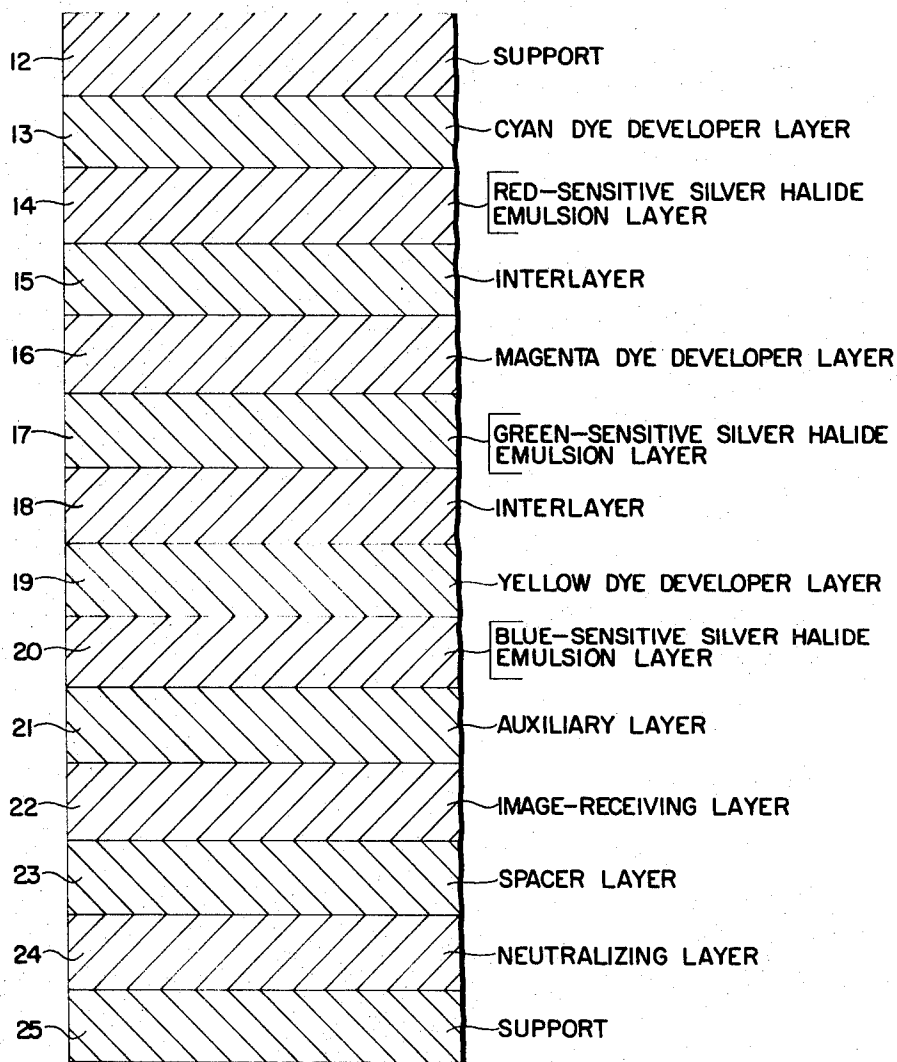


Sept. 4, 1973

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PHOTOGRAPHIC COLOR-DIFFUSION TRANSFER UNITS WHICH
UTILIZE NEUTRALIZING LAYER COMPRISING A
WATER-SOLUBLE POLYMERIC ACID AND
A WATER SOLUBLE BINDER
Filed July 22, 1971

3,756,815



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PHOTOGRAPHIC COLOR-DIFFUSION TRANSFER UNITS WHICH UTILIZE NEUTRALIZING LAYER COMPRISING A WATER-SOLUBLE POLYMERIC ACID AND A WATER SOLUBLE BINDER

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Filed July 22, 1971, Ser. No. 165,171

Int. Cl. G03c 1/04, 5/48, 5/54

U.S. Cl. 96—3

51 Claims

ABSTRACT OF THE DISCLOSURE

Film units for forming color transfer images including a negative component comprising at least one light-sensitive silver halide layer and an associated dye image-providing material and a positive component containing a dyeable stratum, which film units may be developed with an aqueous alkaline processing composition to provide the color transfer image, wherein the film unit further contains a neutralizing layer comprising a water-soluble polymeric acid and a water-soluble binder. The neutralizing layer is preferably associated with the positive component of the film unit.

BACKGROUND OF THE INVENTION

Various diffusion transfer systems for forming color images have heretofore been disclosed in the art. Generally speaking, such systems rely for color image formation upon a differential in mobility or solubility of a dye image-providing material obtained as a function of development so as to provide an imagewise distribution of such material which is more diffusible and which is therefore selectively transferred, at least in part, by diffusion, to a superposed dyeable stratum to impart thereto the desired color transfer image. The differential in mobility or solubility may for example be obtained by a chemical action such as a redox reaction or a coupling reaction.

The dye image-providing materials which may be employed in such processes generally may be characterized as either (1) initially soluble or diffusible in the processing composition but are selectively rendered non-diffusible in an imagewise pattern as a function of development; or (2) initially insoluble or non-diffusible in the processing composition but which are selectively rendered diffusible in an imagewise pattern as a function of development. These materials may be complete dyes or dye intermediates, e.g., color couplers.

As examples of initially soluble or diffusible materials and their application in color diffusion transfer, mention may be made of those disclosed, for example, in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 2,774,668; and 2,983,606. As examples of initially non-diffusible materials and their use in color transfer systems, mention may be made of the materials and systems disclosed in U.S. Pats. Nos. 3,443,939; 3,443,940; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294 and 3,445,228.

In any of these systems, multicolor images are obtained by employing a film unit containing at least two selectively sensitized silver halide layers each having associated therewith a dye image-providing material exhibiting desired spectral absorption characteristics. The most commonly employed elements of this type are the so-called

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tripack structures employing a blue-, a green- and a red-sensitive silver halide layer having associated therewith, respectively, a yellow, a magenta and a cyan dye image-providing material.

