May 22, 1973 T. W. MILLIGAN 3,734,727

PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Oct. 28, 1971 4 Sheets-Sheet 1

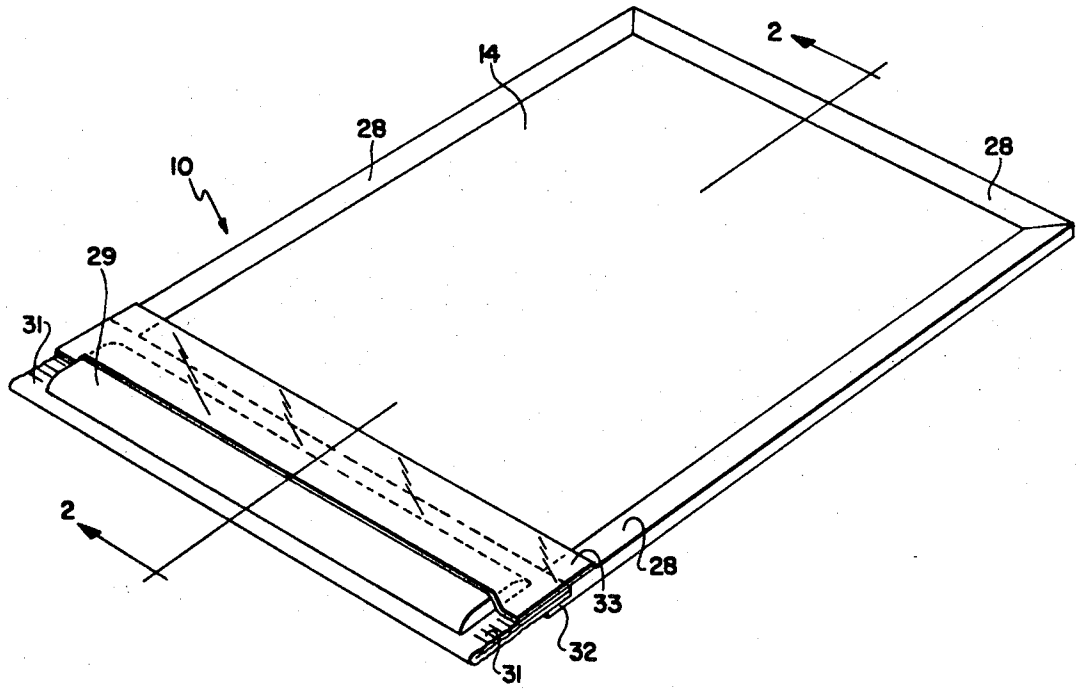

FIG. 1

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PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Oct. 28, 1971 4 Sheets-Sheet 2

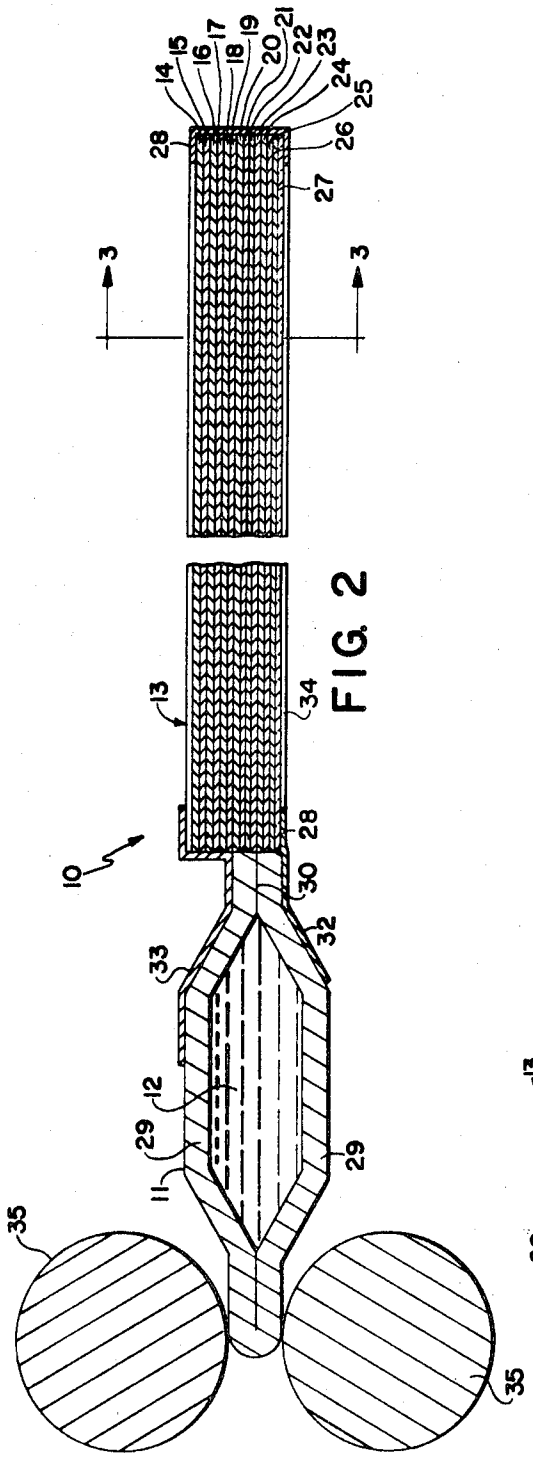

FIG. 2

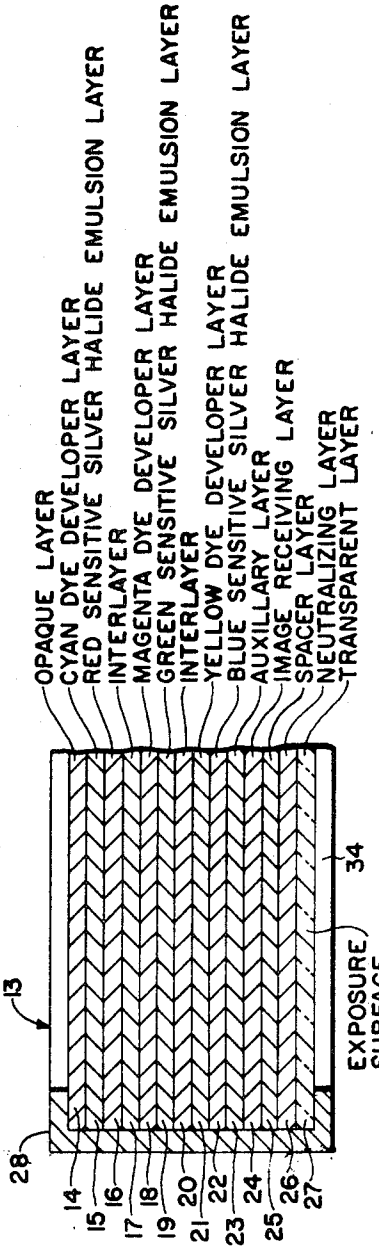

FIG. 3

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PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Oct. 28, 1971 4 Sheets-Sheet 3

