provide a multicolor dye transfer image to that layer which is viewable against the background provided by the reflecting pigment present in processing composition residuum 12 masking cyan, magenta and yellow dye developer remaining associated with blue-sensitive emulsion layer 22, green-sensitive emulsion layer 19 and red-sensitive emulsion layer 16. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline processing composition 12 transfer, by diffusion, to polymeric reception layer 24 whereby the environmental pH of the system decreases as a function of neutralization to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially nondiffusible to thereby provide a stable multicolor dye transfer image and discharge of the pH-sensitive optical filter agent by reduction of the pH substantially below the pKa of such agent to thereby provide maximum reflectivity in terms of the pigment concentration present.

The alkaline solution component of the processing composition, positioned intermediate the photosensitive element and the image-receiving layer, thus permeates the emulsions to initiate development of the latent images contained therein. The respective associated dye developers are mobilized in unexposed areas as a consequence of the development of the latent images. This mobilization is apparently, at least in part, due to a change in the solubility characteristics of 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

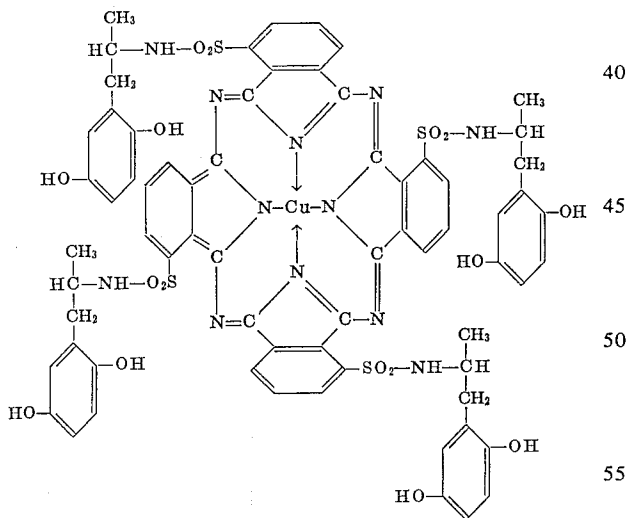
agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsions, the associated dye developer is diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving layer receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image.

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

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

Film units similar to that shown in the drawings may be prepared, for example, by coating, in succession, on a 5 mil. opaque polyester film base, the following layers:

1. a layer of the cyan dye developer

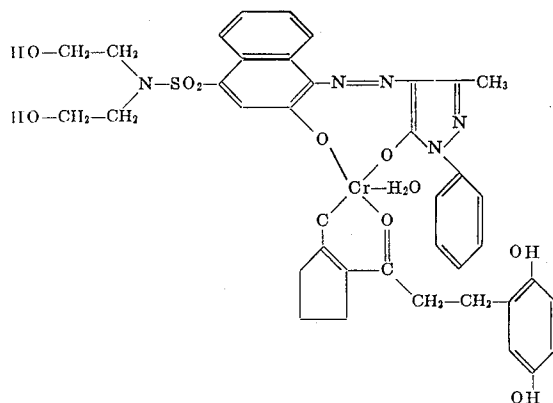


dispersed in gelatin and coated at a coverage of about 75 mgs./ft.² of dye and about 60 mgs./ft.² of gelatin;

2. a red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 140 mgs./ft.² of silver and about 60 mgs./ft.² of gelatin;

3. a layer of butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of about 29:1, respectively, at a coverage of about 180 mgs./ft.²;

4. a layer of the magenta dye developer

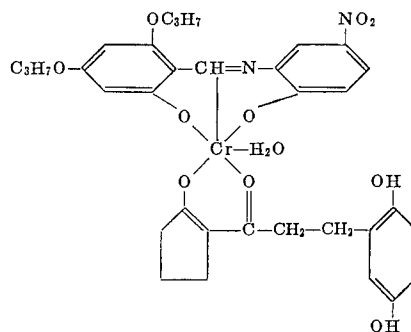


dispersed in gelatin and coated at a coverage of about 110 mgs./ft.² of dye and about 100 mgs./ft.² of gelatin;

5. a green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 100 mgs./ft.² of silver and about 50 mgs./ft.² of gelatin;

6. a layer comprising butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of about 29:4, respectively, at a coverage of about 100 mgs./ft.²;

7. a layer of the yellow dye developer



dispersed in gelatin and coated at a coverage of about 70 mgs./ft.² of dye and about 50 mgs./ft.² of gelatin;

8. a blue-sensitive gelatino-silver iodobromide emulsion and the auxiliary developer 4'-methylphenyl hydroquinone coated at a coverage of about 120 mgs./ft.² of silver, about 30 mgs./ft.² of auxiliary developer and

25

about 60 mgs./ft.² of gelatin; and

9. a layer of gelatin coated at a coverage of about 40 mgs./ft.² of gelatin.

