Sept. 25, 1973 H. G. ROGERS 3,761,271

FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 1

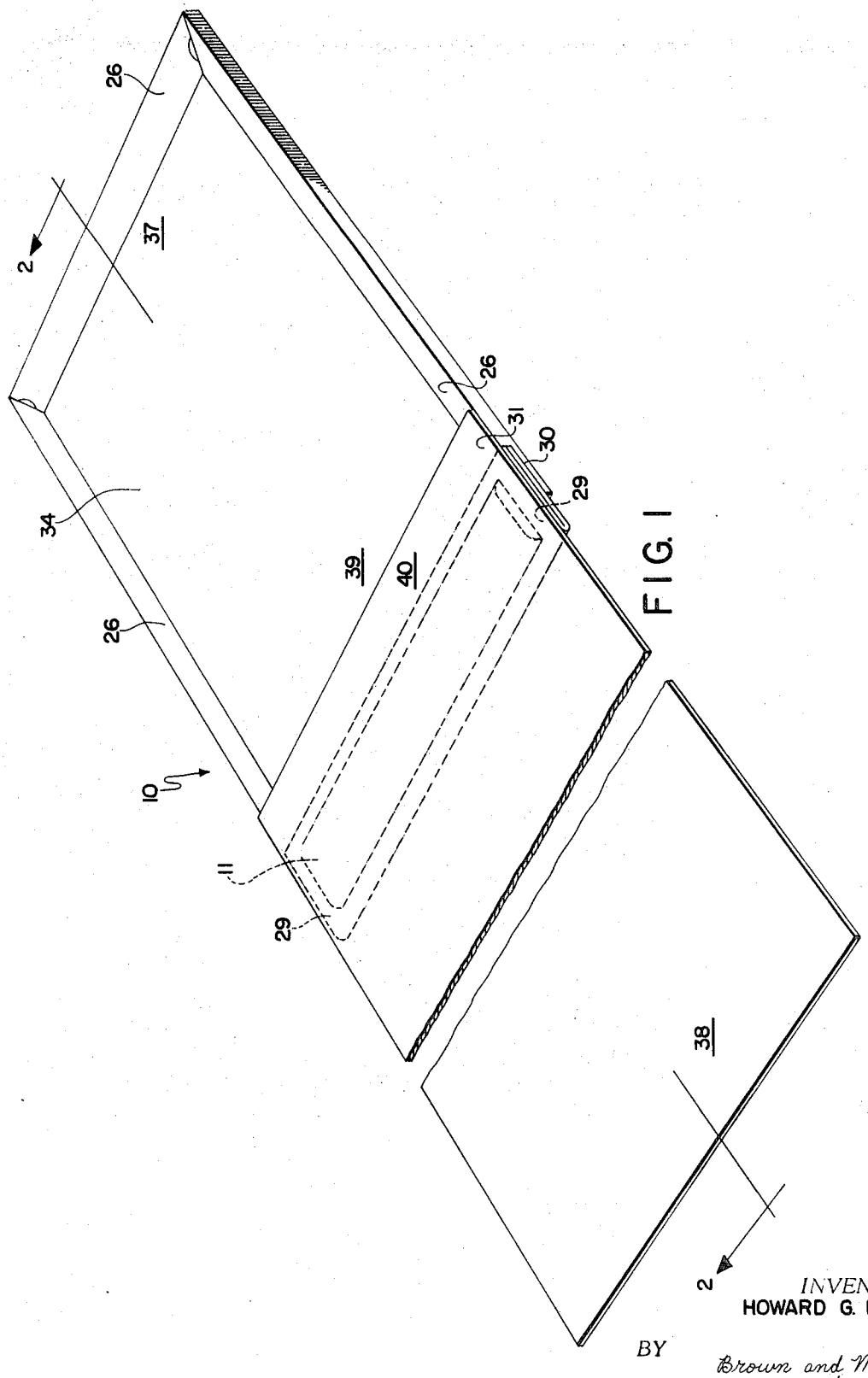


FIG. 1

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 2

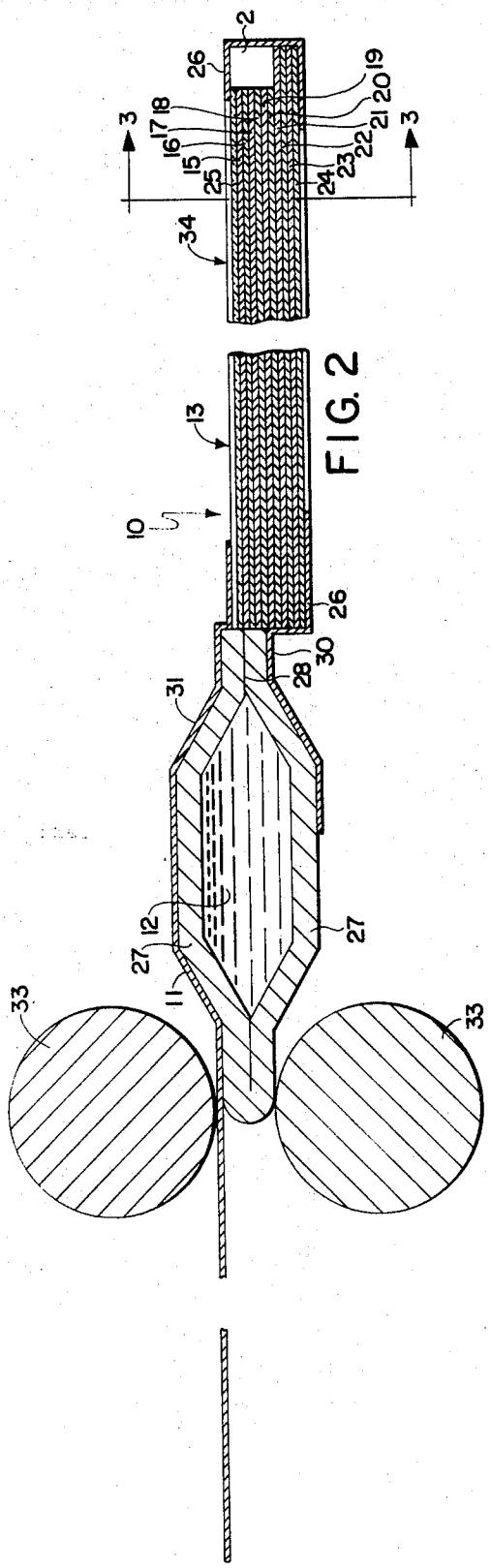


FIG. 2

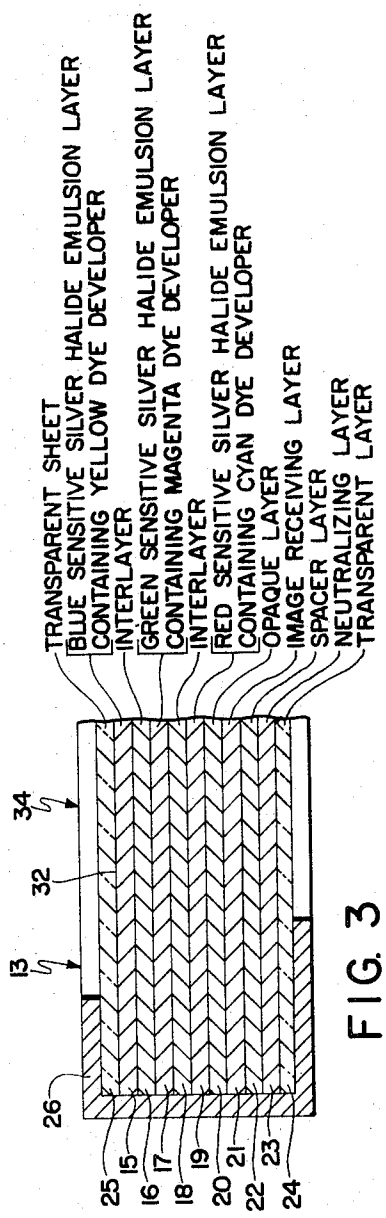


FIG. 3

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 3

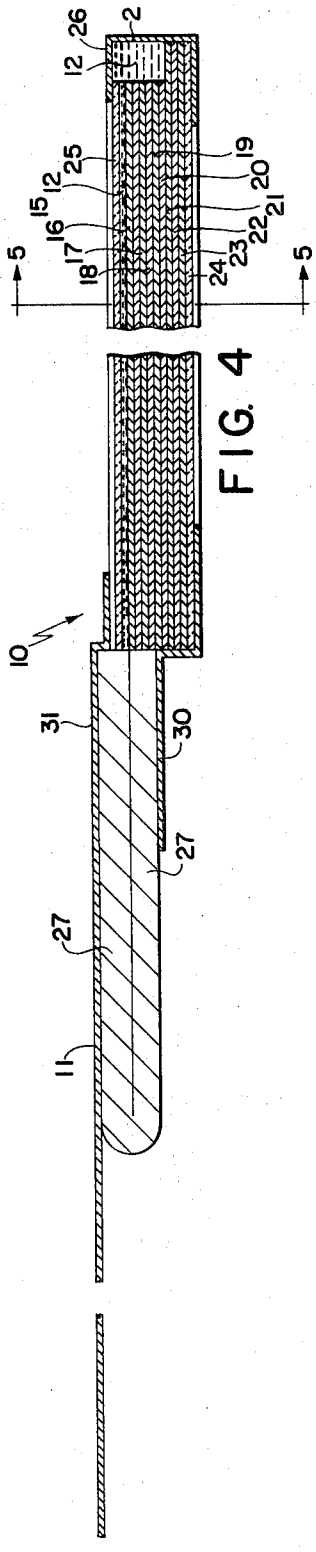


FIG. 4

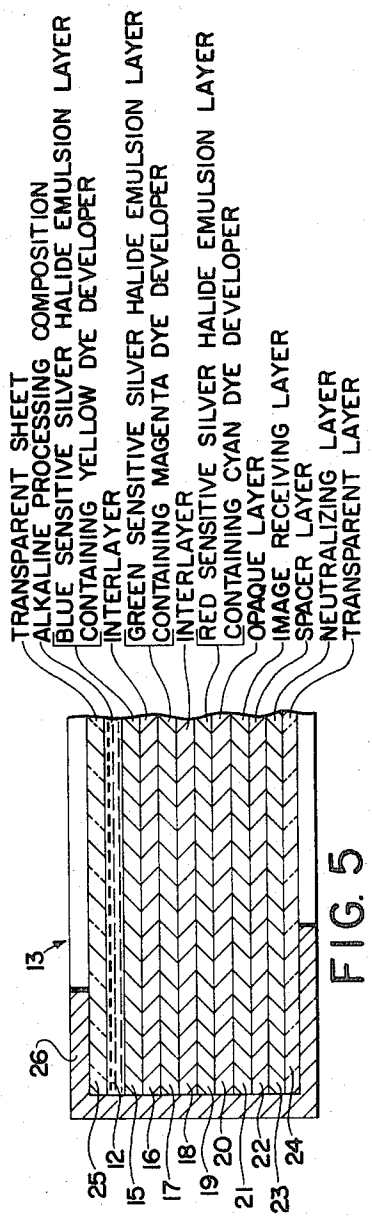


FIG. 5

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

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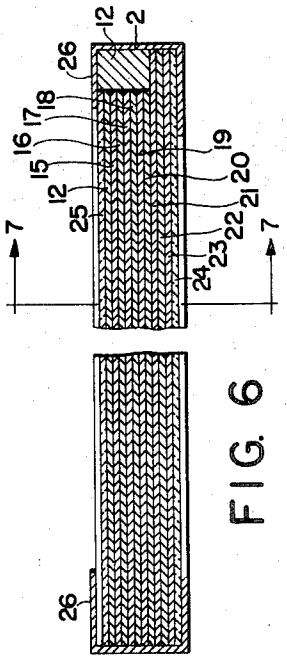