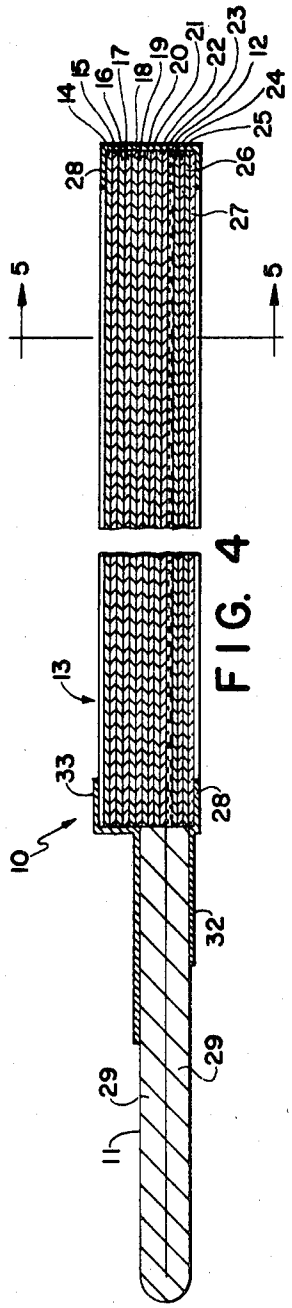

FIG. 4

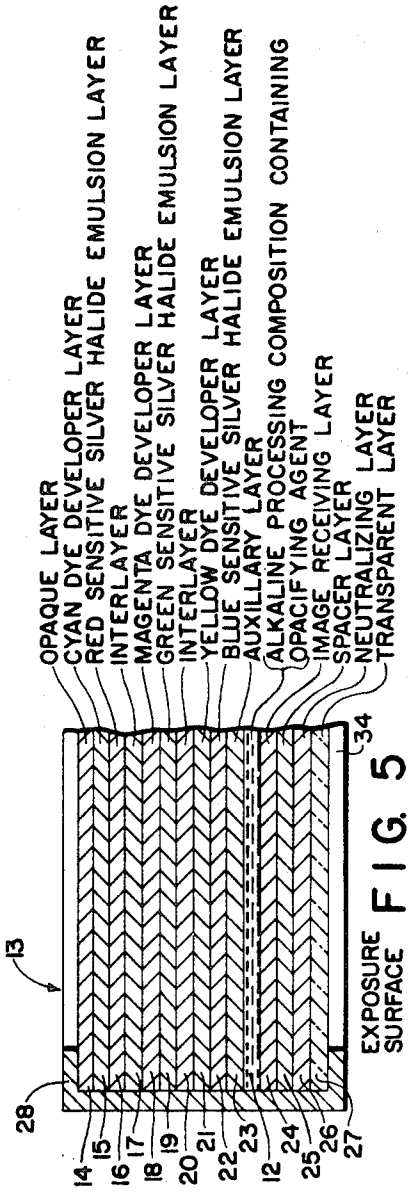

FIG. 5

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PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Oct. 28, 1971 4 Sheets-Sheet 4

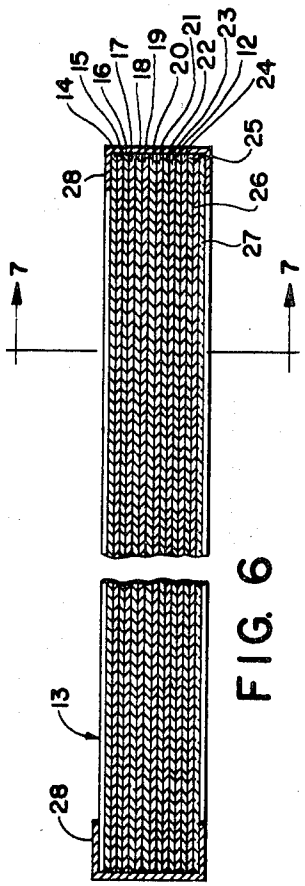

FIG. 6

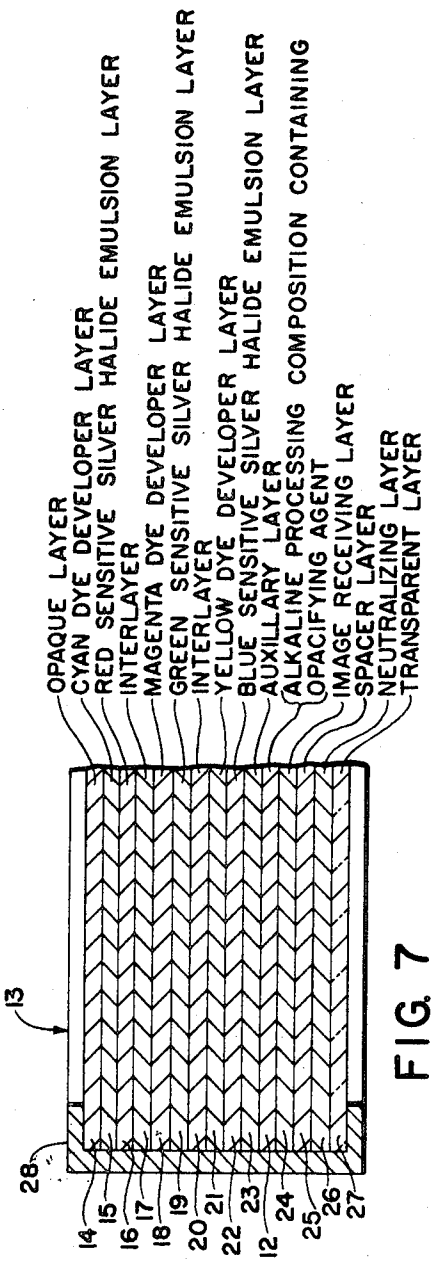

FIG. 7

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United States Patent Office 3,734,727 Patented May 22, 1973

3,734,727

PHOTOGRAPHIC PRODUCTS AND PROCESSES

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Continuation-in-part of abandoned applications Ser. No. 83,479 and Ser. No. 83,480, both Oct. 23, 1970. This application Oct. 28, 1971, Ser. No. 193,480

Int. Cl. G03c 1/48, 5/54, 17/00

U.S. Cl. 96—29 D 41 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to photography and, more particularly, to reflection type diffusion transfer process photographic film units which comprise a composite photosensitive element adapted to provide, by diffusion transfer photographic processing, selective integral negative and positive image recordation of incident actinic radiation as a function of the point-to-point degree of photosensitive element exposure, which includes a plurality of sequential layers including a photosensitive silver halide layer having associated therewith image-forming material which is processing composition diffusible at a first pH as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; and which additionally includes means for providing at least one optical filter agent at a pH above the pK_a of the optical filter agent whose pK_a is below said first pH in a concentration effective to provide, in situ, a layer exhibiting optical transmission density sufficient to provide a barrier with respect to incident visible radiation subsequent to photoexposure of the silver halide layer and means for reducing the initial pH of the layer to a second pH below the pK_a of the optical filter agent, which pH is above the pH necessary for diffusion of said image-forming material and, subsequent to substantial transfer image formation in the reception layer, reducing the pH to a third pH wherein the image-forming material is non-diffusible.

CROSS REFERENCE TO OTHER APPLICATIONS

This application is a continuation-in-part of application Ser. Nos. 83,479 and 83,480, both filed Oct. 23, 1970 and both now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention is directed to providing new and improved reflection type diffusion transfer process photographic film units which comprise a composite photosensitive element adapted to provide, as a function of the point-to-point degree of photoexposure, integral negative and positive images which include a negative image in a superposed relationship with and optically masked from a positive image adapted to be viewed by reflected light.

(2) Description of the prior art

Various film units for forming a color transfer image viewable, without separation from the remainder of the film unit, as a color reflection print, have heretofore been disclosed in the art. Such film units generally comprise a plurality of essential layers including at least one light-sensitive silver halide layer and associated dye image-providing material and a dyeable stratum. These film units also contain means for providing a reflecting layer between the dyeable stratum and the next adjacent silver halide layer and associated dye image-providing material to effectively mask the negative image formed upon development of the film unit and any remaining dye image-providing material and to provide a background for viewing a color transfer image formed in the dyeable stratum, whereby the resulting composite print including the color transfer image may be viewed, by reflected light, without separation, as a reflection print. These essential layers preferably also include a neutralizing layer to reduce the pH following substantial dye transfer to a pH wherein the image-providing material is nondiffusible. The essential layers may be, and preferably are contained between a pair of dimensionally stable layers, at least the one closest to the dyeable stratum being substantially transparent to permit viewing therethrough of the resulting transfer image.

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 for providing an imagewise distribution of a dye which is soluble and diffusible, in alkali, at a first 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 sliver 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 immobilized as a function of the point-to-point degree of the respective silver halide emulsion layer photoexposure, resulting in imagewise distribution 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 transfers, 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.

As disclosed in the copending U.S. patent application Ser. No. 846,441 of Edwin H. Land, filed July 31, 1969 now U.S. Pat. No. 3,615,421 and the copending U.S. patent application Ser. No. 3,646 of Sheldon A. Buckler, filed Jan. 19, 1970 and now U.S. Pat. No. 3,661,585, 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.

In the copending U.S. patent application Ser. No. 786,352 of Edwin H. Land, filed Dec. 23, 1968, 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 nonabsorbing species at the second pH.

In U.S. Pat. No. 3,573,043 of Edwin H. Land, issued Mar. 30, 1971, 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, and the U.S. Pat. No. 3,576,625 of Edwin H. Land, issued April 27, 1971, discloses the employment of particulate acid distributed within the film unit to effect the modulation of the environmental pH.