A particularly useful system for forming color images by diffusion transfer is that described in U.S. Pat. No. 2,983,606, employing dye developers (dyes which are also silver halide developing agents) as the dye image-providing materials. In such systems, a photosensitive element comprising at least one silver halide layer having a dye developer associated therewith (in the same or in an adjacent layer) is developed by applying an aqueous alkaline processing composition. Exposed and developable silver halide is developed by the dye developer which in turn becomes oxidized to provide an oxidation product which is appreciably less diffusible than the unreacted dye developer, thereby providing an imagewise distribution of diffusible dye developer in terms of unexposed areas of the silver halide layer, which imagewise distribution is then transferred, at least in part, by diffusion, to a dyeable stratum to impart thereto a positive dye transfer image. Multicolor images may be obtained with a photosensitive element having two or more selectively sensitized silver halide layers and associated dye developers, a tripack structure of the type described above and in various patents including the aforementioned U.S. Pat. No. 2,983,606 being especially suitable for accurate color recordation of the original subject matter.

In color diffusion transfer systems of the foregoing description, color images are obtained by exposing a photosensitive element or "negative component" comprising at least a light-sensitive layer, e.g., a gelatino silver halide emulsion layer, having a dye image-providing material associated therewith in the same or in an adjacent layer, to form a developable image; developing this exposed element with a processing composition to form an imagewise distribution of a soluble and diffusible image-providing material; and transferring this imagewise distribution, at least in part, by diffusion, to a superposed receiving element or "positive component" comprising at least a dyeable stratum to impart to this stratum a color transfer image. The negative and positive components may be separate elements which are brought together during processing and thereafter either retained together as the final print or separated following image formation; or they may together comprise a unitary structure, e.g., integral negative-positive film units wherein the negative and positive components are laminated and/or otherwise physically retained together at least prior to image formation.

The present invention is directed to the latter type of film units for forming color images by diffusion transfer, i.e., those film units containing a negative or photosensitive component and a positive or image-receiving component in the same structure, as distinguished from those color diffusion transfer systems wherein the photosensitive and image-receiving elements are separate structures adapted to be brought in superposition at some time after photoexposure, e.g., during processing. Generally, such film units comprise a plurality of essential layers including a negative component comprising at least one light-sensitive silver halide and associated dye image-providing material and a positive component comprising dyeable stratum. These components may be laminated together or otherwise secured together in physical juxtaposition as a single structure. Film units intended to provide multicolor images comprise two or more selectively sensitized silver

halide layers each having associated therewith an appropriate dye image-providing material exhibiting desired spectral absorption characteristics. As was heretofore mentioned the most commonly employed negative components for forming multicolor images are of the tripack structure containing a blue-, a green- and a red-sensitive silver halide layer having associated therewith in the same or in a contiguous layer a yellow, a magenta and a cyan dye image-providing material respectively. Interlayers or spacer layers may if desired be provided between the respective silver halide layers and associated dye image-providing materials.

Of particular interest are those integral negative-positive film units adapted for forming color transfer images viewable without separation, i.e., wherein the positive component containing the dye transfer image need not be separated from the negative component for viewing purposes. In addition to the aforementioned essential layers, such film units further include means for providing a reflecting layer between the dyeable stratum and the negative component in order to mask effectively the silver image or images formed as a function of development of the silver halide layer or layers and any remaining associated dye image-providing material and to provide a background for viewing the color image formed in the dyeable stratum, without separation, by reflected light. This reflecting layer may comprise a preformed layer of a reflecting agent included in the essential layers of the film unit or the reflecting agent may be provided after photoexposure, e.g., by including the reflecting agent in the processing composition. These essential layers are preferably contained on a transparent dimensionally stable layer or support member positioned closest to the dyeable stratum so that the resulting transfer image is viewable through this transparent layer. Most preferably another dimensionally stable layer which may be transparent or opaque is positioned on the opposed surface of the essential layers so that the aforementioned essential layers are sandwiched or confined between a pair of dimensionally stable layers or support members, at least one of each is transparent to permit viewing therethrough of a color transfer image obtained as a function of development of the exposed film unit in accordance with the known color diffusion transfer system such as will be detailed hereinafter. In a particularly preferred form such film units are employed in conjunction with a rupturable container of known description containing the requisite processing composition and adapted upon application of pressure of applying its contents to develop the exposed film unit, e.g., by applying the processing composition in a substantially uniform layer between the dyeable stratum and the negative component. It will be appreciated that the film unit may optionally contain other layers performing specific desired functions, e.g., spacer layers, pH-reducing layers, etc.

Opacifying means may be provided on either side of the negative component so that the film unit may be processed in the light to provide the desired color transfer image. In a particularly useful embodiment such opacifying means comprise an opaque dimensionally stable layer or support member positioned on the free or outer surface of the negative component, i.e., on the surface of the film unit opposed from the positive component containing the dyeable stratum to prevent photoexposure by actinic light incident thereon from this side of the film unit and an opacifying agent applied during development between the dyeable stratum and the negative component, e.g., by including the opacifying agent in a developing composition so applied, in order to prevent further exposure (fogging) by actinic light incident thereon from the other side of the film unit when the thus exposed film unit is developed in the light. The last-mentioned opacifying agent may comprise the aforementioned reflecting agent which masks the negative component and provides the requisite background for viewing the transfer image formed thereover.

Where this reflecting agent does not by itself provide the requisite opacity it may be employed in combination with an additional opacifying agent in order to prevent further exposure of the light-sensitive silver halide layer or layers by actinic light incident thereon.