FIG. 6

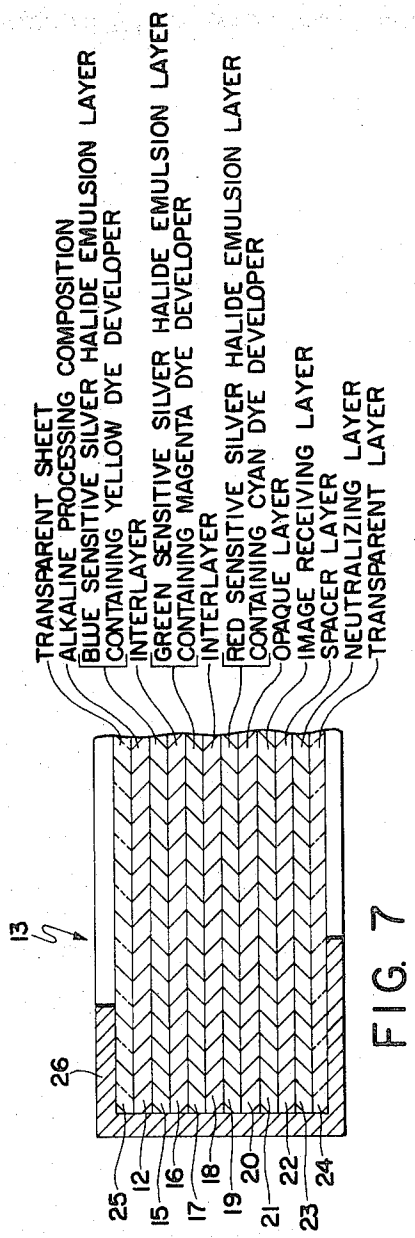


FIG. 7

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 5

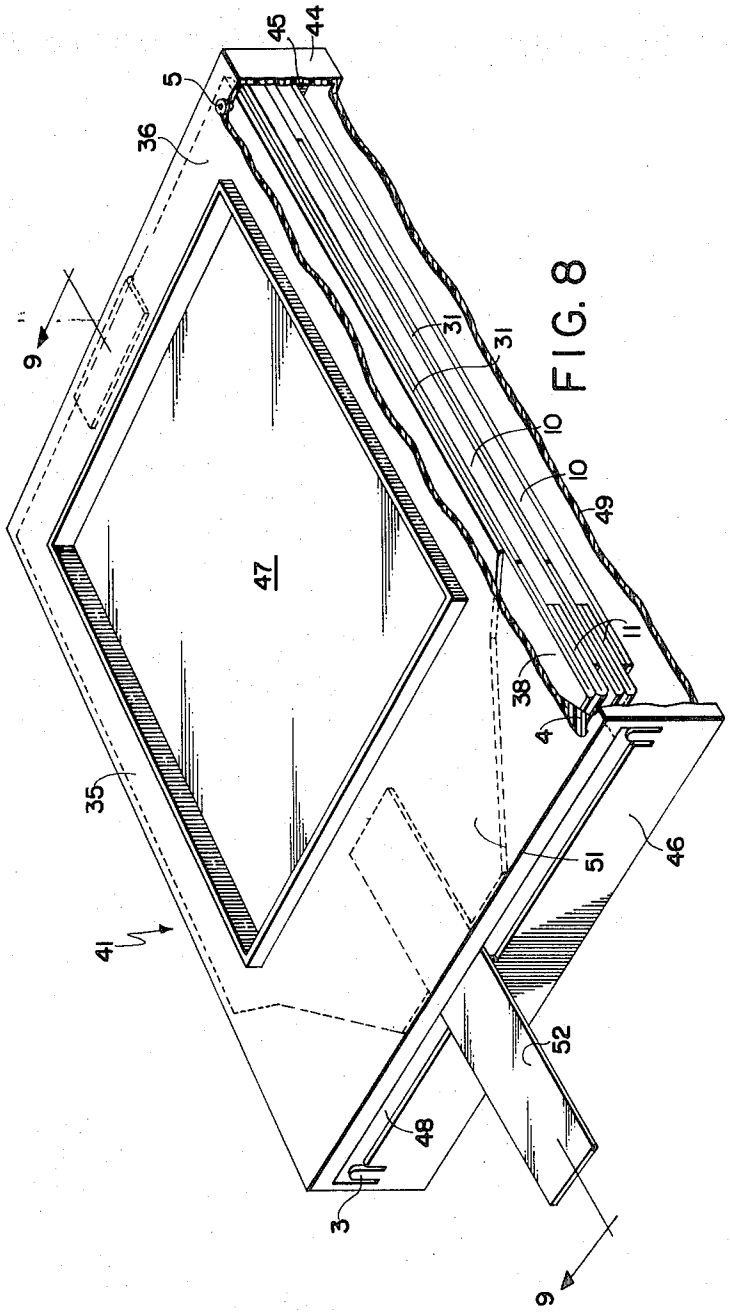


FIG. 8

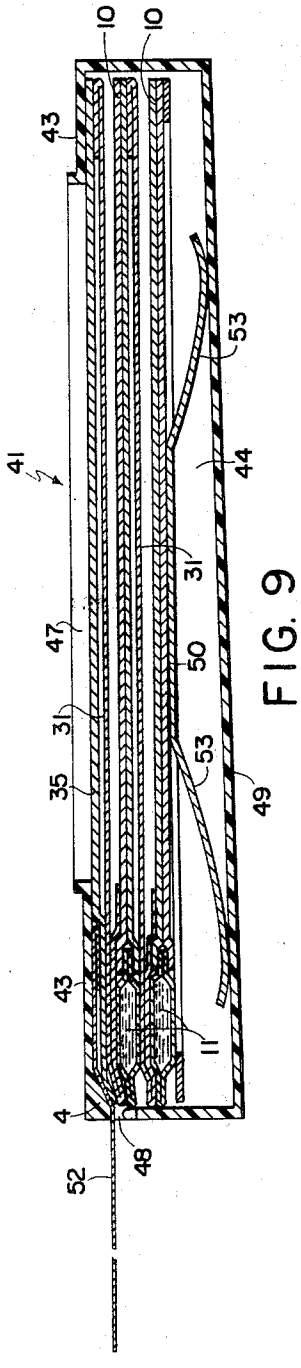


FIG. 9

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 6

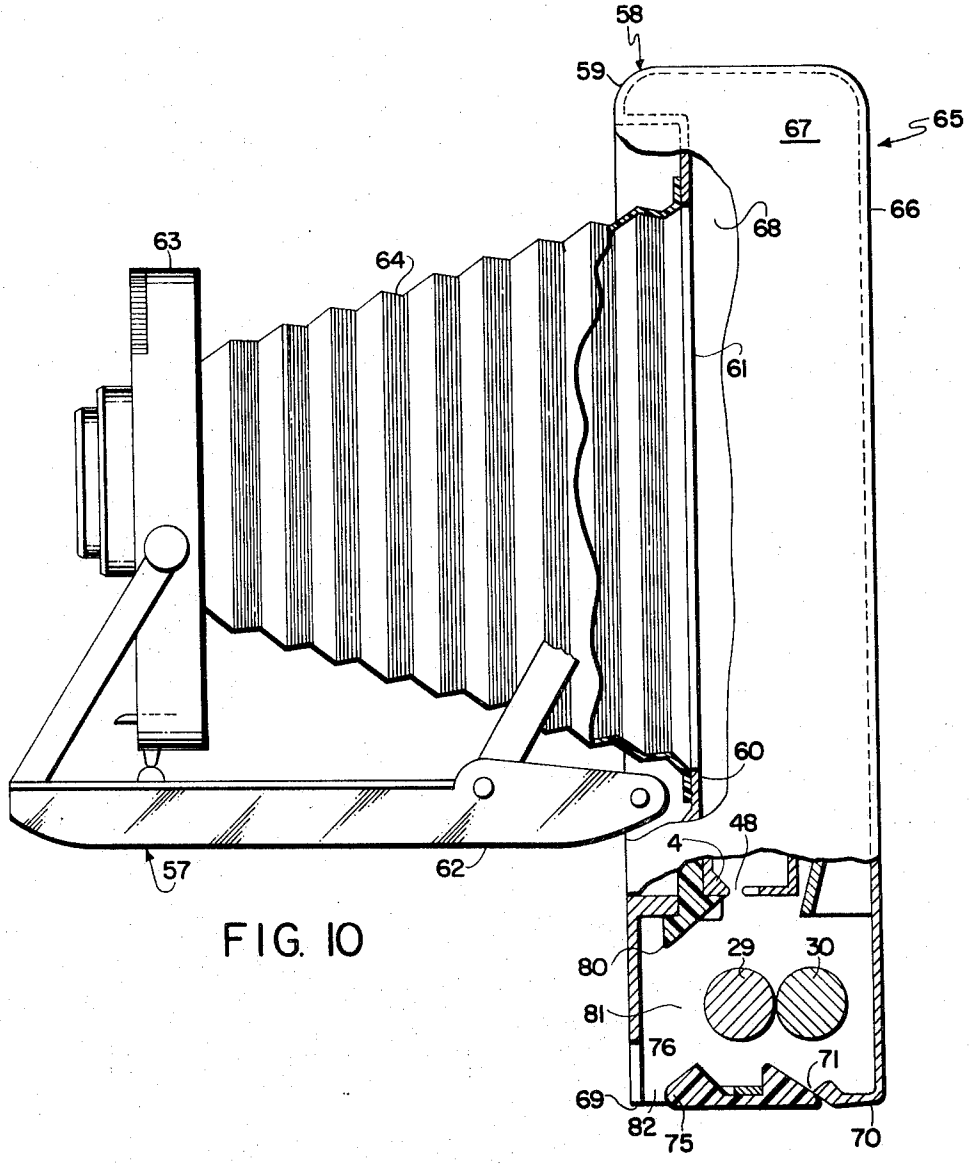


FIG. 10

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FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