Copending application Ser. No. 43,782 filed June 5, 1970, now abandoned, discloses and claims an improved film unit assemblage of the aforementioned general structural parameters and adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation will be fabricated to employ, as the opacifying means interposed intermediate the receptive layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment dispersion containing reflecting pigment dispersion in a concentration per se insufficient, distributed as a layer intermediate the receptive layer and next adjacent silver halide layer, to effectively prevent transmission of radiation actinic to the silver halide layer therethrough and at least one optical filtering agent, at a pH above the pK_a of the optical filter agent, in a concentration also per se insufficient to prevent transmission of actinic radiation therethrough, which concentrations individually and additively are together insufficient to prevent transmission of incident actinic radiation, but in admixture are synergistically effective to provide a barrier to such transmission. Thus, the optical filter agent is empirically effective in combination with the pigment to prevent transmission of radiation actinic to the silver halide layers incident on the layer comprising the dispersion, during processing in the presence of actinic radiation, and sufficiently low to provide substantially immediate viewing of transfer image formation against the background provided by the reflecting pigment. Such effective minimal concentration of filter agent specifically facilitates the acceleration of the clearing time involved in discharging from visual observation the filter agent employed by reduction of the environmental pH as detailed above from above to below the pK_a of the filter agent selected.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved integral negative/positive diffusion transfer process photographic film unit adapted to provide, by diffusion transfer processing, a reflecting print photographic 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 comprises a film unit of the general type set forth above, e.g., in the aforementioned U.S. Pats. Nos. 3,415,644; 3,573,043; 3,576,625; and 3,615,421 and 3,586,501 and copending application Ser. No. 786,352, and may comprise, in essence, a composite photosensitive element which includes a plurality of layers including one or more photosensitive silver halide layers having associated therewith image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; means for interposing, at least one optical filter agent; and means for modulating the pH of the film unit step-wise in at least two pH increments.

A particularly preferred film assemblage of the present invention comprises, in essence, a composite photosensitive element which includes a plurality of layers including, in relative order, a dimensionally stable layer opaque to incident actinic radiation; one or more photosensitive silver halide layers having associated therewith image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; means for interposing, intermediate the silver halide layers and the reception layer, an inorganic reflecting pigment dispersion containing at least one optical filter agent; and means for modulating the pH of the film unit stepwise in at least two pH increments.

In accordance with the present invention, it has been quite unexpectedly discovered that an improved film unit assemblage of the aforementioned general structural parameters and adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation will be fabricated to employ, as the opacifying means interposed intermediate the reception layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment and at least one optical filter agent, the concentrations of which individually and additively are together insufficient to prevent transmission of incident actinic radiation but in admixture are synergistically effective to provide a barrier to such transmission, which film assemblage also contains means for modulating the pH of the system from a first pH wherein the dye image-forming material is diffusible; said first pH being above the pK_a of the optical filter element, to a second pH wherein the optical filter element is rendered substantially ineffective as a light-absorbing barrier, said second pH being below the pK_a of said optical filter element, but at which pH said dye image-forming material is still diffusible, to a third pH at which the dye image-forming material is substantially nondiffusible.

Thus, subsequent to exposure of the photosensitive element and distribution of the aqueous alkaline processing composition and opacifying means intermediate the reception layer and next adjacent silver halide layer, the first pH of the system, as provided by the aqueous alkaline composition, initiates development and the forming of an imagewise distribution of mobile dye image-forming material as a function of the point-to-point degree of emulsion exposure. Subsequent to the diffusion of said dye image-forming material from its initial position in the element, i.e., at a point wherein the mobility of the dye image-forming material has been modulated by the exposed silver halide, the pH of the system is adjusted to a second pH wherein the optical filter agent is substantially ineffective as a light-absorbing barrier; said dye image-forming material being diffusible at said second pH. Subsequent to substantial dye transfer image formation, the

pH of the system is reduced to a third pH wherein said dye image-forming material is substantially nondiffusible.

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; and

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

DETAILED DESCRIPTION OF THE INVENTION

As previously characterized, diffusion transfer photographic processing may be employed to provide a positive reflection image, as a direct function of actinic radiation incident on a film unit assemblage specifically constructed to comprise, in essence, a plurality of sequential layers including a layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material and preferably dye image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide layer photoexposure; and a layer adapted to receive image-forming material diffusing thereto; wherein the assemblage additionally contains means for interposing, intermediate the silver halide layer and the reception layer, an inorganic reflecting pigment and at least one optical filter agent, at a pH above the pK_a of the filter agent, in a concentration effective to provide a light-absorbing barrier between the reception layer and silver halide layer, and means for converting the pH of the dispersion from a pH above the pK_a of the optical filter agent to a second pH below the pK_a of the optical filter agent, whereby the exposure protection is discharged, but at which second pH the diffusibility of the dye image-forming material is not impaired; and means providing for converting said second pH to a third pH at which said dye image-forming material is nondiffusible.

In a particularly preferred embodiment, the aforementioned inorganic reflecting pigment and optical light filter agent as employed in a concentration which provides, at a pH above the pK_a of the filter agent, a layer exhibiting optical transmission density $>\sim 6.0$ density units and optical reflection density $<\sim 1.0$ density units subsequent to photoexposure of the silver halide layer.

It has been found that the film unit assemblage constructed in accordance with the present invention is specifically adapted for processing in the presence of actinic radiation by reason of the protection afforded the silver halide layer's exposure surface by the presence of the pigment and filter agent protecting from exposure such surface, and for the simultaneous viewing of the transfer image carried by the reception layer by reason of the minimal optical reflection density exhibited by the light-reflecting pigment layer, subsequent to photoexposure of the silver halide layer and in situ formation of the pigment layer. There is thus provided by means of the present invention substantially immediate viewing of transfer image formation against a reflecting pigment layer background exhibiting substantially no contamination from the optical reflecting agent employed with the pigment layer to prevent transmission of fog producting actinic radiation through the reflecting layer and thus protecting the silver halide layer during initial stages of transfer processing, i.e., during that period of time required for the silver halide to modulate the mobility of the dye image-providing material. The de minimus concentration of optical filter agent discovered to be capable of effective employment to prevent light transmission when dispersed in intimate relationship with reflecting pigment optimizes discharge of the reflectivity provided by the agent upon decrease of the environmental pH at which the optical filter agent absorbs radiation to that pH at which such agent is substantially innocuous optically, but at which diffusibility of the dye image-forming materials is unimpaired.

It should be understood that reference to modulating the pH of the film unit or system is intended to refer to a pH change in at least those areas of the film unit where the optical filter agent and/or image-forming material is located.

The preferred means for modulating the pH of the system from a first pH wherein the dye image-forming materials are diffusible and the optical filter agent is operative with the inorganic reflecting pigment to provide the above mentioned barrier to actinic radiation, to a second pH wherein the image-forming materials are diffusible but which second pH is below the pK_a of the optical filter agent and which thus discharges the light-absorbing barrier, are non-volatile acids. Any suitable acid may be employed, including high or low molecular weight acids; they may be introduced into the photographic film unit as molecular dispersions, solid dispersions, emulsions or solutions.

The acidic additive may be disposed in any convenient location in the film unit provided it is made available to accomplish the aforementioned clearing of the optical filter agent without adversely effecting the image-forming process or deleteriously effecting the photographic quality of the system. Thus, the acidic additive may be disposed in the photosensitive element, in the image-receiving layer or in a separate layer disposed adjacent either of said layers. Because of the variety of materials suitable for use, and the properties and forms available, the acidic additive can be disposed in a variety of locations and formats to provide the necessary time delay to permit appreciable diffusion of dye image-forming materials and then obtain the relatively precipitous drop of the pH of the system to a point below the pK_a of the optical filter agent. Thus, the time delay may be effected by spatially removing the acidic additive from the locus of the optical filter agent or by locating the acidic additive relatively close to the optical filter agent but providing said acidic additive in such a species that will provide the required time delay.

In a particularly preferred embodiment, the acidic additive is disposed in the layer adapted to receive the image-forming material.

The term acidic additive is intended to include acids and compounds adapted to provide an acidic moiety in the system. It is necessary, however, that the pK_a of the acidic additive be below that of the particular optical filter agent employed.

As examples of suitable acidic additives, mention may be made of the following:

benzoic acid
methane sulfonamide
benzyl malonic acid
phthalic acid
fumaric acid
p-toluene sulfonamide
N-methyl-p-toluene sulfonamide
N-ethyl-p-toluene sulfonamide
citric acid
d-tartaric acid
sulfanilamide
salicylic acid
5-sulfosalicylic acid

sulfoacetic acid
benzene sulfonamide
methane sulfonamide
2-toluene sulfonic acid

In an alternative embodiment, an acid salt of a conventional antifoggant is employed, preferably in the layer adapted to receive the image-forming materials, to provide antifoggant activity and the means for reducing the initial pH to a second pH. As examples of such antifoggants, mention may be made of acid salts of benzotriazole and benzimidazole.