As examples of such integral negative-positive film units for preparing color transfer images viewable without separation as reflection prints, mention may be made of those described and claimed in U.S. Pats. Nos. 3,415,644, 3,415,645, 3,415,646 and 3,473,925; as well as those described in copending applications Ser. Nos. 782,056 and 782,075, filed Dec. 9, 1969, 65,084, filed Aug. 19, 1970, all in the name of Edwin H. Land; and Ser. Nos. 39,646 and 39,666 of Howard G. Rogers, filed May 22, 1970, these applications having issued, respectively, as U.S. Pats. Nos. 3,573,043; 3,573,044; 3,672,890; 3,594,165; and 3,594,164.

In general, the film units of the foregoing description, e.g., those described in the aforementioned patents and/or copending applications, are exposed to form a developable image and thereafter developed by applying the appropriate processing composition to develop exposed silver halide and to form, as a function of development, an imagewise distribution of diffusible dye image-providing material which is transferred, at least in part by diffusion, to the dyeable stratum to impart thereto the desired color transfer image, e.g., a positive color transfer image. Common to all of these systems is the provision of a reflecting layer between the dyeable stratum and the photosensitive strata to mask effectively the latter and to provide a background for viewing the color image contained in the dyeable stratum, whereby this image is viewable without separation, from the other layers or elements of the film unit. In certain of these systems, this reflecting layer is provided prior to photo-exposure, e.g., as a preformed layer included in the essential layers of the laminar structure comprising the film unit, and in others it is provided at some time thereafter, e.g., by including a suitable light-reflecting agent, for example, a white pigment such as titanium dioxide, in the processing composition which is applied between the dyeable stratum and the next adjacent layer to develop the latent image and to form the color transfer image.

The dye image-providing materials which may be employed in such processes generally are selected from those materials heretofore mentioned and disclosed in the illustrative patents which were initially soluble or diffusible in the processing composition but which are selectively rendered non-diffusible as a function of development or those which are initially insoluble or non-diffusible in the processing composition but are selectively rendered diffusible as a function of development. These materials may be complete dyes or dye intermediates, e.g., color couplers.

A preferred opacification system to be contained in the processing composition is that described in the copending application of Edwin H. Land, Ser. No. 43,782, filed June 5, 1970, now abandoned, and Ser. No. 101,968, filed Dec. 28, 1970, and now U.S. Pat. No. 3,647,437, comprising an inorganic reflecting pigment dispersion containing at least one optical filter agent at a pH above the pKa of the optical filter agent in a concentration effective, when the processing composition is applied, to provide a layer exhibiting optical transmission density > than about 6.0 density units with respect to incident radiation actinic to the photosensitive silver halide layer and optical reflection density < than about 1.0 density with respect to incident visible radiation.

In lieu of having the reflecting pigment contained in the processing composition, e.g., as disclosed in the aforementioned copending application Ser. No. 43,782, and U.S. Pat. No. 3,647,437 the reflecting pigment needed to mask the photosensitive strata and to provide the requisite background for viewing the color transfer image formed in the receiving layer may be contained initially in whole or in part as a preformed layer in the film unit. As an

example of such a preformed layer, mention may be made of that disclosed on the copending applications of Edwin H. Land, Ser. Nos. 846,441, filed July 31, 1969, and 3,645, filed Jan. 19, 1970, now U.S. Pats. Nos. 3,615,421 and 3,620,724, respectively. The reflecting pigment may be generated in situ as is disclosed in the copending applications of Edwin H. Land, Ser. Nos. 43,741 and 43,742, both filed June 5, 1970, now U.S. Pats. Nos. 3,647,434 and 3,647,435, respectively.

These film units may, and usually do, further contain pH modulating or adjusting means, e.g., a layer or layers containing a reagent for adjusting the pH following substantial transfer image formation. In those systems employing an aqueous alkaline processing composition, such film units may contain a neutralizing layer or layers, e.g., a polymeric acid layer of the type described, for example, in U.S. Pat. No. 3,362,819. It is also known to employ a spacer layer in conjunction with the neutralizing layer in order to "time" control the pH adjustment by the neutralizing layer. Spacer layers of this description are disclosed, for example, in the aforementioned U.S. Pat. No. 3,362,819, as well as in other patents, e.g., U.S. Pats. Nos. 3,455,686; 3,433,633; 3,421,893; 3,419,389; etc. The neutralizing and spaced layers are preferably contained in the positive component, e.g., as layers disposed on the side of the dyeable stratum opposed from the negative component. However, they may be disposed in the negative component, as is described and claimed in U.S. Pat. No. 3,573,043.

Preferred positive components employed in film units of the foregoing description comprise a transparent support or dimensionally stable layer carrying an acid neutralizing layer, a timing or spacer layer and a dyeable stratum or image-receiving layer. The positive component may also contain additional layers performing specific desired functions.

BRIEF DESCRIPTION OF DRAWING

The figure is an enlarged, fragmentary, diagrammatic, sectional view of a film unit contemplated by this invention.

SUMMARY OF THE INVENTION

In accordance with the present invention, film units of the foregoing description are constructed to contain pH-modulating means comprising a layer containing a water-soluble polymeric acid, as defined hereinafter, and a water-soluble matrix or binder material. This layer, which is preferably disposed in the positive component, may also contain other ingredients performing specific desired functions.

DESCRIPTION OF PREFERRED EMBODIMENT

In the preferred embodiment, the film unit is a so-called tripack employing dye developers as the dye image-providing materials and the positive component includes the aforementioned neutralizing layer in addition to the dyeable stratum.

As was mentioned previously, the present invention relates to diffusion transfer systems for preparing color images utilizing a film unit containing a positive component and a negative component, which components may be laminated or otherwise retained in juxtaposition as an integral negative-positive film unit.

A primary object of this invention, therefore, is to provide novel film units of the foregoing description.

Another object of this invention is to provide novel systems for forming a color transfer image in a stratum wherein the image is viewable, by reflected light, without separation of the stratum containing this image.

Still another object is to provide novel positive components for use in preparing such film units and in photographic systems employing the same.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

As has been stated, the present invention is directed to those film units employing a positive component and a negative component for forming color images by diffusion transfer, and, in particular, to integral negative-positive film units for forming color images viewable without separation of the positive component containing the color transfer image from the negative component.