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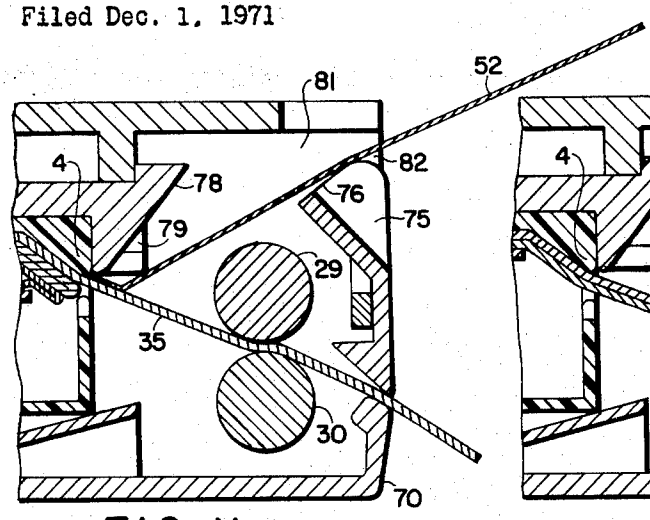


FIG. 11

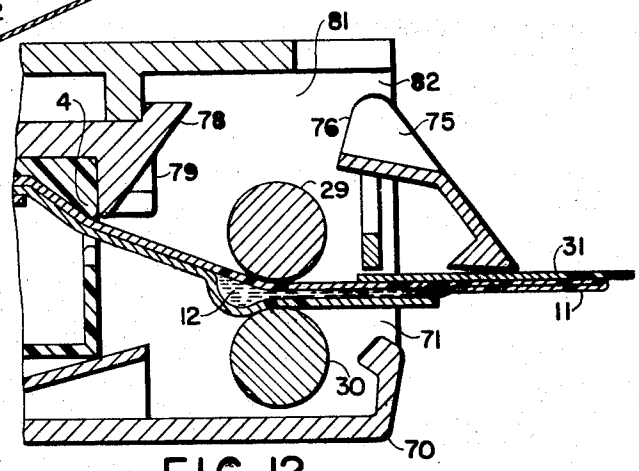


FIG. 12

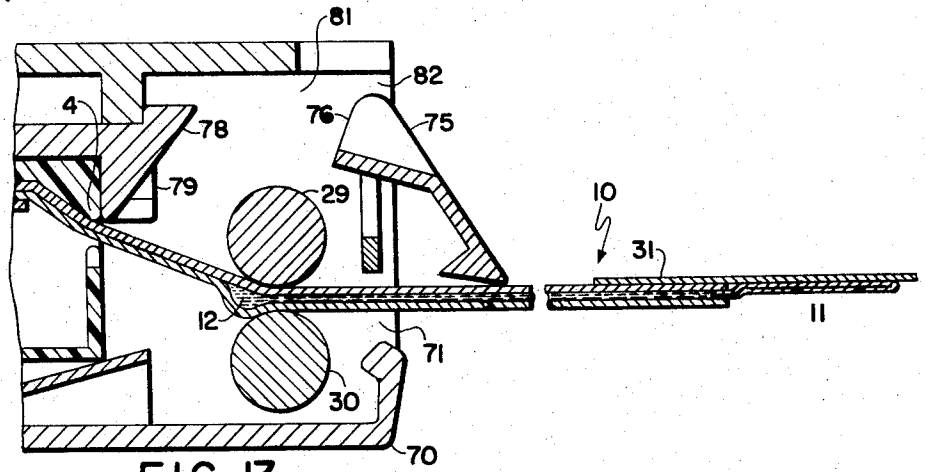


FIG. 13

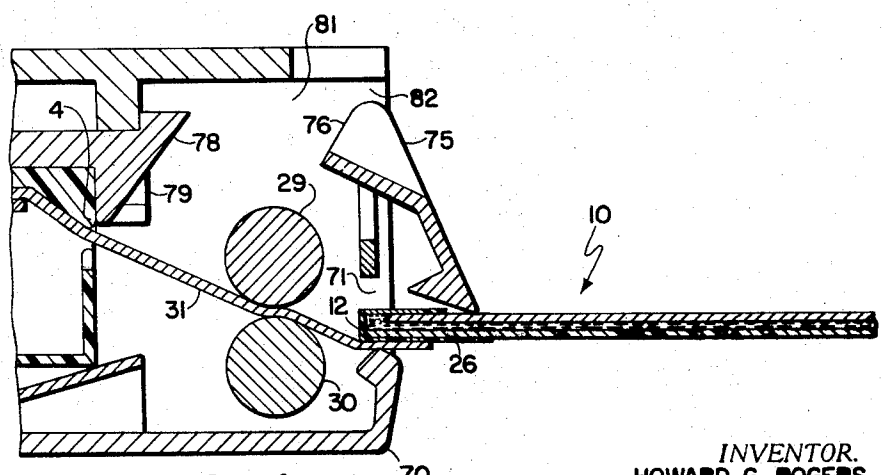


FIG. 14

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Sept. 25, 1973 H. G. ROGERS 3,761,271

FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Filed Dec. 1, 1971 8 Sheets-Sheet 8

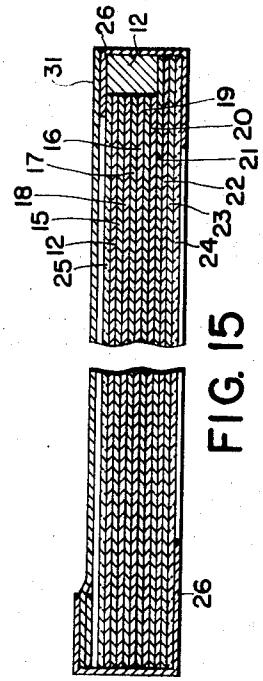


FIG. 15

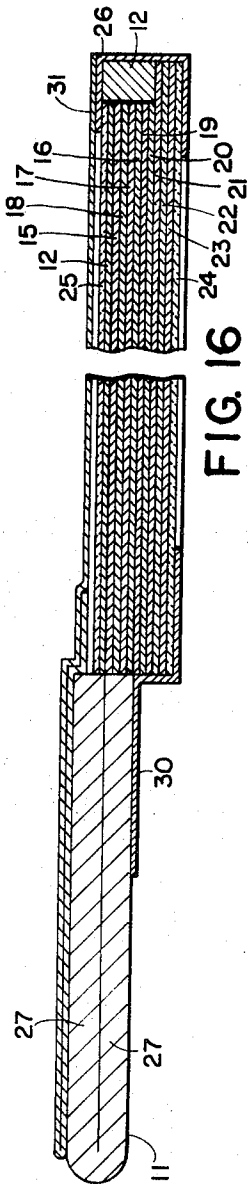


FIG. 16

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United States Patent Office 3,761,271 Patented Sept. 25, 1973

3,761,271

FILM ASSEMBLAGE FOR COLOR DIFFUSION TRANSFER FILM

Howard G. Rogers, Weston, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

Continuation-in-part of application Ser. No. 159,207, July 2, 1971, which is a continuation of application Ser. No. 39,646, May 22, 1970, now Patent No. 3,594,165, which is a continuation-in-part of abandoned application Ser. No. 815,585, Apr. 14, 1969, which in turn is a continuation-in-part of abandoned application Ser. No. 728,535, May 13, 1968. This application Dec. 1, 1971, Ser. No. 203,731

Int. Cl. G03c 1/40

U.S. Cl. 96—77 17 Claims

ABSTRACT OF THE DISCLOSURE

The present invention is directed to a new and improved film assembly for producing diffusion transfer process color reflection prints employing a film pack or magazine type film unit.

The film assembly includes, in essence, a generally rectilinear container selectively retaining, in order, and in stacked relationship, a dark slide and a plurality of color diffusion transfer process film units constructed as detailed.

The assembly specifically comprises, in combination, a generally rectilinear container including a forward wall possessing a light-transmitting section, a side wall possessing a withdrawal orifice through which a dark slide and individual diffusion transfer process color film units are adapted to be selectively withdrawn sequentially, and means for biasing the dark slide and film units toward the light-transmitting section; a dark slide disposed substantially coextensive the light-transmitting section of the container's forward wall and including a leading edge and a trailing end section; a plurality of diffusion transfer process color film units each including a leading end and a trailing end section and comprising a photosensitive laminate containing, as essential layers, in order, a dimensionally stable transparent support layer, a layer adapted to receive a diffusion transfer process dye image-forming material diffusing thereto, an opaque layer, a photosensitive silver halide layer having associated a diffusion transfer process dye image-forming material, a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the transparent support, and a rupturable container retaining a processing composition including an opacifying agent extending transverse the leading edge of the film unit to effect unidirectional discharge of the container's contents between the transparent sheet and the laminate, each of the film units disposed in stacked relationship within the container with its transparent sheet disposed toward the light-transmitting section and the rupturable container toward the withdrawal orifice; and a plurality of leader sheets each comprising a leading and a trailing end section and including a first leader sheet, the leading end section of which extends through the withdrawal orifice and the trailing end section of which is secured to the dark slide rearward of its leading edge, a second leader sheet interconnecting the dark slide and next succeeding film unit with the trailing end section of the leader sheet secured to the leading end section of the film unit, and third leader sheets each interconnecting a preceding film unit and next succeeding film unit in the stack with its trailing end section secured to the leading end section of the next succeeding film unit.

RELATED APPLICATIONS

This application is in part a continuation of my copending U.S. application Ser. No. 159,207, filed July 2, 1971, which is a continuation of Ser. No. 39,646, filed May 22, 1970, now U.S. Pat. No. 3,594,165, which is in part a continuation of Ser. No. 815,585, filed Apr. 14, 1969, now abandoned, and which in turn is in part a continuation of Ser. No. 728,535, filed May 13, 1968, now abandoned.

BACKGROUND OF THE INVENTION

The present invention is concerned with photographic film packs or film magazines particularly adapted for employment in a photographic diffusion transfer process film pack camera of the general type commercially distributed by Polaroid Corporation, Cambridge, Mass., U.S.A.