In an alternative embodiment, the film element includes buffering means to maintain said second pH wherein the optical filter element is rendered substantially ineffective as a light-absorbing barrier, at which pH the dye image-forming material is still diffusible, for a time sufficient to permit substantial dye image-forming material transfer.

In other words, a plot of pH versus time would show a curve indicating pH decrease to a point below the pK_a of the optical filter element whereupon it would plateau while transfer of image-forming material proceeded and then again indicate pH drop to a point where said image-forming material is substantially non-diffusible.

The particular compound employed as the buffering means is selected with respect to the specific pK_a desired, i.e., with respect to the specific optical filter element employed and the period of time during which buffering would occur. Preferably, a compound of relatively high pK_a is employed. More preferably, the compounds are acid salts or acids which will form salts with the aqueous alkaline processing composition. When disposed in the processing composition, the compound must also be stable in alkali and not degrade in storage. It must also not deleteriously interfere with the photographic operation of the film unit.

The compound to provide the buffering means may be disposed in any convenient location in the film unit provided it is made available to accomplish the aforementioned buffering of the processing composition without adversely effecting the image-forming process or deleteriously effecting the photographic quality of the system. Thus, the compound may be disposed in the photosensitive element, in the image-receiving layer or in a separate layer disposed adjacent either of said layers or in the container with the processing composition.

In a particularly preferred embodiment, the compound to provide buffering means is disposed in the processing composition.

As examples of suitable compounds, mention may be made of the following:

sodium ortho silicate
sodium meta silicate
potassium meta silicate
p-toluene sulfonamide
salts of salicylic acid
salts of phosphoric acid
fumed silica
salts of ethylenediamine tetraacetic acid
benzene sulfonamide
N-methyl-p-toluene sulfonamide
N-ethyl-p-toluene sulfonamide
sulfonilamide
methane sulfonamide

It will be recognized that it is necessary to prevent the diffusion to the image-receiving layer of additional dye image-forming material resulting from the exposure of silver halide after discharge of the light absorbing barrier. If the time delay between the discharge of the light-absorbing barrier and the modulation of the pH of the system, wherein the dye image-forming materials are non-diffusing, is sufficiently long, it is not necessary to prevent transfer of dye image-forming materials or to render the silver halide nondevelopable since the mobility of the dye image-forming materials would not permit said materials to reach the dyeable layer in the given time sequence before the pH reduction rendered all components in the film unit immobile.

Alternatively, means may be employed to cause the developable silver halide to remain undeveloped. It has been found that such control may be accomplished by incorporating in a layer of either the photosensitive element or the image-receiving element, or in some instances in the processing composition, a reagent which is made available to the developable silver halide of a given emulsion layer only after a predetermined period during which development is effected without interference by said reagent. Since this added reagent effectively restrains, i.e., minimizes, further development of developable silver halide after this predetermined period, suitable reagents employed for this purpose may be referred to as "development restrainers." While such reagents frequently will have characteristics similar to reagents commonly referred to as "antifoggants", they perform a function herein different from what is normally contemplated as the function of an antifoggant, i.e. their function is not to reduce the fog density in unexposed areas, although under some circumstances, they may also perform this function to a small degree. In some instances, a given reagent may be used in a small concentration in the processing composition wherein it functions as an antifoggant, and an additional quantity is contained in the photosensitive element or in the image-receiving element in a form whereby it is released only after a predetermined period whereupon it acts as a development restrainer.

Reagents which are particularly suitable for use as development restrainers are those which will form products or "complexes with undeveloped silver halide, whether exposed or unexposed, but at least with exposed silver halide, which products or complexes are substantially less developable by a silver halide developing agent, e.g., by the dye developer, and which preferably are substantially insoluble, and hence essentially undevelopable, i.e. developable only with difficulty. In a preferred embodiment, the desired predetermined period during which development is effected without interference is accomplished by incorporating the development restrainer in a chemical form or in a physicial location such that its availability to the developable silver halide is limited or restricted, e.g., as a result of the distance through which it must diffuse to reach the developing silver halide, or as a consequence of a significantly lower diffusion rate than said developing agents. Where the development restrainer is at least initially substantially slower in diffusion than the dye developer, as for example, as a result of the inclusion of a relatively long chain alkyl group, the development restrainer may be positioned in a layer of the multilayer negative, e.g., in the dye layer containing the dye developer or in an interlayer positioned on the side of the dye layer remote from the silver halide emulsion layer. A relatively more diffusible development restrainer may be used provided that it is located sufficiently remote physically from the silver halide emulsion layer upon which it is to act, as by incorporation in the image-receiving layer, i.e., in the image-receiving layer itself or in a layer over the image-receiving layer or in a subcoat beneath the image-receiving layer. Such development restrainers may also be incorporated in a layer in the photosensitive element provided said restrainer is present in such a form as to be only slowly dissolved by the processing composition. Under some circumstances, the development restrainer may be similarly contained in a coating over the outermost or blue-sensitive silver halide emulsion layer.

Development restrainers suitable for use in the processes of this invention will readily suggest themselves to one skilled in the art. By way of illustration, mention may be made of long chain thiobarbituric acids, e.g., dodecyl

thiobarbituric acid, and phenyl-mercaptotetrazoles, e.g., 1-phenyl-5-mercaptotetrazole.

In a preferred embodiment of the invention, the development restrainers are employed, in combination, with an antifoggant initially contained in the processing composition and/or in a layer of the photosensitive element so as to be available for action relatively promptly after the application of the processing composition. Such antifoggants perform the usual function of an antifoggant, i.e., they minimize the development of silver "fog" in unexposed and partially exposed areas of the several photosensitive silver halide emulsions and increase the differentiation between exposed and unexposed silver halide by the developing agent. As previously noted, the development restrainer may and frequently is a compound of the broad class of reagents frequently referred to as antifoggants. An essential distinction between the use of a compound as an antifoggant and as a development restrainer as contemplated by this invention is in the time sequence in which it is available to act upon the silver halide emulsion layer. Furthermore, many useful development restrainers may be found among compounds whose action upon silver halide is too vigorous to be effectively employed as antifoggants, since they would tend to reduce density in the areas intended to be developed. Since it is the purpose of the development restrainers in the instant invention to render the residual developable silver halide substantially undevelopable after a predetermined period of development, we may successfully use a reagent which acts nonimagewise in rendering the remaining undeveloped silver halide, exposed and unexposed, undevelopable by the silver halide developing agent or agents present.

In a particularly preferred embodiment, the film unit includes a compound which is a precursor of the desired development restrainer which is capable of releasing the active species of the compound at a temperature dependent rate. Antifoggant precursors are described and claimed in U.S. Pat. No. 3,575,699 issued Apr. 20, 1971.

In still another alternative embodiment, control of the silver halide may be accomplished by providing means for desensitizing the silver halide, thus rendering it innocuous with respect to providing additional diffusible image-providing material. Conventional desensitizers known to the art may be provided associated with the photosensitive element and adapted to be released substantially contemporaneous with the discharge of the light-absorbing barrier.

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 the 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 halide stratum, a green-sensitive silver halide stratum and a blue-sensitive silver halide 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 strata; 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 halide 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 substractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide 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 stratum comprise 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, preferably

gelatin, are about 1 to 5 microns in thickness; the dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; and each of the dimensionally stable opaque and transparent layers are alkaline solution impermeable, processing composition vapor permeable and about 2 to 6 mils in thickness. It wil 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.

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**; spacer layer **25**; neutralizing layer **26**; 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. Pats. 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-impervious sheet material folded longitudinally upon itself to form two walls **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing 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 illustrated 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 FIG. 6, extension flap **32** of tape **28** is preferably of such area and dimensions that upon, for example, manual separation of container **11** and tape **33**, subsequent to distribution of processing composition **12**, from the remainder of film unit **10**, flap **32** may be folded over 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 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 pK_a of such agent in a quantity sufficient, upon distribution, effective to provide a light-absorbing barrier, preferably a layer exhibiting optical transmission density $>\sim 6.0$ and optical reflection density $<\sim 1.0$ 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%. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of ~85%.

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 <~0.2 micron in diameter and preferably <~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 in excess of ~0.2 micron in diameter and will be coated at a coverage of ~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 pK_a, 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 dispersion 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 pK_a 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 must 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 must possess a pK_a below that of the processing pH and above that of the environmental pH subsequent to transfer image formation, and will be selected for employment in the minimum concentration necessary to provide an optical transmission density >~6.0, at wavelengths at which the silver halide layer is maximally responsive, and in no instance an optical reflection density <~1.0 at such wavelengths.