Film units of this general description have been previously described and will be further understood by reference to the illustrative film unit of the drawing as described in detail hereinafter.

As shown in the drawing, such a film unit may comprise, as the essential layers, a layer 13 of cyan dye developer, red-sensitive silver halide emulsion layer 14, interlayer 15, a layer of magenta dye developer 16, green-sensitive silver halide emulsion layer 17, interlayer 18, yellow dye developer layer 19, blue-sensitive silver halide emulsion layer 20, auxiliary layer 21, image receiving layer or dyeable stratum 22, spacer layer 23, and a pH-reducing or neutralizing layer 24. Layers 13-21 comprise the negative component and layers 22-24 comprise the positive component. These essential layers are shown to be confined between a dimensionally stable layer or support member 12 which is preferably opaque so as to permit development in the light and dimensionally stable layer or support member 25 which is effectively transparent to permit viewing of a color transfer image formed as a function of development in receiving layer or dyeable stratum 22.

Layers 12 and 25 are preferably dimensionally stable liquid-impermeable layers which when taken together may possess a processing composition solvent vapor permeably sufficient to effect, subsequent to substantial transfer image formation and prior to any substantial environmental image degradation to which the resulting image may be prone, osmotic transpiration of processing composition solvent in a quantity effective to decrease the solvent from a first concentration at which the color-providing material is diffusible to a second concentration at which it is not. Although these layers may possess a vapor transmission rate of 1 or less gms./24 hrs./100 in.²/mil., they preferably possess a vapor transmission rate for the 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 advantageously 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. As examples of useful materials of this nature, mention may be made of those having the aforementioned characteristics and which are derived from ethylene glycol terephthalic acid; vinyl chloride polymers; polyvinyl acetate; cellulose derivatives, etc. As heretofore noted layer 12 is of sufficient opacity to prevent fogging from occurring by light passing therethrough, and layer 26 is transparent to permit photoexposure and for viewing of a transfer image formed on receiving layer 23.

The silver halide layers preferably comprise photosensitive silver halide, e.g., silver chloride, bromide or iodide or mixed silver halides such as silver iodobromide or chloriodobromide dispersed in a suitable colloidal binder such as gelatin and such layers may typically be on the order of 0.6 to 6 microns in thickness. It will be appreciated

that the silver halide layers may and in fact generally do contain other adjuncts, e.g., chemical sensitizers such as are disclosed in 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, etc.; as well as other additives performing specific desired functions, e.g., coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, ultraviolet absorbers and/or speed-increasing compounds. While the preferred binder for the silver halide is gelatin, others such as albumin, casein, zein, resins such as cellulose derivatives, polyacrylamides, vinyl polymers, etc., may replace the gelatin in whole or in part.

The respective dye developers, which may be any of those heretofore known in the art and disclosed for example in U.S. Pat. No. 2,983,606, etc., are preferably dispersed in an aqueous alkaline permeable polymeric binder, e.g., gelatin as a layer from about 1 to 7 microns in thickness.

Interlayers 15, 18 and 21 may comprise an alkaline permeable polymeric material such as gelatin and may be on the order of from about 1 to 5 microns in thickness. As examples of other materials for forming these interlayers, mention may be made of those disclosed in U.S. Pat. No. 3,421,892 and the copending applications of Richard J. Haberlin, Ser. No. 854,491, filed Sept. 2, 1969, and Lloyd D. Taylor, Ser. No. 790,648, filed Jan. 13, 1969, now U.S. Pat. Nos. 3,615,422 and 3,575,700, respectively, etc. These interlayers may also contain additional reagents performing specific functions and the various ingredients necessary for development may also be contained initially in such layers in lieu of being present initially in the processing composition, in which event the desired developing composition is obtained by contacting such layers with the solvent for forming the processing composition, which solvent may include the other necessary ingredients dissolved therein.

The image-receiving layer may be on the order of 0.25 to 0.4 mil. in thickness. Typical materials heretofore employed for this layer include dyeable polymers such as nylon, e.g., N-methoxymethyl poly-hexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, etc. Such receiving layers may, if desired, contain suitable mordants, e.g., any of the conventional mordant materials for acid dyes such as those disclosed, for example, in the aforementioned U.S. Pat. No. 3,227,550; as well as other additives such as ultraviolet absorbers, pH-reducing substances, etc. It may also contain specific reagents performing desired functions, e.g., a development restrainer, as disclosed, for example, in U.S. Pat. No. 3,265,498.

The spacer or timing layer may be on the order of 0.1 to 0.7 mil thick. Materials heretofore used for this purpose include polymers which exhibit inverse temperature-dependent permeability to alkali, e.g., as disclosed in U.S. Pat. No. 3,445,686. Materials previously employed for this layer include polyvinyl alcohol, cyanoethylated polyvinyl alcohol, hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral and partial polyvinyl propional, polyvinyl amides such as polyacrylamide, etc.

The neutralizing layer may be on the order of 0.3 to 1.5 mil in thickness. Materials used heretofore in the preparation of this layer include the polymeric acids disclosed in U.S. Pat. No. 3,362,819, e.g., dibasic acid half-ester derivatives of cellulose, which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether

and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether maleic anhydride copolymers; etc.

In accordance with the present invention, the acid neutralizing layer of the aforementioned film units, e.g., layer 24 of the illustrative film unit, comprises a mixture of a water-soluble polymeric acid and a water-soluble matrix or binder material. As used herein, "polymeric acid" is intended to mean polymers which contain acid groups, e.g., carboxylic acid and/or sulfonic acid groups, which are capable of forming salts with alkali metals or with organic bases; or potentially acid-yielding groups, e.g., anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them.

As examples of useful binders or matrices for forming the neutralizing layer, mention may be made of polymeric materials such as polyvinyl alcohol, partially hydrolyzed polyvinyl acetates, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, polymethylvinyl ether, etc.