Film packs or magazines designs of the type adapted to be employed in combination with film pack cameras of the aforementioned type and those of other designs are disclosed in a multiplicity of U.S. patents including, but not limited to, U.S. Pats. Nos. 2,558,856; 2,572,358; 2,909,977; 2,978,971; 3,002,437; 3,053,660; 3,161,118; 3,161,122; 3,161,516; 3,433,636; and the like. Specifically, such film pack or film magazine may be of the type shown in U.S. Pat. No. 3,161,118, issued Dec. 15, 1964, in the name of Richard R. Wareham and may comprise, for example, a container, at least one film unit mounted for exposure within the container and a closure element for preventing the admission of light into the container. As disclosed in that patent, each film unit includes, in combination, a first photosensitive element positioned for exposure within the container; a second nonphotosensitive element, preferably a print-receiving element, adapted to be superposed with the photosensitive element; and frangible container means particularly adapted to releasably retain a fluid processing composition for distribution between the superposed photosensitive and print-receiving elements subsequent to photoexposure of the film unit.

In general, the film pack or container includes an exposure aperture adapted to permit exposure of the photosensitive element; a removable closure element located across the exposure aperture; at least one film unit; and an opening permitting withdrawal of the closure element and film units from the container successively through this opening. The closure element and each film unit includes a leader adapted to project from the film pack through the opening whereby to provide means for selectively withdrawing the closure element, or a film unit, from the film pack into contact, and in engagement, with means adapted to provide individual distribution of the retained fluid processing composition, between superposed photosensitive and nonphotosensitive elements.

Film packs of this type are intended to be employed in photographic apparatus, such as a camera, which include means for maintaining a film pack in position for exposure, means for selectively exposing the photosensitive element of successive film units of the pack, and means for engaging each film unit during withdrawal from the pack, subsequent to photoexposure, and distributing the retained processing fluid between, and in contact with, the contiguous photosensitive and print-receiving elements of the film unit, for effecting photographic diffusion transfer processing of the respective photoexposure film unit. Processing of each film unit may thus be effected manually by grasping a leader attached to the film unit and withdrawing the leader and film unit from both the pack and the camera.

In photographic diffusion transfer process film units commercially available, the photosensitive sheet element

is normally first exposed and then biased into superposed relationship with a second sheet element, which is, in general, photographically inert and aids in the controlled distribution of the processing composition. The photosensitive element may contain an integral print-receiving stratum or the second sheet element may comprise a transfer image-receiving element. The contiguous sheet elements are moved relative to, and between, a pair of suitably opposed members such as gapped parallel pressure rollers or platens. Application of pressure to the frangible fluid-retaining means effects controlled rupture thereof and predetermined unidirectional distribution of its processing composition contents between, and in contact with, the opposed surfaces of the superposed elements. Subsequent to transfer processing, the image-carrying area of the print-receiving element is generally separated from the laminate.

In general, color photographic reproduction may be provided by diffusion transfer processing such as exposing a photoresponsive material, for example, photosensitive silver halide layer having associated therewith dye image-providing material which is processing composition diffusible, as a function of exposure of its associated photosensitive silver halide, such as the dye image-providing materials disclosed in U.S. Pats. Nos. 2,983,605, 2,983,606; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,764; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; 3,209,016; 3,482,972; 3,563,739; 3,551,406; 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,347,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; 2,774,668; 3,087,817; etc., as adapted to provide imagewise differential transfer of dye image-providing material to a contiguous image-receptive element providing dye image formation to such element as a function of the point-to-point degree of silver halide layer photoexposure.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved film assembly for producing diffusion transfer process color reflection prints employing a film pack or magazine type unit. The assembly includes, in essence, a generally rectilinear container selectively retaining, in order and in stacked relationship, a dark slide and a plurality of film units constructed as detailed hereinafter.

Specifically, the assembly comprises, in combination:

(1) a generally rectilinear container including a light-transmitting section, i.e., an exposure aperture positioned in a first wall, a withdrawal orifice positioned in a second wall preferably normal to the first wall through which a dark slide and individual diffusion transfer process color film units are adapted to be selectively withdrawn sequentially, and means for biasing the dark slide and film units toward the exposure aperture;

(2) a dark slide disposed substantially coextensive the exposure aperture and including a leading edge and a trailing end section;

(3) a plurality of diffusion transfer process color film units each including a leading end and a trailing end section and comprising:

(a) a photosensitive laminate containing, as essential layers, in order:

(i) a dimensionally stable transparent support layer;

(ii) a layer adapted to receive a diffusion transfer process dye image-forming material diffusing thereto;

(iii) an opaque layer; and

(iv) a photosensitive silver halide layer having associated therewith a diffusion transfer process dye image-forming material;

(b) a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the transparent support layer; and

(c) a rupturable container retaining a processing composition including an opacifying agent positioned extending transverse the leading end of the film unit to effect, upon application of compressive pressure to the container, unidirectional discharge of the container's contents intermediate the transparent dimensionally stable sheet and the photosensitive laminate,

each of the film units disposed in stacked relationship in the container with the dimensionally stable transparent sheet disposed toward the exposure aperture and the rupturable container disposed toward the second wall containing the withdrawal orifice; and

(4) a plurality of leader sheets each comprising a leading and a trailing end section and including a first leader sheet the leading end section of which extends through the withdrawal orifice and the trailing end section of which is secured to the dark slide rearward of its leading edge, a second leader sheet interconnecting the dark slide and the next succeeding film unit with the trailing end section of the leader sheet secured to the leading end section of the unit, and third leader sheets each interconnecting a preceding film unit and next succeeding film unit in the stack with trailing end section of the leader sheet secured to the leading end section of the succeeding film unit.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary perspective view of one embodiment of a photographic film unit in accordance with 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 as 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 transfer process.

FIG. 8 is a perspective view of a film pack comprising an assembladge of film units;

FIG. 9 is a longitudinal sectional view taken substantially midway between the sides of the film pack of FIG. 8;

FIG. 10 is an elevational view, partially in section, of photographic apparatus in the form of a camera for employing film units; embodying the invention;

FIG. 11 is a fragmentary sectional view, similar to FIG. 10, illustrating passage of the dark slide between a pair of opposed pressure rolls as a function of withdrawal of the dark slide's leader sheet from the camera apparatus of FIG. 10, prior to photoexposure of the first film unit of the assembly;

FIG. 12 is a fragmentary sectional view, similar to FIG. 11, illustrating passage of one film unit between the pair of opposed pressure rolls, rupture of the frangible container and distribution of its fluid processing composition contents between, and in contact with, the opposed surfaces of the superposed sheet elements of the film unit during removal of the film unit from the camera apparatus of FIG. 10;

FIG. 13 is a fragmentary sectional view, similar to FIG. 12, illustrating further passage of the film unit be-

tween the pair of opposed pressure rolls and further distribution of its fluid processing composition between, and in contact with, the opposed surfaces of the superposed sheet elements;

FIG. 14 is a fragmentary sectional view, similar to FIG. 13, illustrating completion of the passage of the film unit between the pair of opposed pressure rolls, the laminate formed by distribution of the fluid processing composition between the superposed sheet elements;

FIGS. 15 and 16 are diagrammatic, enlarged cross-sectional views of the film unit of FIG. 1, similar to FIG. 6, illustrating further embodiments of the film unit at the stage of processing illustrated as FIG. 6.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, the preferred form of the film assemblage for the production of a dye reflection print comprises a photosensitive film unit specifically adapted to be processed in the presence of ambient radiation and the dye reflection print image to be viewed during and subsequent to processing without separation of film unit components including a first photosensitive sheet element comprising a transparent support carrying on one surface a diffusion transfer process dye image receptive layer, an opaque layer and a layer of a photoresponsive material having associated therewith a dye image-providing material, which is processing composition diffusible as a function of the photoexposure of its associated photoresponsive material to produce photographic information recordation. The film unit additionally includes a second transparent sheet element superposed coextensive the surface of the first sheet opposite its transparent support; a rupturable container containing a fluid agent including an opacifying agent for distribution between the first and second sheet elements for reacting with exposed photoresponsive material for forming the image in the image-receptive layer; means including a leader for coupling film units and selectively withdrawing the units sequentially from a film pack or magazine; and the opacifying agent disposed in the processing composition, taken together with the opaque layer, adapted to prevent exposure of the first sheet element's photoresponsive material by radiation actinic thereto incident on the film unit in the processing mode.

The preferred form of film pack or magazine embodying the designated film units comprises a plurality of the film assemblies, each adapted to be individually exposed in a camera, enclosed in a light-proof container which allows the film units to be sequentially exposed. The container includes a forward wall having a light-transmitting section, e.g., an exposure aperture, therein and an opening in one end through which film assembles can be individually withdrawn. The photosensitive film units are positioned together in stacked relationship within the container underlying the exposure aperture with the exposure surface of each film unit uppermost and the rupturable container positioned adjacent the opening through which the film units are withdrawn so that following the exposure of each film unit, the unit is moved, by drawing on the leader of the film unit, and withdrawn from the container through the opening. The film pack is initially provided with a cover element or sheet mounted within the container and extending across the exposure aperture for closing the aperture against the admission of light. The cover element also includes a leader extending from the container through the opening and being removable therethrough.

The film pack is employed by being positioned in a camera, including a pair of juxtaposed pressure-applying members, with the opening located adjacent the pressure-applying members and the exposure aperture disposed approximately in the exposure plane of the camera. A leader of the cover element extends from the pack and from the camera where the last-mentioned leader may be grasped for withdrawing the cover element from the pack through the pressure-applying members and camera to allow the film units of the pack to be selectively exposed. After each successive film unit is exposed, that film unit is then individually withdrawn from the container and camera between the pressure-applying members by withdrawing the leader of the first film unit and of successive film units from the container and camera.

By employing the film assemblages of the present invention, color reflection prints can be provided employing photographic diffusion transfer processing effected external the camera in which the film units were subjected to exposure and in the presence of ambient radiation.