As examples of such pH-sensitive optical filter agents adapted for employment in the practice of the present invention, mention may be made of:

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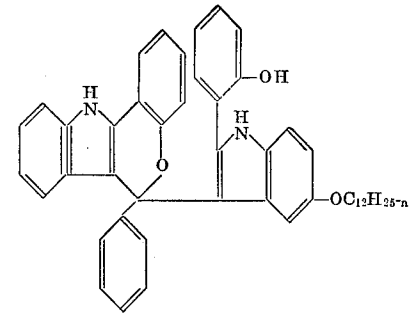

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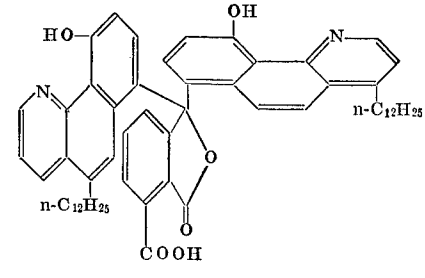

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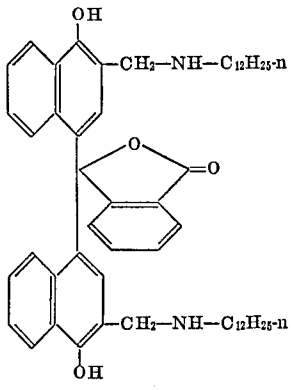

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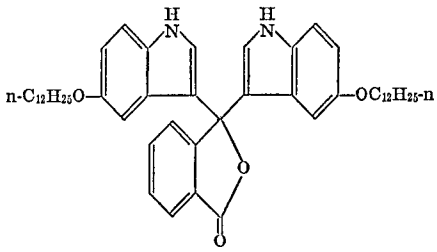

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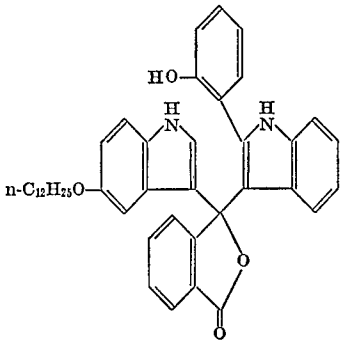

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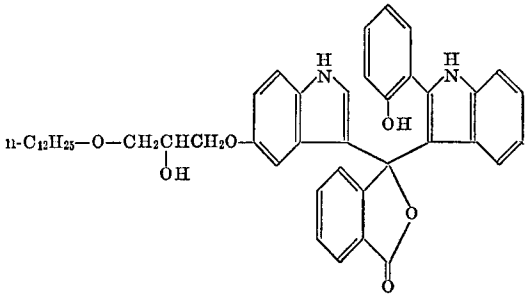

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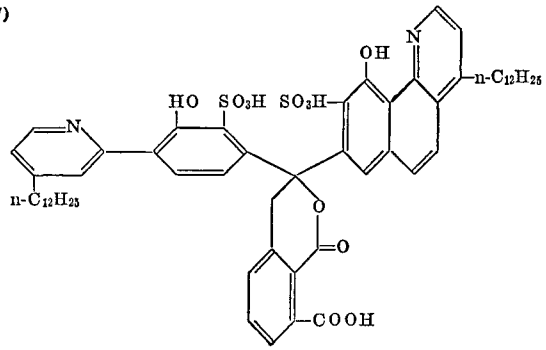

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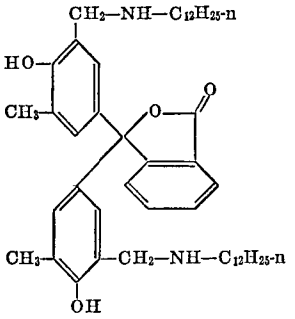

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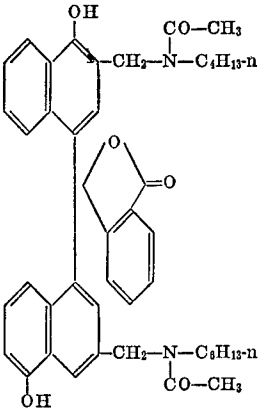

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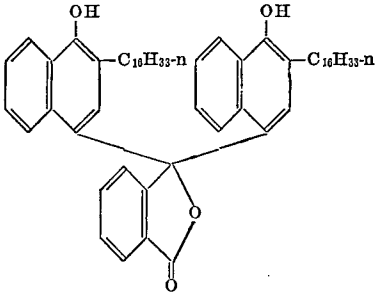

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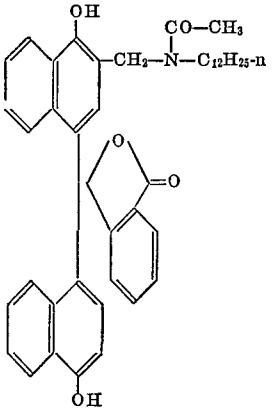

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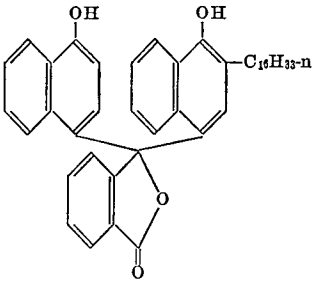

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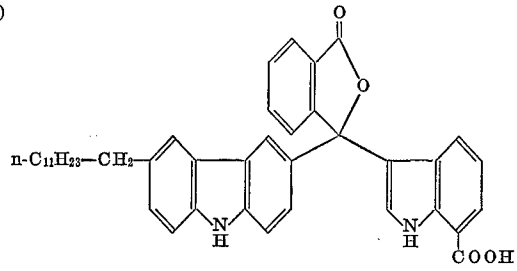

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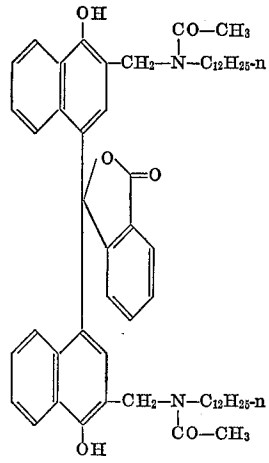

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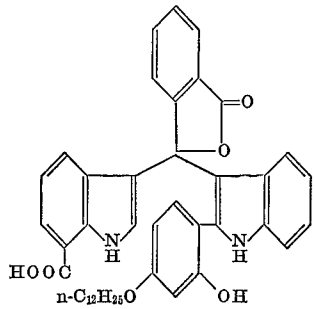

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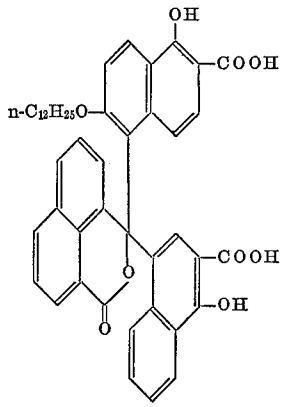

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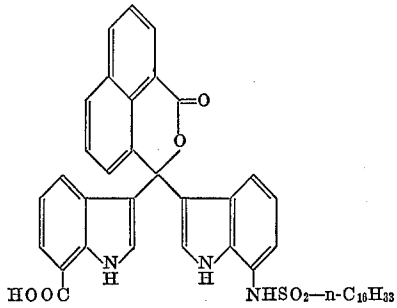

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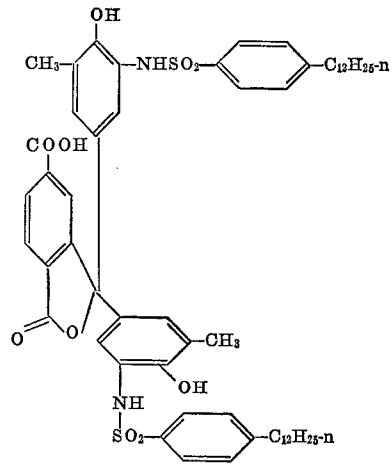

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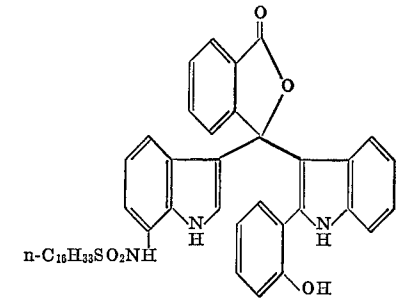

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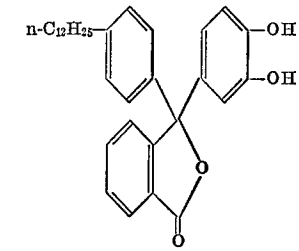