Then a transparent gelatin subcoated 5 mil. polyester film base may be coated with a 8:2 mixture, by weight, of cellulose acetate and poly-4-vinylpyridine, at a coverage of about 1100 mgs./ft.² to provide a polymeric image-receiving layer.

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

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

Water — 150.00 cc.

Potassium hydroxide — 22.00 gms.

Sodium carboxymethyl cellulose — 5.00 gms.

(commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade designation Hercules Type 7H4F providing a viscosity of 3000 cps. at 1% in water at 25° C.)

N-Phenethyl- α -picolinium bromide — 0.80 gms.

N-Benzyl- α -picolinium bromide — 6.00 gms.

Titanium dioxide — 70.00 gms.

6-Methyl uracil — 3.00 gms.

Bis-(β -aminoethyl)-sulfide — 0.20 gms.

Lithium nitrate — 0.60 gms.

6-Benzylamino purine—2.00 gms.

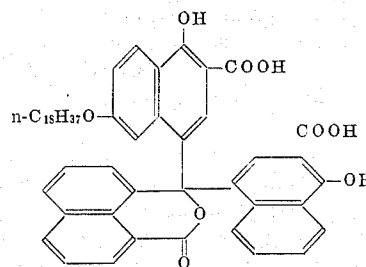
may then be fixedly mounted on the leading edge of each of the laminates, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that, upon application of compressive pressure to a container, its contents may be distributed, upon rupture of the container's marginal seal, between the polymeric image-receiving layer and next adjacent gelatin layer.

The photosensitive composite film units may be exposed through radiation incident on the transparent polyester layer and processed by passage of the exposed film units through appropriate pressure-applying members, such as suitably gapped, opposed rolls, to effect rupture of the container and distribution of its contents. Subsequent to processing, the multicolor dye transfer image formation may be viewed through the transparent polyester layer against the titanium dioxide background provided by distribution of the pigment containing processing composition between Layer 9 and the polymeric image-receiving layer. Multicolor dye transfer image formation will be found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation, within a period of approximately 1.5 to 2 minutes and, in a specific instance, exhibits a cyan, magenta and yellow D_{max} . read to red, green and blue light of 2.26, 2.67 and 2.21, respectively, and D_{min} . read to red, green and blue light of 0.18, 0.26 and 0.26.

For purposes of illustrating the advantageous results achieved by reason of the present invention, film units, fabricated essentially as denoted above, were processed in the stated manner, at processing temperatures of 100° and 40° F.

By addition of about 150 mgs./10 cc. of processing composition

26



to the processing composition, image formation may be immediately viewed upon distribution of the processing composition by reason of the protection against incident radiation afforded the photosensitive silver halide emulsion layers by the composition's optical transmission density of $>$ about 6.0 density units and against the titanium dioxide's effective reflective background afforded by reason of the composition possessing an optical reflection density $<$ about 1.0 density units.

A test film unit was exposed and processed to provide the graphic illustration of the neutralization of the respective dye transfer image, forming the multicolor dye positive image, set forth in FIG. 8.

The detailed neutralization curve was determined by plotting the optical density of the last-mentioned optical filter agent possessing a pKa of about 13 as a function of processing time read on a MacBeth RD-400 densitometer employing a Corion IR Filter and a No. 29 Wratten Filter.