As examples of useful water-soluble polymeric acids, mention may be made of ethylene/maleic anhydride copolymers, poly-(methyl vinyl ether/maleic anhydride), e.g., those commercially available from General Aniline and Film Corporation under the trade names "Gantrez AN-119," "Gantrez AN-139" or "Gantrez AN-169," water-soluble polyacrylic acids, polymethacrylic acids, and copolymers of styrene and maleic acid, etc.

The ratio of acid to binder in the novel neutralizing layers of this invention may vary from about 9:1 to about 1:1. A preferred ratio of acid to binder is on the order of from about 3:1 to about 2:1.

As was heretofore mentioned, the present invention encompasses film units such as those described previously and shown in the illustrative drawing wherein the negative component is exposed through the positive component containing the neutralizing layer. The resulting transfer image is also viewed by light reflected through this layer. In order to minimize distortion and/or to obtain the most optimum resolution as well as clarity in viewing, the neutralizing layer should be as thin and as clear as possible. Thus, while it has been stated previously that the neutralizing layers of the prior art may be on the order of 0.3 to 1.5 mils thick, the neutralizing layers employed in such film units should most ideally be no thicker than about 0.4 mil. Particularly useful neutralizing layers containing the aforementioned acid to binder ratios are obtained by applying the layer as an aqueous coating so as to contain on the order of from about 550 mgs. of acid to about 900 mgs. of acid per square foot of surface area. Lesser amounts of acid in general do not provide the requisite neutralizing capacity; whereas greater amounts of acid generally are not necessary and accordingly should be avoided since these greater amounts would make the neutralizing layer unnecessarily thicker.

In addition to the acid and binder, the neutralizing layer may contain other adjuvants performing specific desired photographic and/or chemical functions. It may, for example, contain a hydrogen bonding inhibitor (e.g., alcohols such as methanol, ethanol, isopropanol, phenol, etc., with alcohols such as isopropanol having a high flash point being most preferred) for maintaining the coating solution at a constant viscosity; cross-linking agents (e.g., formaldehyde, glyoxal, chromium or aluminum nitrate, etc.) to inhibit migration of the salts formed by neutralization and the resulting weakening of the laminar structure or lack of adhesion in the final print.

The neutralizing layer is obtained simply by applying

an aqueous solution of the desired ingredients, e.g., an aqueous solution containing on the order of from about 5-20% by volume of acid and binder by known and conventional coating techniques, e.g., by applying this solution to dimensionally stable layer 25 of the illustrative film unit and then drying to form neutralizing layer 24.

The use of the present aqueous neutralizing layer system employing water-soluble ingredients affords many distinct advantages over the prior solvent systems employing water-insoluble components coated from an organic solvent. One such significant advantage in the preparation of the contemplated film units is that it permits the use of shorter acid molecules with lower equivalent weights, which in turn permits one to employ thinner coatings. As was previously mentioned, the use of thinner coatings provides greater clarity in viewing of the image. In addition, there is evidence indicating unexpectedly that the present aqueous coating system affords greater adhesion of the neutralizing layer to the dimensionally stable layer to which it is applied.

The preferred polymeric binder material comprises partially hydrolyzed polyvinyl acetate. The polyvinyl alcohols of commerce are generally obtained by hydrolyzing polyvinyl acetate and at most contain about 98.2 to about 99% polyvinyl alcohol, the remaining percentage comprising essentially polyvinyl acetate which has not been hydrolyzed to polyvinyl alcohol. Polyvinyl alcohols of lower hydrolysis rates, e.g., as low as 75%, are also available. As used herein, the term "partially hydrolyzed polyvinyl acetate" is intended to exclude the polyvinyl alcohols of commerce which are substantially only polyvinyl alcohol, containing on the order of about 1% polyvinyl acetate, and are thus regarded by those skilled in the art simply as being polyvinyl alcohol. Most preferred are those partially hydrolyzed polyvinyl acetates having a hydrolysis rate of from about 85 to about 92%, i.e., which are about 85-92% polyvinyl alcohol.

These partially hydrolyzed polyvinyl acetates afford certain advantages over the polyvinyl alcohols of commerce which, as noted above, are substantially pure polyvinyl alcohol. With polyvinyl alcohol, e.g., the polyvinyl alcohols of commerce as noted above, it was found that the film unit had a tendency to curl. This curl problem was most evident prior to use, making subsequent processing of the film unit for image formation very difficult. The curl problem was also manifested in the finished print, which of course is undesirable from an aesthetic standpoint. In other words, for optimum functional performance during application of the processing fluid, the film should remain as flat as possible; whereas for optimum physical appearance following image formation, the print should likewise remain flat and not curl. It was further found that when certain of the film units containing a polyvinyl alcohol binder-containing neutralizing layer applied to a transparent dimensionally stable support layer (e.g., layers 24 and 25 of the illustrative film unit) were stored in a hot atmosphere (five days at 100° F.), it was found that the neutralizing layer tended to separate or lift off the base material after processing.

These problems have been obviated by use of the aforementioned partially hydrolyzed polyvinyl acetates, the preferred binder materials of this invention.

An illustrative aqueous coating solution for preparing the neutralizing layers of this invention may comprise:

Ethylene/maleic anhydride	g--	70.0
88-90% hydrolyzed polyvinyl acetate	g--	30.0
Formaldehyde	g--	0.6
Isopropanol	cc--	10.0

dissolved in water to provide a solution containing on the order of 14% by volume of acid and binder.