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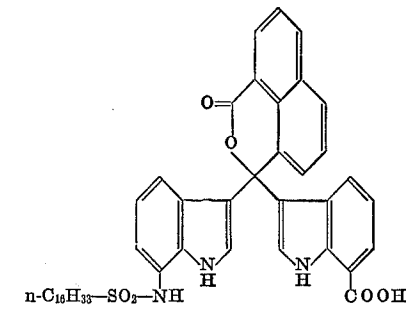

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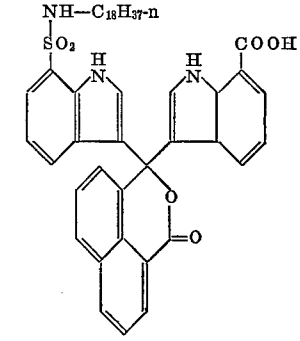

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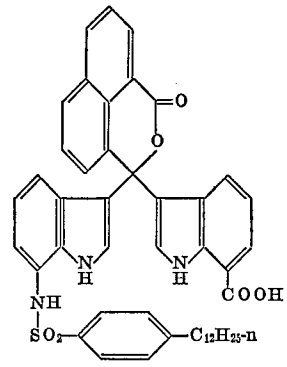

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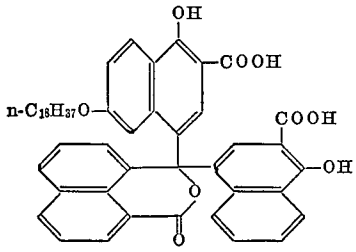

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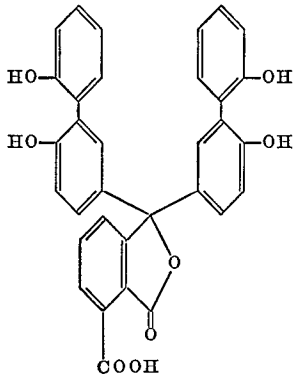

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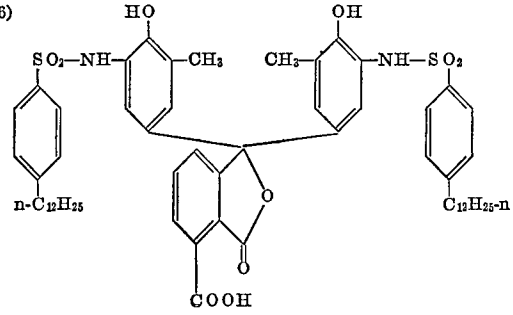


In general, preferred agents, both opacifying and filter, are those which remain immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible materials.

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 c.p.s. at a temperature of approximately 24° C. and preferably in the order of 100,000 c.p.s. to 200,000 c.p.s. 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 **34**, as illustrated in FIG. 2.

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 pK_a 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 reflecting agent precursor layer **25** 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** and 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, through permeable polymeric reception layer **24**, permeable spacer layer **25** to polymeric neutralizing layer **26** 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 pK_a of such agent to thereby provide maximum reflectivity in terms of the pigment concentration present.

Alternatively, subsequent to discharge of the optical filter agent and prior to reduction of the pH to a paint where the dye developers are non-diffusing, the system is buffered for a time sufficient to permit substantial dye image formation.

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 immobilized or precipitated in exposed areas as a consequence of the development of the latent images. This immobilization 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 unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a functon of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image.

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

(1) A layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl-α-methyl]-ethylamino)-5,8 - dihydroxy - anthraquinone dispersed in gelatin and coated at a coverage of about 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 the acrylic latex sold by Rohm and and Haas Co., Philadelphia, Pa., U.S.A., under the trade designation AC–61 and polyacrylamide coated at a coverage of about 150 mgs./ft.^{2} of AC–61 and about 5 mgs./ft.^{2} of polyacrylamide;

(4) A layer of the magenta dye developer 2-(p-[β-hydroquinonylethyl]-phenylazo)-4-isopropoxy-1 - naphthol dispersed in gelatin and coated at a coverage of 70 mgs./ft.^{2} of dye and about 120 mgs./ft.^{2} of gelatin;

(5) A green-sensitive gelatino-silver iodobromide emulsion coated at 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 at a coverage of about 100 mgs./ft.^{2} of B–15 and about 10 mgs./ft.^{2} of polyacrylamide;

(7) A layer of the yellow dye developer 4-(p-[β-hydroquinonylethyl]-phenylazo)-3 - (N,n - hexylcarboxamido)-1-phenyl-5-pyrazolone 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 silver and 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.

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

(1) A 7:3 mixture, by weight, of polyethylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1400 mgs./ft.^{2}, to provide a polymeric acid layer;

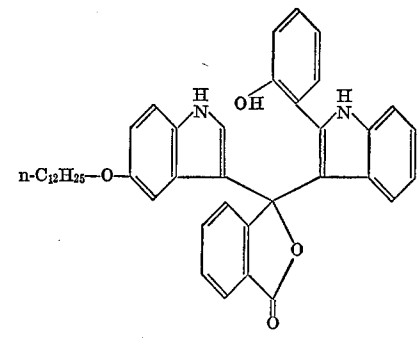
(2) A graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mgs./ft.^{2}, to provide a polymeric spacer layer; and

(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} phenyl mercapto tetrazole, and about 2×10^{-3} moles/ft.^{2} of benzoic acid (in methanol) to provide a polymeric image-receiving layer having associated therewith means adapted to discharge the light-absorbing barrier.

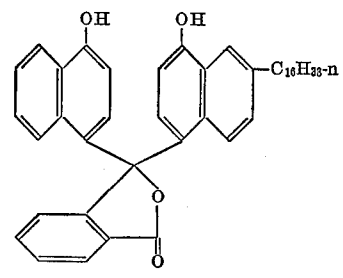
The two components thus prepared may then be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant laminate.

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:

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

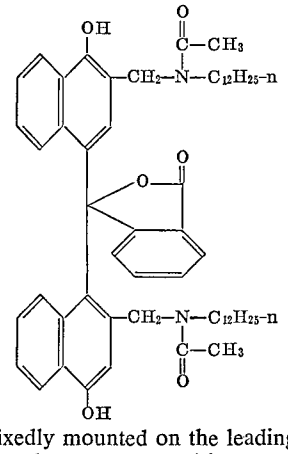


(B)	gms....	0.52



TABLE—Continued

(C) ----------gms-- 1.18



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 step wedges to selectively filter radiation incident on the transparent polyethylene terephthalate 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. During processing, the multicolor dye transfer image formation may be viewed through the transparent polyethylene terephthalate 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 90 seconds. The 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 $>\sim 6.0$ density units and against the titanium dioxide's effective reflective background afforded by reason of the composition possessing an optical reflection density $<\sim 1.0$ density units.

In an alternative embodiment, a film unit was constructed substantially as above except that the image-receiving element did not contain benzoic acid and the processing solution additionally contained 5.7 g. of sodium orthosiilcate. Similar results were obtained with this film unit as with the above-described film unit.

The initial optical transmission density provided by a processing composition substantially as above at the respective $\lambda_{max.}$ of the last-identified optical filter agents measure in situ as a composite formulation comprises ~6.2, 6.2 and 6.1, respectively, of which ~1.25, 1.15 and 1.10, respectively, is contributed by the titanium dioxide content of the processing composition, the remainder contributed by the optical filter agents at a pH above their respective pK_a.

In the absence of the titanium dioxide, the measured optical density provided by the optical filter agents in combination at their respective $\lambda_{max.}$ comprises ~2.4, 2.05 and 2.3. It will be apparent that the optical densities of the optical filter agent individually added to the optical density of the titanium dioxide is insufficient theoretically to provide the required minimum optical transmission density of $>\sim 6.0$ density units, but has been found, by means of the present invention, to unexpectedly provide in combination an optical density in accordance with the

mathematical expression $D_T=EC(l+\Delta l)$, wherein "D_T is transmission density, E is the epsilon of the optical filter agent, C is the concentration and l is the radiation path length; thus directly providing the unexpected advantageous end results discussed in detail above.

The pH and solvent concentration of the alkaline processing solution initially empoyed must possess a pH above the pK_a of the optical filter agents, that is, the pH at which about 50% of the agents are present as the lesser absorbing species and about 50% are present as the greater absorbing species, preferably a pK_a of $>\sim 11$ and most preferably $>\sim 12$ 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 pK_a's of the acidic additives are preferably only slightly lower than that of the particular optical filter agent in order to provide for rapid discharge of the light-absorbing medium.