The pH and solvent concentration of the alkaline processing solution initially employed will possess a pH above the pKa of the optical filter agents where the latter are employed, that is, the pH at which about 50 percent of the agents are present as the lesser absorbing species and about 50 percent are present as the greater absorbing species, preferably a pKa of $>$ about 11 and most preferably $>$ about 12 and a pH at which the dye developers employed are soluble and diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer and optical filter agent, or group of dye developers and filter agents, most particularly desirable dye developers are soluble at pH's above 9 and relatively insoluble at pH's below 9, in reduced form, and relatively insoluble at substantially any alkaline pH, in oxidized form, and the system can be readily balanced accordingly for such dye developers. In addition, although as previously noted, the processing composition, in the preferred embodiment, will include the stated film-forming viscosity-increasing agent, or agents, to facilitate spreading of the composition and to provide maintenance of the spread composition as a structurally stable layer of the laminate, subsequent to distribution, it is not necessary that such agent be employed as a component of the composition.

The preferred silver halide type photosensitive layers employed for the fabrication of the photographic film unit, 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 chloride, together with corresponding iodide and bromide, in an aqueous solution of a peptizing agent such as 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, for example, employing the preferred gelatin ma-

trix material, 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. Pat. Nos. 2,614,928; 2,614,929; 2,728,662, and the like; afterripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for example, chemical sensitizing agents of U. S. Pat. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography Its Materials and Processes*, 6th Ed., 1962.

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

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

As the binder for the photoresponsive material, the aforementioned gelatin may be, in whole or in part, replaced with some other natural and/or synthetic processing composition permeable polymeric material such as albumin; casein; or zein or resins such as cellulose derivatives, as described in U. S. Pat. Nos. 2,322,085 and 2,541,474; vinyl polymers such as those described in an extensive multiplicity of readily available U. S. and foreign patents or the photoresponsive material may be present substantially free of interstitial binding agent as described in U. S. Pat. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, *Comment on Non-Gelatin Film*, B. J. O. P., 434, Sept. 15, 1961; and Belgian Pat. Nos. 642,557 and 642,558.

In preferred embodiments of the present invention, the photosensitive silver halide emulsions employed will be emulsions adapted to provide a Diffusion Transfer Process Exposure Index > about 50, which Index indicates the correct exposure rating of a diffusion transfer color process at which an exposure meter, calibrated to the ASA Exposure Index, must be set in order that it give correct exposure data for producing color transfer prints of satisfactorily high quality. The Diffusion Transfer Process Exposure Index is based on a characteristic H & D curve relating original exposure of the photosensitive silver halide emulsion to the respective curve densities forming the resultant transfer image. Thus, the Diffusion Transfer Exposure Index is based on the exposure to which the photosensitive silver halide emulsion, for use in color diffusion transfer processes, must be subjected in order to obtain an acceptable color transfer image by that process and is a direct guide to the exposure setting to be entered in a camera in order to obtain proper exposure of the film unit.

Excellent diffusion transfer dye image characteristic curve shape control, i.e., control of the transfer image characteristics represented graphically by the curve in-

tegrating dye density of the transfer image as a function of the log exposure of the photosensitive silver halide layer, may be obtained by utilization of a photosensitive silver halide layer which comprises a blend of differentially photosensitive silver halide dispersions at least one of the dispersions comprising, for example, a silver iodochlorobromide dispersion in admixture, for example, with a silver chlorobromide, -bromide, -iodobromide or -iodochlorobromide dispersion or dispersions, which blend preferably may possess a mean particle size within the range of about 0.3 to 3.0 microns.

Specifically, blending the aforementioned differentially sensitive silver halide dispersions, the characteristic curve of the dye transfer image resultant from employment of the blend may assume the "shoulder," i.e., low photosensitive silver halide layer photoexposure region, "speed," i.e., relative measurement defined as a value representing the reciprocal of the exposure required to produce a predetermined result, of the fastest silver halide dispersion and the "toe," i.e., high photosensitive layer photoexposure region, "speed" of the slowest silver halide dispersion, thus increasing the exposure latitude range and lowering the resultant slope or gamma of the curve.

There is thus provided the capacity for controlled formulation of photosensitive layers exhibiting a selectively extended range of predetermined gammas or contrasts and "exposure latitudes" or "dynamic ranges", i.e., the relative measurement of the range of exposure from which a useful dye transfer image may be derived; thereby providing the capability of a high maximum density, low minimum density and extended dynamic range dye diffusion transfer imaging system and thus adapted to more advantageously reproduce, as dye transfer image differences, the luminance differences existing in an object to be photographically reproduced, including optimization of the minimum useful exposures required to reproduce minimum differences existing in the shadow regions of the object to be reproduced by means of some minimum density differences in resultant dye transfer image conformation.