A film unit similar to that shown in the drawing may be prepared, for example, by coating, in succession, on

a gelatin subbed, 4 mil opaque polyethylene terephthalate film base, the following layers:

(1) A layer of cyan dye developer dispersed in gelatin and coated at a coverage of about 80 mgs./ft.² of dye and about 100 mgs./ft.² of gelatin;

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 225 mgs./ft.² of silver and about 50 mgs./ft.² of gelatin;

(3) A layer of acrylic latex sold by Rohm and Haas Co. under the trade designation AC-61 and polyacrylamide coated with a coverage of about 100 mgs./ft.² of AC-61 and about 5 mgs./ft.² of polyacrylamide;

(4) A layer of magenta dye developer dispersed in gelatin and coated at a coverage of 70 mgs./ft.² of dye and about 120 mgs./ft.² of gelatin;

(5) A green-sensitive gelatino-silver iodobromide emulsion coated in a coverage of about 120 mgs./ft.² of silver and 60 mgs./ft.² of gelatin;

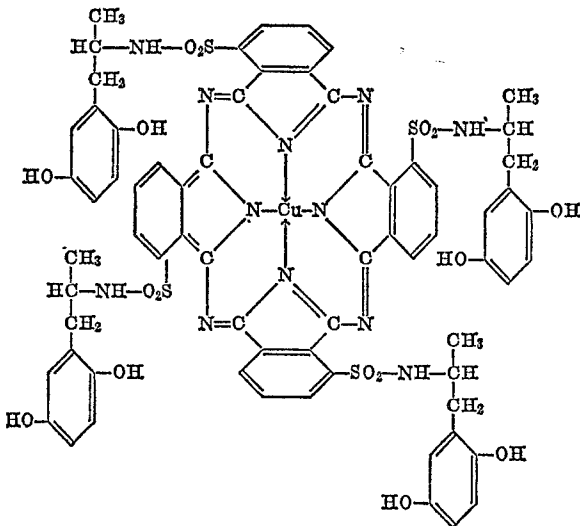
(6) A layer comprising the acrylic latex sold by Rohm and Haas Co. under the trade designation B-15 and polyacrylamide coated in a coverage of about 100 mgs./ft.² of B-15 and about 10 mgs./ft.² of polyacrylamide;

(7) A layer of a yellow dye developer and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 50 mgs./ft.² of dye, about 15 mgs./ft.² of auxiliary developer and 50 mgs./ft.² of gelatin;

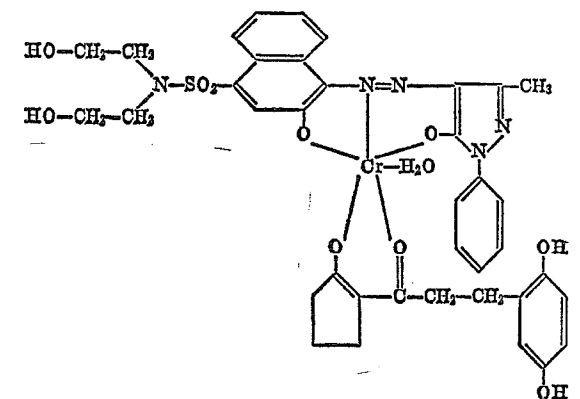
(8) A blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 75 mgs./ft.² of gelatin; and

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

The three dye developers employed above may be the following:

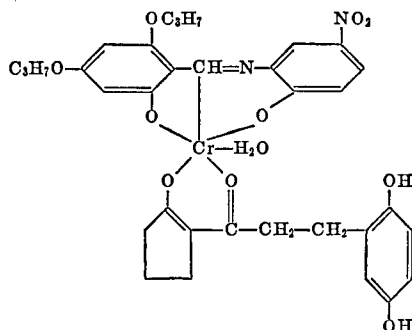


a cyan dye developer;



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a magenta dye developer; and



a yellow dye developer.

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

(1) the aforementioned illustrative aqueous coating solution to provide a polymeric acid neutralizing layer containing a 7:3 mixture, by weight, of polyethylene/maleic anhydride copolymer and 88-90% hydrolyzed polyvinyl acetate at a coverage of about 1000 mgs./ft.²;

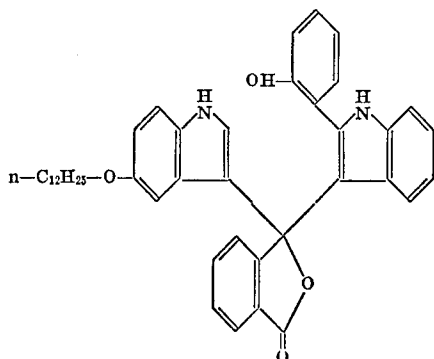
(2) a graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mgs./ft.², to provide a polymeric spacer or timing layer; and

(3) a 2:1 mixture, by weight, of polyvinyl alcohol and poly - 4 - vinylpyridine, at a coverage of about 900 mgs./ft.² and including about 20 mgs./ft.² of 1-phenyl-5-mercaptotetrazole, to provide a polymeric image-receiving layer containing development restrainer.

The two components may then be laminated together to provide an integral film unit of the type shown in the drawing.

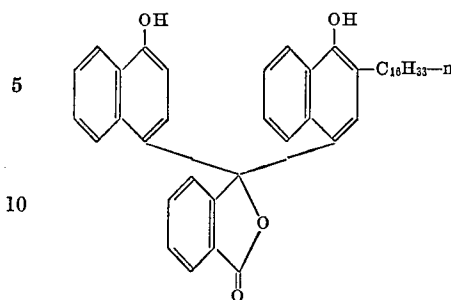
A rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising the following proportions of ingredients:

Water.....	100 cc.
Potassium hydroxide.....	11.2 gms.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250].....	3.4 gms.
N-phenyl- α -picolinium bromide.....	2.7 gms.
Benzotriazole.....	1.15 gms.
Titanium dioxide.....	50.0 gms.
(A).....	2.08 gms.