Neutralizing means, for example, a polymeric acid layer of the type discussed above will be incorporated, as stated, in the film unit of the present invention, to provide reduction of the alkalinity of the processing solution from a pH at which the dyes are diffusible to a pH 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 neutraliizng 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. No. 3,362,819 which, most preferably, includes the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the image-receiving layer.

As set forth in the last-mentioned patent, the neutralizing 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 hydogen 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.

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 is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer 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 be accurately so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer 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 components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the polymer layer may be effected by mixing acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only an acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also there disclosed that the layer containing the polymeric acid may contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats are employed to help the various polymeric layers adhere to each other during storage and use.

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

As disclosed in aforementioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, for example, at 95 to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

However, as disclosed in U.S. Pat. No. 3,455,686 preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processess relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective with the temperature range of optimum transfer processing. Conversely, at temperature below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its color definition.

It is further stated in the last-mentioned U.S. Pat. No. 3,455,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

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

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

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

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 concentration from a solvent concentration at which dye diffusion or transfer is operative to a solvent 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, multicolor transfer 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 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 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.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. 3,148,061, issued Sept. 8, 1964.

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

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

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH 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 compiliation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Pats. Nos. 2,983,605, 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

As additional examples of synthetic, film-forming, permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl-α,β-unsaturated carboxamides

and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinylphthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl and N-cycloalkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,296; and the like.

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

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

Although the invention has been discussed in detail throughout employing dye developers, the preferred 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. Pats. 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. Pats. Nos. 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.

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

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

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

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

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivatives, as described in U.S. Pats. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

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 $>\sim 50$, 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 emulsions 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 emulsions, 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.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively 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 developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye image-providing material and the use of a mixture of dye image-providing material adapted to provide a black-and-white trnasfer 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 produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

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 be 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, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

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

What is claimed is:

1. A photographic film unit which comprises a plurality of sequential layers including a layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material which is processing composition diffusible at a first pH as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; means for interposing, intermediate the silver halide layer and the reception layer, an inorganic reflecting pigment dispersion comprising at least one optical filter agent at a pH above the pK_a of said optical filter agent whose pK_a is below said first pH and above a second pH, in a concentration effective to provide a layer exhibiting optical transmission density sufficient to provide a barrier to incident radiation actinic to the photosensitive silver halide layer and means for reducing the initial pH of the film unit at the location of the optical filter agent to a second pH below the pK_a of the optical filter agent, said image-forming material being diffusible at said initial pH and said second pH, and, subsequent to substantial diffusion of image-forming material to the layer adapted to receive image-forming material diffusing thereto, means for reducing the pH of the film unit at the location of the image-forming material to a third pH wherein said image-forming material is substantially nondiffusible.

2. A photographic film unit as defined in claim **1** wherein said means for providing said barrier comprises a processing composition permeable layer, intermediate the silver halide layer and the reception layer, which includes an inorganic light-reflecting pigment dispersion containing at least one pH sensitive dye at a pH below the pK_a of the dye and a concentration effective upon contact with a processing composition possessing a pH above the pK_a of the dye to provide a layer exhibiting optical transmission density $\geq \sim 6.0$ density units and optical reflection density $\leq \sim 1.0$ density units.

3. A photographic film unit as defined in claim **2** wherein the means for introducing the photographic processing composition comprises a rupturable container retaining the processing composition positioned extending transverse an edge of the film unit, whereby application of compressive pressure to the container, discharges the container's processing composition contents intermediate the silver halide layer and the reception layer.

4. A photographic film unit as defined in claim **1** wherein the image-forming material is a dye image-forming material.

5. A photographic film unit as defined in claim **4** wherein the dye image-forming material comprises a dye which is a silver halide developing agent.

6. A photographic film unit as defined in claim **5** including, intermediate the opaque layer and the reception layer, at least two selectively sensitized silver halide emulsion layers each having a dye which is a silver halide developing agent of predetermined color associated therewith, each of the dyes soluble and diffusible in processing composition at said first and second pH as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

7. A photographic film unit as defined in claim **6** wherein each of the selectively sensitized silver halide emulsion layers possesses predominant spectral sensitivity to regions of the spectrum and the dye associated with each of said silver halide emulsion layers possesses a spectral absorption range subsequent to processing subtantially complementary to the predominant ensitivity image of its associated emulsion layer.

8. A photographic film unit as defined in claim **7** wherein at least one optical filter agent exhibits, at a pH above its pK_a, major spectral absorption in the spectral region within which a selectively sensitized silver halide emulsion layer possesses predominant spectral sensitivity.

9. A photographic film unit as defined in claim **1** wherein the pH above the pK_a of the filter agent is an alkaline pH above 7.

10. A photographic film unit as defined in claim **9** including at least one layer positioned in the film unit and adapted to reduce the pH of an aqueous alkaline processing solution to said third pH at which the dye is substantially nondiffusible subsequent to substantial transfer of dye to the reception layer.

11. A photographic film unit as defined in claim **1** wherein said means for reducing the pH of the film unit

from said first pH to said second pH includes an acidic additive.

12. A photographic film unit as defined in claim 11 wherein said acidic additive is disposed in said reception layer.

13. A photographic film unit as defined in claim 11 wherein said acidic additive is benzoic acid.

14. A photographic film unit as defined in claim 11 wherein said acidic additive is salicylic acid.

15. A photographic film unit as defined in claim 11 wherein said acidic additive is methyl sulfonamide.

16. A photographic film unit as defined in claim 12 wherein said acidic additive is an acid salt of an antifoggant.

17. A photographic film unit as defined in claim 16 wherein said antifoggant is benzotriazole.

18. A photographic film unit as defined in claim 1 wherein the means for reducing the pH of said film unit from said first pH to said third pH includes buffering means to maintain said second pH for a time sufficient to provide for substantial diffusion of said image-forming material to said reception layer.

19. A photographic film unit as defined in claim 18 wherein said buffering means is disposed in a layer adjacent to said reception layer.

20. A photographic film unit as defined in claim 18 wherein said buffering agent is sodium ortho silicate.

21. A photographic film unit as defined in claim 18 wherein said buffering agent is sodium meta silicate.

22. A photographic film unit as defined in claim 18 wherein said buffering agent is fumed silicia.

23. A photographic film unit as defined in claim 18 wherein said buffering agent is a salt of salicylic acid.

24. A photographic film unit as defined in claim 18 wherein said buffering agent is a salt of ethylenediamine tetraacetic acid.

25. A photographic film unit as defined in claim 10 wherein said inorganic light-reflecting pigment comprises titanium dioxide.

26. A photographic film unit as defined in claim 25 wherein the optical filter agent comprises a phthalein pH-sensitive dye possessing a pK_a below said first pH and above said second pH.

27. A photographic film unit as defined in claim 26 wherein said pH-sensitive dye is substantially nondiffusible from said inorganic light-reflecting pigment dispersion.

28. A photographic film unit as defined in claim 25 adapted to be processed by passing the 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, 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 and a dye which is a silver halide developing agent and is soluble and diffusible, in alkaline processing composition at said first pH, associated with each of the silver halide emulsion layers and possessing a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion layer; an alkaline solution permeable and dyeable polymeric layer; a dimensionally stable transparent layer; and means securing the layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing composition possessing said first pH and retaining substantially uniformly disposed therein titanium dioxide and an optical filter agent substantially nondiffusible from the processing composition and possessing a pK_a below said first pH and above said second pH wherein the filter agent exhibits spectral absorption substantially complementary to the predominant sensitivity range of the selectively sensitized silver halide emulsion layers at said first pH and said titanium dioxide and said filter agent are present in a quantity sufficient, upon distribution of the alkaline processing composition possessing said first pH as a layer intermediate the dyeable polymeric layer and next adjacent selectively sensitized silver halide emulsion layer, to provide to the layer an optical transmission density $>\sim 6.0$ density units with respect to incident radiation actinic to said silver halide emulsion layers and an optical reflection density $<\sim 1.0$ density units with respect to incident visible radiation, said rupturable container is positioned and extends transverse an edge of said 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; means for reducing the pH at the location of said optical filter agent from said first pH to a second pH; and

a polymeric layer possessing acid capacity effective to reduce the pH of said alkaline processing composition possessing said second pH to said third pH at which said dyes are substantially nondiffusible.

29. A photographic film unit as defined in claim 28 wherein said silver halide is present in a concentration within the range of $\sim$125 to 500 mgs./ft.^{2}.

30. A photographic film unit as defined in claim 29 wherein the titanium dioxide is distributed intermediate said dyeable polymeric layer and said silver halide emulsion layer next adjacent at a coverage within the range of $\sim$1500 to 4000 mgs./ft.^{2}.