Neutralizing means, for example, a polymeric acid layer of the type discussed above may be incorporated, as stated, in the film unit of the present invention, to provide further reduction of the alkalinity of the processing solution from a pH above the pKa of the optical filter agent selected at which the dyes are soluble to a pH below the pKa of the agent at which the dyes are substantially nondiffusible, in order to advantageously further stabilize and optimize reflectivity of the dye transfer image. In such instance, the neutralizing layer may comprise particulate acid reacting reagent disposed within the film unit or a polymeric acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mils. in thickness, positioned intermediate the transparent support and image-receiving layer, and/or the opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer, for example, approximating 0.1 to 0.7 mil. in thickness, next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

Specifically, the film units may employ the presence of a polymeric acid layer such as, for example, of the type set forth in U. S. Pat. Nos. 3,362,819 and 3,362,821 which, most preferably, include the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the next adjacent layer.

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

As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14 and the pKa of the selected optical filter agents will accordingly preferably be in the order of 13 or greater. The polymer layer optionally employed may be constructed to contain acid groups adapted to amplify rate and/or concentration wise reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid also be accurately so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, as previously stated, the pH of the image layer must be kept at a functional transfer level, for example, 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to a pH below that at which dye transfer may be accomplished, for example, at least about 11 and preferably about pH 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming com-

ponents thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has been accomplished.

The 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 sub-coats are employed to help the various polymeric layers adhere to each other during storage and use.

Employment of the detailed and preferred film units of the present invention, according to the herein described color diffusion transfer process, specifically provides for the production of a highly stable transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by in process adjustment of the environmental processing composition solvent and pH concentration from a solvent and pH concentration at which dye diffusion or transfer is operative to a solvent and pH concentration at which dye transfer is inoperative subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during exposure, processing, viewing, and storage of the unit. Accordingly, by means of the present invention, multi-color transfer images may be provided over an extended processing temperature range which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit construction and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

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

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

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

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH and solvent concentration required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

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

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U. S. Pat. No. 2,983,606 and in the various copending U. S. applications referred to in that patent, especially in the table of U. S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U. S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U. S. Pat. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808;

3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

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

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

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U. S. Pat. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U. S. Pat. No. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having asso-

ciated therewith, respectively a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye image-forming material in or behind in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye image-forming material.

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

Where in the specification, the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produce on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

Where separation of the image receptor from the remainder of the film unit, subsequent to dye transfer image formation, is contemplated, it will be understood and appreciated that the support for and/or the receptor layer retaining the transfer image, especially when self-sustaining, may be constituted as a projection or transparency image or print or, at the election of the operator, a reflection print, the latter readily accomplished by appropriate selection of an opaque, preferably reflecting, support member and/or the addition or distribution of reflecting adjuvant associated with the dye image carried by the receptor layer.

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

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, and that any one or more of the described layers may comprise a composite of two or

more strata of the same, or different, components and which may be contiguous, or separated from, each other.

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

What is claimed is:

1. A photographic diffusion transfer color process film unit which comprises a plurality of layers including a photosensitive silver halide layer having associated therewith a diffusion transfer process dye image-forming material adapted to provide a dye image to a contiguous image-receiving layer during processing of the unit as a function of the point-to-point degree of the photosensitive layer's exposure to radiation actinic thereto and an image-receptive layer, adapted to receive dye image-forming material diffusing thereto, which is a substantially continuous polymeric layer consisting essentially of a synthetic neutral polymer which provides acid as a function of alkaline hydrolysis, upon contact with aqueous alkaline processing composition, adapted to reduce the alkalinity of said image-receptive layer, subsequent to substantial dye image formation in said image-receptive layer by diffusion of dye image-forming material to said layer, at least one pH unit, and having associated therewith in said layer a mordant adapted to mordant dye image-forming material diffusing to said layer.