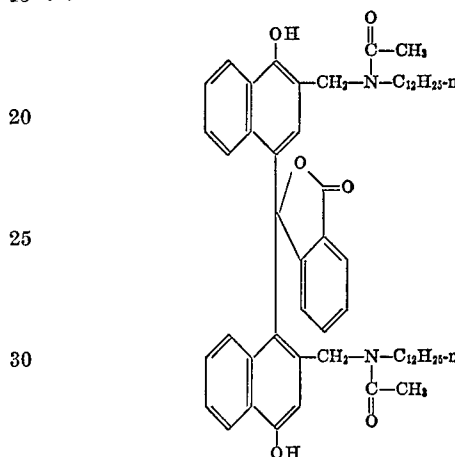


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(B)..... 0.52 gms.



15 (C)..... 1.18 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 dyeable stratum and the next adjacent layer of the negative component.

While in the preferred film units contemplated by this invention the neutralizing layer is contained in the positive component, e.g., on the side of the dyeable stratum opposed, or adapted to be opposed, from the negative component, the neutralizing layer may, as heretofore mentioned, be disposed in the negative component.

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

What is claimed is:

1. In a film unit for forming color transfer images including a negative component comprising at least one light-sensitive silver halide layer and an associated dye image-providing material and a positive component containing a dyeable stratum, said film unit further containing a neutralizing layer in said positive or negative components for lowering the pH of an alkaline processing composition applied to develop said negative component and to form said transfer image after substantial transfer image formation;

the improvement which comprises employing as said neutralizing layer a layer comprising a water-soluble polymeric acid and a water-soluble binder.

2. A film unit as defined in claim 1 wherein said neutralizing layer is disposed in said positive component.

3. A film unit as defined in claim 1 including means for applying an aqueous alkaline processing composition between said negative and positive components.

4. A film unit as defined in claim 3 including means for applying a layer of a light-reflecting agent between

said positive and negative components, said layer of light-reflecting agent being adapted for effectively masking said negative component and for providing a background for viewing a color transfer image formed in said dyeable stratum, without separation, as a reflection print.

5 5. A film unit as defined in claim 4 wherein said light-reflecting means comprises a preformed layer disposed in said film unit between said dyeable stratum and said negative component.

6. A film unit as defined in claim 4 wherein said light-reflecting means is applied in a layer between said negative component and said dyeable stratum at some time following photoexposure of said film unit.

7. A film unit as defined in claim 1 wherein said dye image-providing material is a dye or dye intermediate which is insoluble and non-diffusible in an aqueous alkaline medium.

8. A film unit as defined in claim 1 wherein said dye image-providing material is soluble and diffusible in an aqueous alkaline medium.

9. A film unit as defined in claim 1 wherein the ratio of acid to binder in said neutralizing layer being from about 9:1 to about 1:1.

10. A film unit as defined in claim 9 wherein said neutralizing layer is no thicker than about 0.4 mil.

11. A film unit as defined in claim 10 wherein said neutralizing layer contains from about 550 to about 900 mgs. of said acid per square foot of surface area.

12. A film unit as defined in claim 1 wherein said binder comprises a mixture of polyvinyl alcohol and polyvinyl acetate.

13. A film unit as defined in claim 12 wherein said mixtures consists essentially of partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of below about 92%.

14. A film unit as defined in claim 1 wherein the aqueous solution employed to provide said neutralizing layer includes a reagent for maintaining said solution at a constant viscosity.

15. A film unit as defined in claim 1 wherein the aqueous solution employed to provide said neutralizing layer includes a cross-linking agent.

16. An image-receiving element for use in preparing color transfer images and which may be employed as the positive component in film units including a negative component comprising at least one light-sensitive silver halide layer and an associated dye image-providing material to form said transfer image which may be viewed without separation of said components, said image-receiving element comprising a support carrying, on one side thereof, in order, a neutralizing layer comprising a water-soluble polymeric acid and a water-soluble binder; and a dyeable stratum.

17. An element as defined in claim 16 wherein said support is transparent.

18. An element as defined in claim 17 including a spacer layer positioned between said dyeable stratum and said neutralizing layer.

19. An element as defined in claim 16 wherein said binder comprises a mixture of polyvinyl acetate and polyvinyl alcohol, the ratio of acid to binder being from about 9:1 to about 1:1.

20. An element as defined in claim 19 wherein said neutralizing layer is no thicker than about 0.4 mil, and said acid is present at a coverage of from about 550 to about 900 mgs. of acid per square foot of surface area.

21. An element as defined in claim 20 wherein said binder comprises partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of from about 85 to about 92%.

22. In a film unit for forming color transfer images including a negative component comprising a red-sensitive silver halide layer having a cyan dye image-providing material associated therewith, a green-sensitive silver halide

layer having a magenta dye image-providing material associated therewith, and a blue-sensitive silver halide layer having a yellow dye image-providing material associated therewith; a positive component including a dyeable stratum; a polymeric acid layer; and means for applying a layer of a light-reflecting agent between said positive and negative components, said layer of light-reflecting agent being adapted for effectively masking said negative component and for providing a background for viewing a color transfer image formed in said dyeable stratum, without separation, as a reflection print;

the improvement which comprises employing as said neutralizing layer, a layer comprising a water-soluble polymeric acid and a water-soluble binder.

23. A film unit as defined in claim 22 wherein said neutralizing layer is no thicker than about 0.4 mil.

24. A film unit as defined in claim 22 wherein said components are contained on a transparent support.

25. A film unit as defined in claim 24 wherein said support is positioned closest to said positive component.

26. A film unit as defined in claim 25 wherein said neutralizing layer is positioned between said dyeable stratum and said support.

27. A film unit as defined in claim 25 wherein said means for applying said layer of light-reflecting pigment comprises a preformed layer of a white pigment positioned between said dyeable stratum and said negative component.

28. A film unit as defined in claim 27 including a quantity of an aqueous alkaline processing composition adapted for spreading on the surface of said film unit.

29. A film unit as defined in claim 22 wherein said components are confined between a pair of supports, at least the support closest to the positive component being transparent to permit viewing therethrough of a color transfer image imparted to said dyeable stratum as a function of exposure and development of said film unit.