31. A process for providing a photographic diffusion transfer image which comprises, in combination, the steps of:

(a) exposing to incident electromagnetic radiation a photographic film unit which comprises a plurality of sequential layers including a layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material which is processing composition diffusible at a first pH as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; employing means for interposing, intermediate the silver halide layer and the reception layer, an inorganic reflecting pigment dispersion containing at least one optical filter agent at a pH above the pK_a of the optical filter agent whose pK_a is below said first pH and above a second pH in a concentration effective to provide a layer exhibiting optical transmission density sufficient to provide a barrier to incident radiation actinic to the photosensitive silver halide layer; and means for reducing the initial pH of the film unit in the location of the optical filter agent to a second pH below the pK_a of the optical filter agent, said image-forming material being diffusible at said second pH (and, subsequent to substantial diffusion of solubilized image-forming material to the layer adapted to receive image-forming material diffusing thereto, reducing said second pH to a third pH in the location of the image-forming material wherein said image-forming material is substantially nondiffusible;

(b) interposing the inorganic reflecting pigment dispersion intermediate the silver halide layer and the reception layer;

(c) contacting the photoexposed silver halide layer with a processing composition adapted to effect development of the silver halide layer;

(d) effecting thereby development of the photoexposed silver halide layer;

(e) forming thereby an imagewise distribution of mobile image-forming material as a function of the

point-to-point degree of silver halide layer photoexposure;

(f) transferring, by diffusion, at least a portion of the imagewise distribution of mobile image-forming material to the layer adapted to receive image-forming material diffusing thereto to thereby provide an image in terms of the imagewise distribution;

(g) reducing said first pH to a second pH below the pK_a of the optical filter agent, said image-forming material being diffusible at said second pH; and

(h) reducing, subsequent to substantial transfer of mobile image-forming material to the layer adapted to receive image-forming material diffusion thereto, the pH of the film unit in the location of said image-forming material to a third pH below which said image-forming material is substantially nondiffusible.

32. A process for providing a photographic diffusion transfer image as defined in claim **31** wherein said means for providing said barrier comprises including within the photographic film unit, intermediate the silver halide layer and the reception layer, a preformed processing composition permeable layer which includes an inorganic light-reflecting pigment dispersion containing at least one pH-sensitive dye at a pH below the pK_a of the dye and a concentration effective upon contact with a processing composition possessing a pH above the pK_a of the dye to provide a layer exhibiting the optical transmission density $>\sim 6.0$ density unit and the optical reflection density $<\sim 1.0$ density units, and including the step of contacting the pH-sensitive dye, subsequent to photoexposure of the film unit, with a processing composition possessing a pH above the pK_a of the dye to provide a layer exhibiting the optical transmission density $>\sim 6.0$ density units and the optical reflection density $<\sim 1.0$ density units.

33. A process for providing a photographic diffusion transfer image as defined in claim **31** wherein the means for interposing the processing composition comprises a rupturable container retaining the processing composition positioned transverse an edge of the film unit, whereby application of compressive pressure to the container, subsequent to photoexposure of the silver halide layer, discharges the processing composition intermediate the silver halide layer and the reception layer.

34. A process for providing a photographic diffusion transfer image as defined in claim **31** wherein the image-forming material comprises a dye which is a silver halide developing agent.

35. A process for providing a photographic diffusion transfer image as defined in claim **31** wherein said means for reducing the pH of the film unit from said first pH to said second pH includes an acidic additive.

36. A process for providing a photographic diffusion transfer image as defined in claim **35** wherein said acidic additive is disposed in said reception layer.

37. A process as defined in claim **31** wherein said means for reducing the pH from said first pH to said third pH includes buffering means to maintain said second pH for a time sufficient to provide for substantial diffusion of said image-forming material to said reception layer.

38. A process for providing a multicolored diffusion transfer image as defined in claim **31** which comprises, in combination, the steps of:

(a) exposing to incident actinic radiation a composite photographic film unit which comprises a plurality of sequential layers including a dimensionally stable layer opaque to incident actinic radiation; at least two selectively sensitized silver halide emulsion layers possessing predominant spectral sensitivity to separate regions of the visible electromagnetic spectrum and a dye which is a silver halide developing agent and is soluble and diffusible in aqueous alkaline processing composition, at a first pH, associated with each of the silver halide emulsion layers and possessing spectral absorption range, subsequent to processing, substantially complementary to the predominant sensitivity range of its associated silver halide emulsion layers; an alkaline solution dyeable polymeric layer; a dimensionally stable layer transparent to incident actinic radiation; at least one layer possessing neutralizing capacity effective to reduce the alkaline processing composition stepwise ot a second pH at which the dyes are soluble and diffusible and subsequently to a third pH at which the dyes are substantially nondiffusible positioned intermediate at least one of the dimensionally stable opaque or transparent layers and next adjacent essential layer; and means of securing the layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing composition possessing said first pH and retaining substantially uniformly dispersed therein an inorganic light-reflecting pigment and at least one optical filter agent, substantially nondiffusible from the processing composition and possessing a pK_a below the first pH and above the second pH, exhibiting spectral absorption substantially complementary to the predominant sensitivity range of the selectivity sensitized silver halide emulsion layers, at the first pH, and the light-reflecting pigmen and optical filter agent are present in a quantity sufficient, upon distribution of the alkaline processing composition possessing the first pH as a layer intermediate the dyeable polymeric layer and next adjacent selectively sensitized silver halide emulsion layer, to provide a layer exhibting an optical transmission density $\gtrsim 6.0$ density units with respect to incident radiation actinic to the silver halide emulsion layers and an optical reflection density $\lambda 1.0$ density units with respect to incident visible radiation, and the rupturable container is positioned and extends transverse an edge of the photosensitive element to effect discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the selectively sensitized silver halide emulsion layer next adjacent;

(b) effecting discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent;

(c) effecting thereby development of each of the silver halide emulsions;

(d) immobolizing the dye associated with each of the silver halide emulsions as a function of the point-to-point degree of exposure thereof;

(e) forming thereby an imagewise distribution of mobile dye as a function of development;

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

(g) reducing the pH at the location of the optical filter agent to a second pH below the pK_a of said optical filter agent;

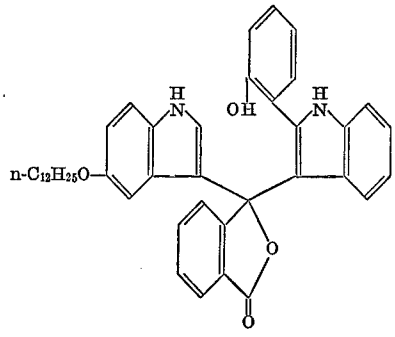
(h) transferring, by diffusion, subsequent to substantial dye transfer image formation, a sufficient portion of the ions of the alkaline processing composition to the neutralizing layer to thereby reduce the alkalinity of the composition from the second pH at which the dyes associated with the silver halide emulsions are soluble and diffusible to a third pH at which the dyes associated with the silver halide emulsions are substantially nondiffusible; and

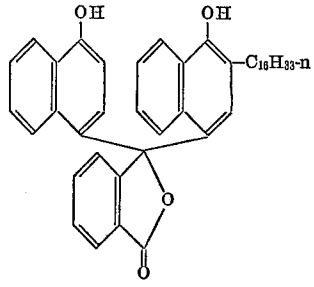
(i) maintaining the composite structure intact subsequent to processing.

39. A process for providing a photographic diffusion transfer multicolor image as defined in claim **38** which includes buffering means for maintaining said second pH for a time sufficient to provide substantial dye transfer to said dyeable polymeric layer.

40. A process for providing a photographic diffusion transfer multicolor image as defined in claim **38** wherein said inorganic light-reflecting pigment is titanium dioxide and is distributed intermediate the dyeable polymeric layer and the blue-sensitive silver halide emulsion layer at a coverage within the range of 1500 to 4000 mgs./ft.^{2}.

41. A process for providing a photographic diffusion transfer multicolor image as defined in claim **40** wherein the pH-sensitive dyes are





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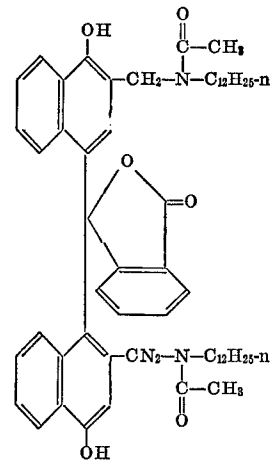

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