2. A photographic diffusion transfer color process film unit as defined in claim 1 wherein said diffusion transfer process dye image-forming material is diffusible at a first alkaline pH as a function of the photoexposure of said film unit and is substantially nondiffusible at a second pH at least one pH unit lower than said first pH and said neutral polymer is adapted to be hydrolyzed by contact with aqueous alkaline processing composition possessing said first pH to provide acid in a concentration effective to reduce the pH of said processing composition in contact with said image-receiving layer to said second pH at which said dye image-forming material is substantially nondiffusible subsequent to substantial dye image formation in said image-receiving layer.

3. A photographic diffusion transfer color process film unit as defined in claim 1 wherein said polymer comprises an alkaline processing composition hydrolyzable polymeric ester.

4. A photographic diffusion transfer color process film unit as defined in claim 3 wherein said polymeric ester is a polycarboxylic acid ester.

5. A photographic diffusion transfer color process film unit as defined in claim 4 wherein said polycarboxylic acid ester is cellulose acetate.

6. A photographic diffusion transfer color process film unit as defined in claim 5 wherein said cellulose acetate contains an acetate substituent ratio of 1.5 to 2.8 acetate groups per anhydroglucose unit.

7. A photographic diffusion transfer color process film unit as defined in claim 1 including opacifying agent, in a quantity sufficient to mask dye image-forming material associated with said photosensitive silver halide layer, adapted to be disposed intermediate said photosensitive silver halide layer and said layer

adapted to receive dye image-forming material diffusing thereto.

8. A photographic diffusion transfer color process film unit as defined in claim 1 including a rupturable container retaining said processing composition positioned extending transverse an edge of the film unit to effect, upon application of compressive pressure to said container, discharge of said container's processing composition contents into contact with said photosensitive silver halide layer.

9. A photographic diffusion transfer color process film unit as defined in claim 8 wherein said rupturable container retaining said processing composition is adapted, upon application of compressive pressure to the container, to discharge the container's processing composition contents intermediate said photosensitive layer and the layer adapted to receive dye image-forming material diffusing thereto.

10. A photographic diffusion transfer color process film unit as defined in claim 9 wherein said processing composition includes opacifying agent in a quantity sufficient to mask dye image-forming material associated with said photosensitive layer.

11. A photographic diffusion transfer color process film unit as defined in claim 10 including a dimensionally stable opaque layer positioned contiguous the surface of said photosensitive layer opposite said layer adapted to receive dye image-forming material diffusing thereto.

12. A photographic diffusion transfer color process film unit as defined in claim 11 including a separate dimensionally stable transparent layer positioned contiguous the surface of said layer adapted to receive dye image-forming material diffusing thereto opposite said photosensitive layer.

13. A photographic diffusion transfer color process film unit as defined in claim 8 including a dimensionally stable transparent layer positioned contiguous the surface of said photosensitive silver halide layer opposite said layer adapted to receive dye image-forming material diffusing thereto, an opaque layer adapted to reflect incident visible radiation positioned intermediate said photosensitive silver halide layer and the layer adapted to receive dye image-forming material diffusing thereto and said rupturable container retaining said processing composition is adapted, upon application of compressive pressure to the container, to discharge the container's processing composition contents intermediate said photosensitive silver halide layer and said dimensionally stable transparent layer.

14. A photographic diffusion transfer color process film unit as defined in claim 1 wherein said dye image-forming material is a dye which is a silver halide developing agent.

15. A photographic diffusion transfer color process film unit as defined in claim 1 wherein said mordant is a basic mordant adapted to mordant an acid dyestuff.

16. A photographic diffusion transfer color process film unit as defined in claim 1 wherein said polymer is an alkali hydrolyzable polymeric salt.

17. A photographic diffusion transfer color process film unit as defined in claim 1 including at least two selectively sensitized silver halide layers each having a dye image-forming material associated therewith.

18. A photographic diffusion transfer color process film unit as defined in claim 17 wherein each of the selectively sensitized silver halide layers possesses pre-

dominant spectral sensitivity to separate regions of the spectrum and the dye image-forming material associated with each of said silver halide layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated silver halide layer.