30. A film unit as defined in claim 29 wherein said other support is opaque and said means for applying said layer of light-reflecting pigment comprises a liquid reagent including a white reflecting pigment adapted for spreading in a substantially uniform layer between said dyeable stratum and said negative component.

31. A film unit as defined in claim 22 wherein the aqueous solution employed to prepare said neutralizing layer includes a hydrogen bonding inhibitor and a cross-linking agent.

32. A film unit as defined in claim 31 wherein said hydrogen bonding inhibitor is isopropanol and said cross-linking agent is formaldehyde.

33. In a photographic film unit comprising a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer, an alkaline solution permeable polymeric layer containing a cyan dye image-providing material, a red-sensitive silver halide emulsion layer, an alkaline solution permeable polymeric layer containing a magenta dye image-providing material, a green-sensitive silver halide emulsion layer, an alkaline solution permeable polymeric layer containing a yellow dye image-providing material, a blue-sensitive silver halide emulsion layer, said dye image-providing materials being capable of forming, as a function of development of said photosensitive element with an aqueous alkaline processing composition an imagewise distribution of dyes which are soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable polymeric layer dyeable by said dyes, an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of processing solution having said first pH to a second pH at which said imagewise distribution of dyes is substantially insoluble and non-diffusible, a dimensionally stable alkaline solution impermeable transparent layer, and means for applying between said blue-sensitive silver halide emulsion

and said dyeable polymeric layer an aqueous alkaline processing composition having said first pH and containing dispersed therein a white light-reflecting agent;

the improvement wherein said polymeric acid layer comprises a layer containing a water-soluble polymeric acid and a water-soluble binder, the ratio of acid to binder in said layer being from about 9:1 to about 1:1, said acid being present in amount from about 550 to about 900 mgs./ft.² of surface area.

34. A film unit as defined in claim 33 wherein said binder consists essentially of partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of below about 92%.

35. A film unit as defined in claim 33 including an alkaline solution permeable polymeric spacer layer positioned between said dyeable polymeric layer and said polymeric acid layer.

36. A film unit as defined in claim 35 wherein each of said dye image-providing materials is a dye developer.

37. In a photographic film unit comprising, in combination, a photosensitive element including a composite structure containing, as essential layers, in sequence, a blue-sensitive silver halide emulsion layer, an alkaline solution permeable polymeric layer containing a yellow dye image-providing material, a green-sensitive silver halide emulsion layer, an alkaline solution permeable polymeric layer containing a magenta dye image-providing material, a red-sensitive silver halide emulsion layer, an alkaline solution permeable polymeric layer containing a cyan dye image-providing material, each of said dye image-providing materials being soluble and diffusible, in alkali, at a first pH, as a function of development of said photosensitive element, an alkaline solution permeable layer of a white reflecting agent, an alkaline solution permeable polymeric layer dyeable by said dyes, an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of processing solution having said first pH to a second pH at which said imagewise distribution of dyes is substantially insoluble and non-diffusible, and a dimensionally stable alkaline solution-impermeable transparent layer; a spreader sheet disposed in superposition with the surface of said photosensitive element opposed from said transparent layer and means for applying an aqueous alkaline processing composition having said first pH between said spreader sheet and said photosensitive element;

the improvement wherein said polymeric acid layer comprises a layer containing a water-soluble polymeric acid and a water-soluble binder, the ratio of acid to binder in said layer being from about 9:1 to about 1:1, said acid being present in amount from about 550 to about 900 mgs./ft.² of surface area.

38. A film unit as defined in claim 37 wherein said binder consists essentially of partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of below about 92%.

39. A film unit as defined in claim 37 including an alkaline solution permeable polymeric spacer layer positioned between said dyeable polymeric layer and said polymeric acid layer.

40. A film unit as defined in claim 37 wherein each of said dye image-providing materials is a dye developer.

41. A film unit as defined in claim 37 wherein each of said dye image-providing materials is a dye or dye intermediate which is insoluble and non-diffusible in an aqueous alkaline medium.

42. A process for forming a color transfer image com-

prising the steps of exposing a film unit as defined in claim 1 to form a developable image; and thereafter applying an aqueous alkaline processing composition to develop said image and to form said color transfer image.

43. A process as defined in claim 42 wherein said film unit includes a layer of a light-reflecting agent disposed between said dyeable stratum and said negative component, said agent being present in a quantity sufficient to mask effectively said negative component and to provide a background for viewing said color transfer image as a reflection print.

44. A process as defined in claim 42 wherein said processing composition is applied in a layer between said negative component and said dyeable stratum and said composition includes a light-reflecting agent in a quantity sufficient to mask effectively said negative component and to provide a background for viewing said color transfer image as a reflection print.

45. A process as defined in claim 42 wherein said dye image-providing material is a dye developer.

46. A process as defined in claim 42 wherein said dye image-providing material is a dye or dye intermediate which is insoluble and non-diffusible in said aqueous alkaline composition.

47. A process as defined in claim 42 wherein said binder comprises a mixture of polyvinyl alcohol and polyvinyl acetate.

48. A process for forming a color transfer image comprising the steps of exposing a film unit as defined in claim 29 to form a developable image; and applying said processing composition between said blue-sensitive silver halide emulsion and said dyeable polymeric layer to form a color-transfer image in said dyeable polymeric layer, said color image being viewable by reflected light through said transparent layer.

49. A process as defined in claim 48 wherein said binder consists essentially of partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of below about 92%.

50. A process for forming a color transfer image comprising the steps of exposing a film unit as defined in claim 33 to form a developable image; and applying said aqueous alkaline processing composition between said spreader sheet and said photosensitive element to form a color transfer image in said dyeable layer, said color image being viewable by reflected light through said transparent layer.

51. A process as defined in claim 48 wherein said binder consists essentially of partially hydrolyzed polyvinyl acetate having a hydrolysis rate to polyvinyl alcohol of below about 92%.

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U.S. Cl. X.R.

96—29 D, 77—84 R