Multicolor images may be obtained using color image-forming components in the diffusion transfer process of the present invention by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing, for example, dye developers as dye image-providing materials by employment of an integral multilayer photosensitive element, such as is disclosed in aforementioned U.S. Pat. No. 2,983,606 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 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 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 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 orthodihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion, in a preferred embodiment, or in a separate layer behind the respective silver halide stratum. Specifically, the dye developer may, for example, be in a coating or layer behind or directly disposed in the respective silver halide stratum and such dye developer

structure may be applied by use of a coating solution about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

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, at least two selectively sensitized silver halide emulsion strata each having dye image-providing material of predetermined image color subsequent to processing associated therewith which is soluble and diffusible, in alkali, at a first pH, as a function of the photoexposure of its associated silver halide emulsion stratum; an alkaline solution permeable opaque layer; an alkaline solution permeable polymeric layer dyeable by the dye image-providing materials; an alkaline solution permeable polymeric layer containing sufficient acidifying capacity to effect reduction, subsequent to substantial multicolor transfer dye image formation, of a processing composition having the first pH to a second pH, at which the dye image-providing material is substantially non-diffusible; and the dimensionally stable transparent layer.

The silver halide emulsions 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 the first pH, possessing subsequent to photoexposure or processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion. Specifically preferred dyes comprise dyes which exhibit major spectral absorption outside of the primary regions of the spectrum to which the associated silver halide emulsion is sensitive and a spectral transmission substantially complementary to that absorption, during exposure of the emulsion, and major spectral absorption within the spectral range to which the associated silver halide emulsion is sensitive and spectral transmission substantially complementary to said absorption, subequent to exposure or processing of said emulsion, for example, of the type disclosed in U.S. Pat. No. 3,307,947.

In one embodiment each of the emulsion strata, and its associated dye, may be spaced from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers and the dyeable polymeric layer next adjacent the polymeric acid layer may be separated from that layer by an alkaline solution permeable polymeric spacer layer, most preferably a polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

In such preferred embodiments of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself may be dispersed in an aqueous alkaline solution permeable 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 alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; the alkaline solution polymeric spacer layer is transparent and about 0.1 to 0.7 mil in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mils in thickness; and the dimensionally stable transparent layer is alkaline solution impermeable and about 2 to 6 mils in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

In view of the fact that the preferred dye image-providing materials comprise dyes which are silver halide developing agents, as stated above, the present invention will be further described hereinafter in terms of such dyes without limitation of the invention to the illustrative dyes.

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 yellow dye developer/blue-sensitive emulsion unit, a cyan dye developer/red-sensitive emulsion unit and a 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.

In those instances, where either or both the respective yellow and magenta dye developers, employed in a preferred tripack configuration which positions the yellow dye developer/blue-sensitive emulsion unit distal the dimensionally stable transparent layer and the cyan dye developer/red-sensitive emulsion unit proximal the transparent layer to provide the multicolor transfer image, comprise a dye developer which exhibits major spectral absorption outside of the primary region of the spectrum to which its associated silver halide emulsion is sensitive and a spectral transmission substantially complementary to that absorption, during exposure of the emulsion, then, in ordinary circumstances, it may be advantageous to incorporate filter agents adapted to insure the correct selective exposure of the respective emulsions less proximal the exposure surface of the laminate. Specifically, in the instance where the yellow dye developer exhibits major spectral absorption outside of the primary regions of the spectrum to which its associated silver halide emulsion is sensitive, that is, the blue region of the visible spectrum, during exposure of the emulsions, then a yellow filter agent may advantageously be incorporated intermediate the blue-sensitive emulsion and the remaining green- and red-sensitive emulsions, in order to prevent undesired exposure of the latter emulsions by reason of their inherent sensitivity to actinic radiation within the blue range of the spectrum generally present. In the instance where the magenta dye developer employed exhibits major spectral absorption outside of the primary region of the spectrum to which its associated silver halide emulsion is sensitive, that is, the green region of the visible spectrum, during exposure of the emulsions, a magenta filter agent may be advantageously incorporated intermediate the green- and red-sensitive emulsions in instances wherein the red-sensitive emulsion possesses sensitivity to actinic radiation within the green region of the spectrum.

Where desired, the yellow dye developer employed in such preferred embodiment also may be disposed in the processing composition retained within the container and distributed contiguous the exposure surface of the blue-sensitive emulsion, subsequent to exposure of the photosensitive laminate, during processing of the exposed film unit, to provide the desired multicolor transfer image formation. In the latter embodiment, it may be desirable to incorporate a yellow filter agent intermediate the blue- and green-sensitive emulsion units of the photosensitive laminate for the reasons stated above.

Employment of the detailed film unit of the present invention, according to the hereinafter described color diffusion transfer photographic process, is specifically adapted to provide for the production of a color transfer image accomplished by a diffusion transfer process which may include in-process adjustment of the environmental pH of the film unit, from a pH at which transfer processing is operative to a pH at which dye transfer is substantially inoperative, subsequent to substantial transfer

image formation, in order to obviate the previously discussed disadvantages of the prior art products and processes. The color transfer image is thus obtained and maintained irrespective of the fact that the film unit comprises an integral laminate unit during exposure, processing and subsequent viewing, and storage of the unit. Accordingly, by means of the present invention, color transfer images and specifically multicolor images may be obtained, employing an integral laminate film unit, which exhibit desired maximum and minimum dye densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation, over an extended period of time, as compared with prior art disclosed film materials. 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.

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 alkaline solution **12**, photosensitive laminate **13** including, in order, blue-sensitive silver halide emulsion layer **15** containing yellow dye developer; interlayer **16**; green-sensitive silver halide emulsion layer **17** containing magenta dye developer; interlayer **18**; red-sensitive silver halide emulsion layer **19** containing cyan dye developer; opaque layer **20**; image-receiving layer **21**; spacer layer **22**; neutralizing layer **23**; and dimensionally stable transparent layer **24**; and dimensionally stable transparent sheet **25**; both layer **24** and sheet **25** preferably comprising an actinic radiation transparent and processing composition impermeable flexible sheet material.

The composite may be provided with a binding member extending around, for example, the specified edges of composite, maintaining the laminate and sheet element comprising the composite intact except at the interface between the elements during distribution of processing composition **12**. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape **26** securing the sheet and laminate elements together at the composite's specified edges. Tape **26** will also act to maintain processing composition **12** intermediate sheet **25** and photosensitive laminate **13** upon application of compressive pressure to container **11** and distribution of its contents intermediate the stated elements. Under such circumstances, binder tape **26** will act to prevent leakage of processing composition from the film unit during and subsequent to photographic processing. In the preferred embodiment illustrated, that portion of binding sheet **26** which overlies the lateral edge section of transparent sheet **25** is less than the portion of transparent support layer **24** overlaid by sheet **26** in order to insure processing distribution and resultant dye image formation at least equal to the viewing frame area circumscribed by the binding sheet overlying transparent sheet **24** through which the dye image is to be viewed.

In addition, as illustrated, binding sheet **26** overlying and secured to the trailing edge sections of transparent sheet **25** and transparent support layer **24** cooperates with the trailing edge of the sheet and support layer to provide an enclosed chamber or trap area **2** adapted to secure and retain excess processing composition **12**, employed to insure adequate processing composition coverage upon distribution, discharged from between the trailing edge sections of the transparent sheet and support layer. To further facilitate distribution of processing composition **12** between transparent sheet **25** and photosensitive laminate **13**, binding member **26** may be provided with one or more air release vents **1** associated with the trailing edge section of the film unit and preferably in direct communication with trap chamber **2** in order to facilitate release of air from the film unit during distribution of processing composition **12**.

Rupturable container **11** may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,491; 3,056,492; 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 **27** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing solution **12** is retained. The longitudinal marginal seal **28** is made weaker than the end seals **29** 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 **27** of the container.

As illustrated in FIGS. 1, 2 and 4, 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** intermediate transparent sheet **25** and surface **32** of blue-sensitive silver halide emulsion layer **15**, 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 **28** directed toward the leading edge of surface **32**. As shown in FIGS. 1, 2 and 4, container **11** is fixedly secured to laminate **13** by extension **30** of tape **26** extending over a portion of one wall **27** of the container, in combination with a separate retaining member such as illustrated retaining tape **31** extending over a portion of the other wall **27** of the container and a portion of laminate **13**'s surface **32** generally equal in area to about that covered by tape **26**.

Transparent sheet **25**, as illustrated in the figures in the preferred embodiment, is fixedly maintained superposed on and coextensive with surface **32** of blue-sensitive emulsion layer **15**, at least during processing, to facilitate distribution of processing composition **12** upon compressive rupture of container **11** and uniderectional discharge of its contents on surface **32**.

As illustrated in FIGS. 1, 2 and 4, extension flap **30** of tape **26** may be of such area and dimensions that upon, for example, manual separation of container **11** and leader **31**, subsequent to distribution of the composition, from the remainder of film unit **10**, flap **30** may be folded over the edge of laminate **13**, previously covered by leader **31**, 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 **24**. Preferably, however, the film unit will be maintained intact subsequent to processing including retention of the exhausted container, the processing composition and transparent sheet in the spacial position assumed during processing. In such instance, the processing composition employed should possess the requisite adhesive capacity, in both the fluid and dry states, to enhance the integrity and stability of the spacial arrangement assumed.

In general, in a particularly preferred embodiment, the opacity of processing composition **12** when distributed will be sufficient to prevent further exposure of the film unit's

silver halide emulsion or emulsions, by actinic radiation incident on transparent sheet **25**, during processing of the unit in the presence of radiation actinic to the emulsion or emulsions. Accordingly on the film unit may be processed, subsequent to exposure, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of the laminate are appropriately protected from incident radiation, at one major surface by the opaque layer or layers **20** and at the remaining major surface by opaque processing composition **12** as further described hereinafter. If the illustrated binder tapes are also opaque, as stated above, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The selected opaque layer or layers **20**, however, 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 permeable opaque layer may be employed, it is preferred that a layer be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, a layer 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 opaque layers will be those providing a white background, for viewing the transfer image, and specifically those adapted to be employed to provide background for reflection photographic prints and, especially, those layers possessing the optical properties desired for reflectance of incident radiation.

The opaque layer may comprise substantially any opacifying agent compatible with the photographic system, such as, for example, barium sulfate, zinc oxide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica and the like, which may be distributed in a permeable polymeric matrix or binder, such as, for example, gelatin, polyvinyl alcohol, and the like.

A particularly preferred opaque layer comprises titanium dioxide due to its highly effective reflection properties. In general, a coating composition, for example, hydroxyethylcellulose, containing sufficient titanium dioxide to provide a percent reflectance of about 85 to 99%, respectively, will be employed. In the most preferred embodiments, the percent reflectance desired thus will be in the order of about 85%.

Where it is desired to increase the opacifying capacity of a layer containing, for example, titanium dioxide, beyond that ordinarily obtained, an additional opacifying agent such as carbon black, for example, in a concentration of about 1 part carbon black to 100 to 500 parts titanium dioxide may be provided to the layer. Preferably, however, such additonal opacifying capacity will be provided by constituting the opacifying layer as a plurality of more or less discrete layers, the layer next adjacent the transparent support comprising a reflection layer and the succeeding layer or layers comprising one or more opacifying agents possessing greater opacifying capacity than tha ordinarily obtained from the reflecting agent or agents employed.