19. A photographic diffusion transfer color process film unit as defined in claim 18 which comprises, in combination:

a photosensitive element including a composite structure containing, as essential layers, a dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsion layers possessing predominant spectral sensitivity to separate regions of the visible electromagnetic spectrum, said silver halide emulsion layers having associated therewith a dye which is a silver halide developing agent and is soluble and diffusible, in alkaline processing composition, at a first pH, possessing a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion layer; an alkaline solution dyeable mordant retaining polycarboxylic acid ester layer adapted to provide, as a function of contact with an alkaline processing composition, acid in a concentration effective subsequent to substantial dye transfer image formation in said dyeable polymeric layer to reduce alkaline processing composition possessing said first pH at which said dyes are soluble and diffusible to a second pH at least one pH unit lower than said first pH at which said dyes are substantially nondiffusible; a dimensionally stable transparent layer; and means securing the layers in substantially fixed relationship; and

a rupturable container retaining an alkaline processing composition possessing said first pH at which said dyes are soluble and diffusible and opacifying agent in a quantity sufficient to mask dye associated with said selectively sensitized silver halide emulsion layers, said rupturable container positioned and extending transverse an edge of the photosensitive element to effect unidirectional discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the selectively sensitized silver halide emulsion layer next adjacent thereto.

20. A photographic diffusion transfer color process film unit as defined in claim 19 adapted to be processed by passage of said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye, said cyan, magenta and yellow dyes comprising silver halide developing agents soluble and diffusible, in alkaline processing composition, at a first pH; an alkaline solution dyeable mordant retaining cellulose acetate layer adapted to provide upon contact with alkaline processing composition acid in a concentra-

tion effective to reduce an alkaline processing composition having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible to a second pH at least one pH unit lower than said pH at which said cyan, magenta and yellow dyes are substantially nondiffusible; a dimensionally stable alkaline solution impermeable transparent layer; and means securing said layers substantially in fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible and opacifying agent in a quantity sufficient to mask, upon distribution of the aqueous alkaline processing composition as a layer, intermediate the dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, cyan, magenta and yellow dye associated with said red-, green-, and blue-sensitive emulsion layers, said container fixedly positioned and extending transverse an edge of the photosensitive element to effect, upon application of compressive force to said container, unidirectional discharge of the container's aqueous alkaline processing composition contents intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer.

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

- a. exposing a photographic film unit which comprises a plurality of layers including a photosensitive silver halide layer having associated therewith a diffusion transfer process dye image-forming material adapted to provide a dye image to a contiguous image-receiving layer during processing of the unit as a function of the point-to-point degree of the photosensitive layer's exposure to radiation actinic thereto and an image-receptive layer, adapted to receive dye image-forming material diffusing thereto, which is a substantially continuous polymeric layer consisting essentially of a neutral synthetic polymer which provides acid as a function of alkaline hydrolysis, upon contact with aqueous alkaline processing composition, adapted to reduce the alkalinity of said image-receptive layer at least one pH unit, having associated therewith in said layer a mordant adapted to mordant dye image-forming material diffusing to said layer;
- b. contacting said photosensitive silver halide layer with an aqueous alkaline processing composition;
- c. effecting thereby development of the photoexposed silver halide layer;
- d. forming thereby an imagewise distribution of diffusible dye image-forming material, as a function of the point-to-point degree of the silver halide layer's exposure to incident actinic radiation;
- e. transferring, by diffusion, at least a portion of said imagewise distribution of said diffusible dye image-forming material to said image-receptive layer to provide a dye image to said layer in terms of said imagewise distribution; and
- f. reducing, subsequent to substantial transfer of said diffusible dye image-forming material to said image-receptive layer, the pH of said image-receptive layer at least one pH unit.

22. A process of forming transfer images in color as defined in claim 21 wherein said diffusion transfer process dye image-forming material is diffusible at a first

alkaline processing pH as a function of the photoexposure of said film unit and is substantially nondiffusible at a second pH at least one pH unit lower than said first pH and said neutral polymer is adapted to interact with said aqueous alkaline processing composition possessing said first pH to provide by hydrolysis acid in a concentration effective, subsequent to substantial dye transfer image formation, to reduce said processing composition in contact with said image-receptive layer to said second pH at which said dye image-forming material is substantially nondiffusible.

23. A process of forming transfer images in color as defined in claim 22 wherein said hydrolyzable polymer comprises an aqueous alkaline processing composition hydrolyzable polymeric ester.

24. A process of forming transfer images in color as defined in claim 23 wherein said hydrolyzable polymeric ester is a polycarboxylic acid ester.