The opacifying agent dispersed in processing composition **12** may be any of the multiplicity of such agents known in the art such as carbon black, iron oxide, titanium (III) oxide, titanium (III) hydroxide, and the like. In preference, the agent or agents should be selected which possess the maximum opacifying capacity per unit weight, is photographically nondeleterious and is substantially nondiffusible throughout the film unit subsequent to distribution. A particularly preferred agent has been found to comprise carbon black employed in a concentration effective to provide the opacity required to prevent undesired physical fogging of the emulsion formulations selected and employed by radiation transmitted through the speed processing composition.

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 **33** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **28** and distribution of processing composition **12**, containing an opacifying agent and having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate transparent sheet **25** and blue-sensitive silver halide emulsion layer **15** on a coextensive surface **32**.

Processing composition **12** permeates emulsion layers **15**, **17** and **19** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **15**, **17** and **19**, 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, magneta 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 transfer, by diffusion, to processing composition permeable polymeric layer **21** to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous composition **12** transfer, by diffusion, through permeable polymeric layer **21**, permeable spacer layer **22** and to permeable polymeric acid layer **23** whereby solution **12** decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image viewable through dimensionally stable transparent layer **24**.

Subsequent to distribution of processing solution **12**, container **11**, optionally, may be manually dissociated from the remainder of the film unit, as described above.

As previously stated, the multicolor dye transfer image is viewable through dimensionally stable transparent layer **24** both during and subsequent to transfer image formation, in the preferred embodiment detailed above. In addition, a multicolor dye image, negative with respect to the transfer image, may be viewed subsequent to processing, through surface **34** of the laminate, in embodiments wherein sheet **25** and processing composition are separated from the remainder of the photosensitive laminate subsequent to processing.

The present invention will be further illustrated and detailed in conjunction with the following illustrative constructions which set out representative construction of the photographic film units employed in the practice of this invention, which, however, are not limited to the details herein set forth and are intended to be illustrative.

Film units similar to that set forth in the drawings may be prepared, for example, by coating, in succession, on a transparent cellulose triacetate film base:

(1) The partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing for 14 hours, about 300 grams of high viscosity poly-(ethylene/maleic anhydride), about 140 grams of n-butyl alcohol and about 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.75 mil thick;

(2) A solution of hydroxy propyl cellulose in water to provide a polymeric spacer layer approximately 0.075 mils thick;

(3) A 2:1 mixture, by weight, of polyvinyl alcohol and

poly-4-vinylpyridine, at a coverage of approximately 600 mgs./ft.^{2}, to provide a polymeric image-receiving layer approximately 0.40 mils thick;

(4) A layer of titanium dioxide dispersed in hydroxyethyl cellulose and coated at a coverage of about 1200 mgs./ft.^{2} of titanium dioxide and about 30 mgs./ft.^{2} of hydroxyethyl cellulose;

(5) A layer of gelatin coated at a coverage of about 200 mgs./ft.^{2};

(6) A layer of the acrylic latex sold by Rohm and Haas Co., Philadelphia, Pa., under the trade designation Rhoplex AC–61 coated at a coverage of about 110 mgs./ft.^{2};

(7) A layer of carbon black dispersed in hydroxyethyl cellulose coated at a coverage of about 150 mgs./ft.^{2} carbon black and about 3.0 mgs./ft.^{2} hydroxyethyl cellulose;

(8) A layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl - α - methyl] - ethyl-amino)-5,8-dihydroxyanthraquinone and carbon black dispersed in gelatin and coated at a coverage of about 50 mgs./ft.^{2} of dye, about 180 mgs./ft.^{2} of carbon black and about 63 mgs./ft.^{2} of gelatin;

(9) A red-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 120 mgs./ft.^{2} of silver and about 22 mgs./ft.^{2} of gelatin;

(10) A layer of Rhoplex AC–61 coated at a coverage of about 80 mgs./tf.2;

(11) A layer of the magenta dye developer 4-isopropoxy - 2 - [p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-ethoxy acetate dispersed in a green-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 80 mgs./ft.^{2} of dye, about 110 mgs./ft.^{2} of silver and about 150 mgs./ft.^{2} of gelatin;

(12) A layer of the last-mentioned magenta dye developer dispersed in gelatin at a coverage of about 20 mgs./ft.^{2} of dye and about 30 mgs./ft.^{2} gelatin;

(13) A layer of Rhoplex AC–61 coated at a coverage of about 110 mgs./ft.^{2};

(14) A layer of the yellow dye developer 4-(p-[β-hydroquinonyl ethyl] - phenylazo) - 3-(N-n-hexylcarboxamido)-1-phenyl-5-pyrazolone dispersed in gelatin and coated at a coverage of about 140 mgs./ft.^{2} of dye and about 175 mgs./ft.^{2} of gelatin;

(15) A blue-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 150 mgs./ft.^{2} of silver and about 28 mgs./ft.^{2} of gelatin; and

(16) A layer containing 4'-methylphenyl hydroquinone dispersed in gelatin at a coverage of about 20 mgs./ft.^{2} of 4'-methylphenyl hydroquinone and about 30 mgs./ft.^{2} of gelatin.

Transparent cellulose triacetate film base may then be superposed on the external surface of coating No. 16 and the two components then taped together, in composite form, at their respective edges by means of opaque pressure-sensitive binding tape extending around, on contact with, and over the edges of the resultant film unit.

A rupturable container comprising an outer layer of paper, an intermediate 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]	gms..	3.4
N-benzyl-α-picolinium bromide	gms..	1.5
Benzotriazole	gms..	1.0
Carbon black	gms..	6.4

may then be fixed mounted on the leading edge, of each of the composites, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that upon application of compressive pressure to the container, its contents will be distributed, upon rupture of the container's marginal seal, intermediate the cellulose triacetate sheet and the 4'-methylphenyl hydroquinone containing layer.

The photosensitive laminates may be exposed through step wedges to selectively filtered radiation incident on the cellulose triacetate sheet and processed as detailed herein. During processing, a multicolor dye transfer image formation may be viewed through the cellulose triacetate film base and such image formation is found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation within a period of about 1 to 3 minutes.

The pH and solvent concentration of the alkaline processing solution initially employed must be a pH at which the dye developers employed are diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer, or group of dye developers, most particularly desirable developers are soluble at pH's above 9 and relatively insoluble at pH's below 9, in reduced 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. In the latter instance, however, it will be preferred that the concentration of solvent, that is, water, etc., comprising the composition be the minimum amount necessary to conduct the desired transfer process, in order not to adversely effect the structural integrity of the laminate and that the layers forming the laminate can readily accommodate and dissipate the solvent throughout during processing and drying without effecting undesirable dimensional changes in the layers forming the laminate.

Naturalizing 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 soluble to a pH below the pKa of the agent at which the dyes are substantially nondiffusible, in order to advantageously further stabilize and optimize reflectivity of the dye transfer image. In such instance, the neutralizing layer may comprise particulate acid reacting reagent disposed within the film unit or a polymeric acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mils in thickness, positioned intermediate the transparent support and amido)-1-phenyl-5--pyrazolone dispersed in gelatin 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 suppot and the image-receiving layer.

As set forth in the last-mentioned patent, the polymeric acid layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, retained in the polymer layer. In the preferred embodi-

ments disclosed, the polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters 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 from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid 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 distribtued 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 processes 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 temperatures 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 resultant degradation of the positive transfer images' 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 depend-

ent 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 may 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 in-process adjustment of the environmental pH concentration from a pH concentration at which dye transfer is inoperative subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during processing, viewing and storage of the reflection print. The multicolor transfer images may be provided over an extended processing temperature range which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation and customer utilization of the unit.

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. No. 3,148,061, issued Sept. 8, 1964.

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 components may be varied over a wide range and when desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The dimensionally stable layers and sheet referred to may comprise any of various types of conventional transparent rigid or flexible materials, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include alkaline solution impermeable materials such as paper; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers, polyvinyl acetal; polyamides such as nylon; polyester such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate or acetate-butyrate. It will be recognized that one or more of the designated layers may not be required where the remaining layers of the laminate are such as to provide the functions of these layers in the absence of same, for example, where the remaining layers of the laminate provide the requisite dimensional stability and radiation filtering properties.

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

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U.S. patents detailing the 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 vinyl phthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-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. 3,069,264; and the like.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric, or colloidal, matrix such as ball-milling and the like techniques, the preparation of the dye developer disper-

sion may also be obtained by dissolving the dye in an appropriate solvent, or mixture of solvents, and the resultant solution distributed in the polymeric binder, with optional subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic color-providing materials in polymeric binders, specifically for the formation of component layers of photographic film units, reference may be made to U.S. Pats. 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; 3227,554; 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 or dye formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. Nos. 2,744,668 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 which, as disposed in the film unit, are initially diffusible or nondiffusible in the processing composition selected and are capable of providing an imagewise distribution of processing composition diffusible dye image-forming material 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 alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. 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 derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; and vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

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 image-forming material in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen may 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, for example, 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, for example, dye developers adapted to provide a black-and-white transfer image, for example, the employment of dye developers of the three subtractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

Where in the specification, the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image 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 as image produced on the image-carrying layer.

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.

In addition, the polymeric neutralizing layer disclosed to be optionally disposed, in a preferred embodiment, intermediate the dimensionally stable transparent support and next adjacent essential layer may, where desired, by disposed carrier by the transparent sheet element on the surface of that element next adjacent the photosensitive laminate and adapted to effect the stated in situ process modulation of the environmental pH, subsequent to substantial dye transfer image formation. In such structure, the pH modulating acidic component may be appropriately insulated to a substantial extent from deleterious interaction with the remainder of the photographic system during storage, exposure and initial processing of the film unit by means of, for example, a polymeric diffusion control barrier or spacer timing layer of the general type and design discussed above and may be employed alone or in combination with the polymeric neutralizing layer discussed hereinbefore. The in situ process modulation referred to may also optimally be in whole or in part accomplished by the employment of particulate acidic material distributed within the film unit and selectively available to effect the desired pH reduction in accordance with techniques disclosed in the copending U.S. Pat. No. 3,576,625 incorporated by reference herein.

Reference is now made to FIGS. 9 through 14 of the drawings wherein there are illustrated film units and an assemblage of film units in the form of a film pack.

As disclosed in the drawings, there is attached to leading end section **39** of each film unit **10** a leader sheet **31** having a trailing end section **40** at which the leader sheet **31** is coupled with the film unit. Leader sheet **31** including leading and trailing end sections **38** and **40** is approximately equal in width to the film unit **10** and leading end section **38** of each leader sheet **31** is secured to the film unit or cover sheet next preceding in the direction of the exposure aperture, preferably secured to the trailing end section of the preceding element.

The length of leader sheet **31** between its leading edge attachment to one film unit and the trailing edge to the next succeeding film unit is substantially equal to the length of the film units between their leading and trailing edges.

The rupturable container is of the type shown and described in U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,674,532; 2,702,146; 2,723,051; 2,750,075; 3,056,491; and 3,056,492, and may comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls which are sealed to one another along the longitudinal and end margins to form a cavity in which the processing fluid is contained. Longitudinal marginal seal **28** is made weaker than the end seal so as to become unsealed in response to hydraulic pressure generated within the fluid contents of the container by the application of compressive pressure to the walls of the container. Container **11** is mounted at film unit **10**'s leading end section **39** with the longitudinal marginal seal directed to facilitate restricted unidirectional flow of fluid contents **12** upon compressive rupture of container **11** intermediate transparent sheet **25** and blue-sensitive silver halide emulsion layer **15**.

A film pack or assemblage of film units **10** is shown in FIGS. 8 and 9 of the drawings. This film pack, designated **41**, comprises a generally rectilinear container or box **42** for holding and enclosing a plurality of film units **10**. Container **42** is shown as comprising a forward wall **43**, side walls **44**, a trailing end wall **45**, a leading end wall **46**, and a rear wall **49** and may be formed of a resilient plastic material. Forward wall **43** is provided with a generally rectangular exposure aperture **47** for transmitting light for exposing the photosensitive sheets of film units carried within the container. Leading end wall **46** is provided with a generally rectangular slot or exit orifice to provide a passage **48** at the leading end of the container through which film units **10** carried by the container are adapted to be individually withdrawn. In order to insure that only one film unit at a time will pass through opening **48**, stop means, for example, in the form of one or more projections or extensions such as those illustrated as **3** in FIG. 8 may be provided. Extensions **3**, which as illustrated is an integral part of end wall **46**, projects into the orifice to a position whereat it sufficiently obstructs passageway **48** to insure restriction of passage to the forwardmost film unit **10** in the stack, that is, the film unit positioned next adjacent exposure aperture **47**. Projection **3** may comprise a resilient construction adapted to provide a degree of resiliency such that as the leading film unit is withdrawn through orifice **48** the leading edge of the film unit will engage and deflect projections **3** to a position whereat the forward film unit only is allowed to move through orifice **48**. In addition, forward wall **43** at its leading end contiguous leading end wall **46** is provided with a guide plate **4** approximately equal in width to film units **10** extending generally in the direction of slot **48** and providing a slide surface facilitating passage of cover sheet **35** and film units **10** from container **41** through orifice **48**.

The stack arrangement within container **41** of a plurality of film units **10** (two are shown) is illustrated in FIGS. 8 and 9. Each film unit is arranged in overlying relation with exposure surface **13** of the film unit facing in the direction of exposure aperture **47**. Trailing end section **40** of leader sheet **31** is folded or curved in the direction of trailing end wall **45** of container **42** adjacent the leading end section **39** of film unit **10** intermediate that end section and the film unit in the stack, or the cover sheet in the instance of the film unit contiguous therewith, next adjacent exposure aperture **47** and extends in a plane parallel to the film unit for the distance necessary to allow the leader sheet to extend through the withdrawal orifice the required distance necessary for manual withdrawal of the film unit upon withdrawal of the preceding unit to which leading end section **38** of the leader is attached. Specifically, leading end section **38** of leader sheet **31** is folded or curved in the direction of leading end wall **46** of container **42** so that leading portions of leading end section **38** interconnect leader sheet **31** and the next preceding film unit **10** or cover sheet **35**; and specifically leading end section **38** of sheet **31** is disposed adjacent and secured to trailing end section **37** of the film unit **10** or trailing end section **36** of dark slide **35**. The film pack is provided with a generally flat, rectangular pressure plate **50** located intermediate rear wall **49** of container **42** and the portions of the film unit stack distal exposure aperture **47** for supporting the film unit next adjacent aperture **47** against the inner surface of forward wall **43** in position for exposure through the aperture **47**. Pressure plate **50** is provided with springs **53** formed from the rear wall and biased outwardly for engaging rear wall **49** and biasing pressure plate **50** toward forward wall **43** to retain film units **10** next adjacent thereto in position for exposure.

The means for withdrawing each film unit **10** from container **41** between a pair of pressure-applying members comprises a relatively narrow elongated leader **52** secured at the trailing end of the leader to tapered end section **51** of cover sheet **35** rearward of the leading edge **54** of tapered end section **51**. Leader **52** is of substantially uniform width throughout its length. The areas of adher-

ence of leader 52 to tapered end section 51 extend substantially in the direction of movement of the leader, and comprise any suitable adhesive material which will form a bond preferably at least equal in strength to the sheet materials (paper) comprising the leader and tapered end section, sufficient in resistance to the application of tension, in a direction of the plane of tapered end section 51, to prevent shearing. The adhesive bond is such that the application of a suitable shearing force to leader 52, effective by applying tension to the leader in a direction at an angle from the plane of tapered end section 51, causes leader 52 to disengage from contact with tapered end section 51. By virtue of this construction, as long as the leader and film unit coupled therewith are being moved in approximately the same direction, then the leader is in tension and does not fail. However, when the direction of movement of leader 52 and tapered end section 51 diverges sufficiently (as shown in FIG. 11), the trailing end section of the leader is subjected to a shearing force which causes the leader to tear and thereby become detached from tapered end section 51.

Leader 52 extends from container 41 through opening 48 therein and, when drawn from the container, advances cover sheet 35 within the container 41 towards opening 48 releasing storage restraint of cover sheet 35 within container 41, for example, by withdrawal pressure separation of sheet 35 from restraining staple 5 or the like selective restraining means. As leader 52 commences to advance towards opening 48, tapered end section 51 of sheet 35 transports through the opening in response to movement of cover sheet 35.

The film units incorporating the invention and comprising film pack 41 are adapted to be employed in photographic apparatus such as a hand-held camera 57, illustrated in FIGS. 10 through 14 of the drawings. Camera 57 comprises a housing including a forward section 58 having a forward wall 59 with a recessed or reentrant section 60 and an aperture 61 in the reentrant section for transmitting light for exposing film unit 10 of a film pack positioned for exposure within the camera. A hinged door 62 is provided for covering recessed section 60 and for mounting a lens and shutter assembly 63, the latter being connected to recessed section 60 by a collapsible bellows 64 secured at one end to the lens and shutter assembly and secured at its other end to the recessed section in surrounding relation to aperture 61. In lieu of door 62, lens and shutter assembly 63 and bellows 64, the camera housing can be constructed in the form of a camera back of film pack adapter intended to be mounted on or coupled with a camera or other photographic exposure device.

The camera housing includes a rear section 65 having a rear wall 66 and side walls 67 cooperating with forward housing section 58 to provide a chamber 68 to the rear of forward wall 59 and aperture 61 for containing the film pack in position for exposure through aperture 61. Film pack 41 is mounted within chamber 68 with the wall of the pack located against the rear surface of reentrant section 60 and with aperture 47 in the forward wall of the pack aligned with aperture 61. Rear housing section 65 is preferably pivotably secured to forward housing section 58 adjacent one end of the housing, herein shown and designated for purposes of description as the upper end, by a hinge which permits the two housing sections to be moved apart from one another to allow leading of a film pack into chamber 68. The camera housing includes a lower end wall comprising end wall 69 on forward housing section 58 and another end wall 70 on rear housing section 65. A film withdrawal passage 71 is provided in lower end wall of the housing to permit withdrawal of a film unit from the housing. Suitable latch means (not shown) of a conventional type are also provided in the lower portion of the housing for retaining the two housing sections together in the closed or operative position shown in the drawings.

Camera 57 includes a pair of juxtaposed pressure-applying members in the form of pressure-applying rolls 29 and 30 within chamber 68 adjacent film withdrawal passage 71. Pressure-applying rolls 29 and 30 are mounted for pivotal movement with their axes substantially in a common plane, and resilient means are provided for biasing the rolls toward one another into juxtaposition so as to apply compressive pressure to a film unit during movement thereof between the rolls. The pressure-applying rolls cooperate to form a convergent (and divergent) passage through which the film unit is moved for effecting the processing of the film unit, and this passage between the pressure-applying rolls is located in substantial alignment with withdrawal passage 71. In the arrangement of the pressure-applying rolls shown in the drawings, both rolls are mounted on rear housing section 65 so that when the housing sections are pivoted apart from one another, an assemblage of film units may be loaded into the camera with leader 52 thereof extending from the camera past and to one side (forward) of the pressure-applying rolls. Portions of end walls 69 and 70 cooperate to define an opening 82 between the forward and rear housing sections through which the leaders extend from the camera housing.

Camera 57 includes means for guiding the tapered end section 51 of cover sheet 35 between pressure-applying rolls 29 and 30 in response to withdrawal movement of leader 52 past rolls 29 to the front thereof and through opening 71. In the form shown in FIG. 10, this guide means comprises a guide bar 75 mounted on rear housing section 65 closely adjacent roll 29 and having a substantially straight guiding edge extending from side to side of the camera housing and lying substantially in a plane through the convergent passage between pressure-applying rolls 29 and 30, i.e., tangent to the rolls. Section 76 of guide bar 75, comprising the forward edge of the guide bar is located with its forward edge approximately in line with the forwardmost portion of roll 29, and guide bar 75 may be provided with facing end surfaces spaced from one another by a distance slightly greater than the width of leader 52. A guide plate 78, approximately equal in length to the width of leader 52, including facing end sections 79 spaced from one another by a distance slightly greater than the width of leader 52, is mounted on forward housing section 58, and extends toward the rear of the camera adjacent guide bar 75 at its forwardmost extremity 80. The rearmost edge of guide plate 78 may be cured, where desired. Guide bar 75, facing end sections 79, and guide plate 58 cooperate with one another to define a guide passage extending generally in a direction toward end wall 70 of the camera and having a width, measured from side to side of the camera, just slightly greater than the width of leader 52, so that the leader may be moved through passage 81. It will be noted that tapered end section 51, at the leading edge thereof, is wider than leader 52 so that tapered end section 51 is unable to enter passage 81. Facing surfaces 79 of guide plate 78 function to guide tapered end section 51 of the cover sheet into the convergent passage between pressure-applying rolls 29 and 30.