25. A process of forming transfer images in color as defined in claim 24 wherein said polycarboxylic acid ester is cellulose acetate.

26. A process of forming transfer images in color as defined in claim 25 wherein said cellulose acetate comprises an acetate group substituent ratio 1.5 to 2.8 acetate groups per anhydroglucose unit.

27. A process of forming transfer images in color as defined in claim 26 wherein said mordant is poly-4-vinyl pyridine.

28. A process of forming transfer images in color as defined in claim 21 wherein said mordant is a basic mordant adapted to mordant an acid dyestuff.

29. A process of forming transfer images in color as defined in claim 21 wherein said dye image-providing material is a dye which is a silver halide developing agent.

30. A process of forming transfer images in color as defined in claim 21 wherein said photosensitive element comprises in contiguous relationship at least two selectively sensitized silver halide layers having associated therewith a dye image-providing material which is diffusible during processing as a function of the point-to-point degree of the photoexposure of its associated silver halide layer.

31. A process of forming transfer images in color as defined in claim 30 wherein said selectively sensitized silver layers possess predominant spectral sensitivity to separate regions of the visible spectrum and the dye image-providing material associated with each of said emulsion layers provides a dye possessing subsequent to processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion layer.

32. A process of forming transfer images in color as defined in claim 31 wherein said photosensitive element contains, as essential layers, in sequence, a support layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of said cyan, magenta and yellow dyes being a silver halide developing agent.

33. A process of forming transfer images in color as defined in claim 21 wherein said film unit possesses a rupturable container retaining said aqueous alkaline processing composition positioned extending transverse an edge of said film unit adapted to effect, upon

application of compressive pressure to said container, discharge of said container's processing contents into contact with said photosensitive silver halide layer, and including the step of applying compressive pressure to said container and discharging said container's processing composition contents into contact with said photosensitive layer.

34. A process of forming transfer images in color as defined in claim 33 wherein said aqueous alkaline processing composition includes an opacifying agent.

35. A process of forming transfer images in color as defined in claim 33 wherein said aqueous alkaline processing composition is discharged intermediate said photosensitive silver halide layer and said image-receptive layer.

36. A process of forming transfer images in color as defined in claim 33 wherein said film unit contains an aqueous alkaline processing composition permeable opaque layer disposed intermediate said photosensitive silver halide layer and said image-receptive layer.

37. A photographic diffusion transfer color process image-receiving element which comprises a dye image-receiving layer, adapted to receive diffusion transfer process dye image-forming material diffusing thereto, which is a substantially continuous polymeric layer consisting essentially of a synthetic neutral polymer, adapted to react with aqueous alkaline processing composition in contact with said layer to provide, as a function hydrolysis, acid in a concentration effective to reduce the alkalinity of said layer at least one pH unit, having associated therewith in said layer a mordant adapted to mordant diffusion transfer process dye image-forming material diffusing to the layer.

38. A photographic diffusion transfer color process image-receiving element as defined in claim 37 wherein said image-receiving layer is carried on a separate dimensionally stable support.

39. A photographic diffusion transfer color process image-receiving element as defined in claim 38 wherein said dimensionally stable support is substantially transparent with respect to visible light.

40. A photographic diffusion transfer color process image-receiving element as defined in claim 38 wherein at least the surface of the dimensionally stable support next adjacent the image-receiving layer is reflective with respect to visible light.

41. A photographic diffusion transfer color process image-receiving element as defined in claim 37 wherein said polymer is an aqueous alkaline processing composition hydrolyzable polymeric ester adapted to generate acid as a function of hydrolysis.

42. A photographic diffusion transfer color process image-receiving element as defined in claim 41 wherein said polymeric ester is a polycarboxylic acid ester.

43. A photographic diffusion transfer color process image-receiving element as defined in claim 42 wherein said polycarboxylic acid ester is cellulose acetate.

44. A photographic diffusion transfer color process image-receiving element as defined in claim 43 wherein said cellulose acetate contains an acetate ratio of 1.5 to 2.8 acetate groups per anhydroglucose unit.

45. A photographic diffusion transfer color process image-receiving element as defined in claim 44 wherein said cellulose acetate contains an acetate ratio of 2.3 acetate groups per anhydroglucose unit.

* * * * *

35

40

45

50

55

60

65