In the loading and operation of the camera, the forward and rear housing sections are pivoted apart from one another and a film pack 41 is positioned within the forward housing section 58 with the forward wall 43 of pack 41 resting against section 60 of the forward wall 59 of forward housing section 58, and with leader 52 projecting from the pack extending across and to the rear of guide plate 78 and end wall 69. Rear housing section 65 is then pivoted into the operative position shown, causing the intermediate section 82 of guide bar 75 to engage leader 52 displacing it forwardly so that it extends through passage 81 toward the forward wall of the camera, past pressure-applying roll 29 and through opening 82 in end walls 69 and 70. As a leader 52 is withdrawn from the camera through opening 71, the tapered end section 51 is withdrawn from the pack and, being unable to enter

passage **81**, is guided by the guide bar, guide members and guide plate into the convergent passage between the pressure-applying rolls.

Film and cover sheet withdrawal passage **71**, in the lower end wall **70** of the camera housing, is at least equal in width to the width of cover sheet **35** and film units **10** whereas passage **81** need be of a width only sufficient to allow the passage of leader **52** to project from the camera where the leader may be grasped. As leader **52** is withdrawn through opening **71**, the leader is attached to tapered end section **51** and results in separation of the leader at these areas.

Application of withdrawing force on tapered end section **51**, advancing dark slide element **35** between pressure-applying rolls **29** and **30** through the position shown in FIG. 11.

In the operation of the film unit of the invention, thus leader **52** is pulled from the camera advancing tapered end section **51** between pressure-applying rolls **29** and **30** to the position shown in FIG. 11 at which leader **52** extends from its point of attachment to tapered end section **51** at almost a right angle from the plane of the tapered end section. At this position, the leading end of tapered end section **51** projects through passage **71** a sufficient distance to permit the tapered end section to be grasped, and the application of a continued pulling force on leader **52** results in the exertion of a shearing force to leader **52** at its area of attachment to cover sheet **35**.

Continued withdrawing force on cover sheet **35** between pressure-applying rolls **29** and **30** to the position shown in FIG. 12 provides withdrawal of cover sheet **35** from the camera and projection of leader sheet **31** possessing its leading end section **38** secured to the trailing end section **36** of the cover sheet **35** through passage **71** a sufficient distance to uncover the exposure surface of the next succeeding film unit **10** the leading end section of which is secured to the trailing end section **40** of leader sheet **31** and to permit leader sheet **31** to be grasped for withdrawal of film unit **10** subsequent to photoexposure. Cover sheet **35** may optionally be detached from leader sheet **31** subsequent to the leader sheet being threaded through the pressure rolls at the election of the operator or alternatively leader sheet **31** may be comprise a continuation of and be unitary with the dark slide.

As further illustrated in FIGS. 13 and 14, subsequent to photoexposure each film unit **10** may be sequentially withdrawn from container **42** selectively transported intermediate pressure rolls **29** and **30** to effect rupture of processing container **11** and distribution of its fluid processing contents **12** intermediate transparent sheet **25** and the photo sensitive laminate component of the film unit to effect processing thereof as detailed hereinbefore.

Withdrawal of each film unit **10** in effect succeeds in projecting leader **31** secured to the next succeeding film unit through passage **71** for the distance necessary to selectively withdraw that film unit for processing subsequent to photoexposure in the manner stated above. Where desired the leader may be selectively detached from the preceding and succeeding film unit subsequent to the selected film units' withdrawal from the camera.

It will be recognized that although in the preferred embodiment of the present invention the leading end section **38** of the leader sheet **31** is secured to either major surface of the preceding elements trailing end section provided that by position or composition when secured to the exposure surface it does not interfere with exposure of the unit. Leading end section **38** of leader sheet **31** may be secured to the preceding element, i.e., film unit or dark slide, on its surface opposite the exposure aperture forward that element's trailing end section provided that the length of the leader is sufficient to extend through the withdrawal orifice a sufficient distance to be grasped, possesses the requisite slip capacity, e.g., by composition or coating, to allow, upon the detachment of the leader from the preceding element as practically required of this embodiment, the latter element to complete its withdrawal from the camera including between the opposed pressure-applying rolls; and is readily dissociated from the preceding element external the camera and within grasping capacity of the operator.

The dark slide and leader sheet materials employed may comprise any one or more of the conventional paper and/or polymeric materials, for example, those previously identified, sufficiently flexible to perform the function denoted which with respect to the leader material, be opaque, translucent or transparent, and may optionally be either separated from the film unit subsequent to processing, for example, with or without separation of the frangible container, or alternatively adhered to, for example, the exposure surface, or if transparent, to the viewing surface, of the film unit, preferably coextensive therewith for asthetic purposes, as illustrated in FIGS. 15 and 16, by means of conventional selectively adhering adhesives available from a multiplicity of commercial sources which may be carried by a proposed contact surface. In those instances wherein the leader is maintained with the processed film unit, the decorative aspects of the leader sheet, i.e., color, texture and design will be selected to provide the desired visual appearance.

Since certain changes may be made in the above product 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 assembly which comprises, in combination:

(1) a container including a light-transmitting section positioned in a wall, a withdrawal orifice positioned in a wall through which a dark slide and individual diffusion transfer process color film units are adapted to be selectively withdrawn sequentially and means for biasing a dark slide and film units toward the exposure aperture;

(2) a dark slide disposed substantially coextensive the light-transmitting section and including a leading edge and a trailing end section;

(3) a plurality of diffusion transfer process color film units each including a leading end and a trailing end section and each comprising:

(a) a photosensitive laminate containing, as essential layers, in order:

(i) a dimensionally stable transparent support support layer;

(ii) a layer adapted to receive a diffusion transfer process dye image-forming material diffusing thereto;

(iii) an opaque layer; and

(iv) a photosensitive silver halide layer having associated therewith a diffusion transfer process dye image-forming material;

(b) a transparent dimensionally stable sheet superposed substantially coextensive the surface of the photosensitive laminate opposite the transparent support layer; and

(c) a rupturable container retaining a processing composition including an opacifying agent positioned extending transverse the leading end of the film unit to effect, upon application of compressive pressure to the container, unidirectional discharge of the container's contents intermediate the transparent dimensionally stable sheet and the photosensitive laminate,

each of the film units disposed in stacked relationship in the container with the transparent dimensionally stable sheet disposed toward the light-transmitting section and the rupturable container disposed toward the withdrawal orifice; and

(4) a plurality of leader sheets each comprising a

leading end and a trailing end section and including a first leader sheet, the leading end section of which extends through the withdrawal orifice and the trailing end section of which is secured to the dark slide rearward of its leading edge, a second leader sheet interconnecting the dark side and the next succeeding film unit in the stack, the trailing end section of the second leader sheet secured to the leading end section of the film unit, and third leader sheets each interconnecting a preceding film unit and next succeeding film unit in the stack, the trailing end section of each third leader sheet being secured to the leading end section of the succeeding film unit.

2. A photographic film assembly as defined in claim 1 wherein the leading end section of the second leader sheet is secured to the trailing end section of the dark slide.

3. A photographic film assembly as defined in claim 1 wherein the leading end section of each of the third leader sheets is secured to the trailing end section of the preceding film unit in the stack.

4. A photographic film assembly as defined in claim 1 wherein the trailing end section of the first leader sheet is secured to the surface of the dark slide next adjacent the light-transmitting section of the container.

5. A photographic film assembly as defined in claim 1 wherein the dark slide is a flexible sheet material and the second leader sheet comprises an extension of the trailing end section of the dark slide.

6. A photographic film assembly as defined in claim 1 including a binding sheet extending around the lateral and trailing edges of each film unit overlying and secured to the lateral and trailing external surface edge sections of each of the transparent sheets and the transparent support layer.

7. A photographic film assembly as defined in claim 6 wherein the portion of the lateral edge section of the transparent sheet which the binding sheet overlies is less than the portion of the transparent support layer overlaid by the binding sheet.

8. A photographic film assembly as defined in claim 6 wherein the binding sheet overlying and secured to the trailing edge sections of the transparent sheet and the transparent support layer cooperates with the trailing edge of the sheet and support layer to provide an enclosed chamber adapted to receive and retain processing composition entering the chamber from intermediate the trailing edge sections of the transparent sheet and transparent support layer.

9. A photographic film assembly as defined in claim 8 including at least one air-release means associated with the chamber to vent air therefrom.

10. A photographic film assembly as defined in claim 1 wherein the opaque layer is adapted to reflect electromagnetic radiation incident thereon.

11. A photographic film assembly as defined in claim 10 wherein the reflecting layer comprises titanium dioxide disposed in a polymeric matrix permeable to processing composition solubilized dye image-forming material.

12. A photographic film assembly as defined in claim 11 wherein the opacifying agent included in the processing composition comprises carbon black.

13. A photographic film asembly as defined in claim 1 wherein the photosensitive laminate contains at least two selectively sensitized silver halide layers each having associated therewith a dye image-forming material adapted to provide a dye image of predetermined color as a function of the photo-exposure of its associated silver halide layer.

14. A photographic film assembly as defined in claim 13 wherein each of the selectively sensitized silver halide layers possesses predominant spectral sensitivity to separate regions of the spectrum and the dye image-forming material associated with each of the silver halide layers is adapted to provide a dye transfer image possessing a spectral absorption range subsequent to processing substantially complementary to the predominanat sensitivity range of its associated silver halide layer.

15. A photographic film assembly as defined in claim 14 wherein the processing composition comprises an aqueous alkaline processing composition and the color film units each include means for converting the pH of the processing composition, subsequent to substantial diffusion dye image-forming materials to the receiving layer, from the initial pH to a second pH at which the dye transfer image provided by the dye image-forming materials exhibits increased stability.

16. A photographic film assembly as defined in claim 15 wherein the photosensitive laminate includes, as essential layers, a red-sensitive silver halide emulsion layer having associated therewith a diffusion transfer process cyan dye image-forming material, a green-sensitive silver halide emulsion layer having associated therewith a diffusion transfer process magenta dye image-forming material and a blue-sensitive silver halide emulsion layer having associated therewith a diffusion transfer process yellow dye image-forming material.

17. A photographic film assembly as defined in claim 16 wherein the opaque layer comprises a first alkaline process-composition permeable polymeric layer containing titanium dioxide and, contiguous the surface of the titanium dioxide containing layer intermediate that layer and the surface of the laminate opposite the transparent support layer, a second alkaline processing composition permeable polymeric layer containing carbon black.

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U.S. Cl. X.R.

95—19; 96—72, 3, 29, 76