United States Patent [19]

Land

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[54] **PHOTOGRAPHIC PRODUCTS COMPRISING AN OPACIFYING AGENT IN ASSOCIATION WITH A REFLECTING AGENT**

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[52] **U.S. Cl.** .... **96/77,** 96/76 C

[51] **Int. Cl.** **G03c 1/48,** G03c 5/54, G03c 7/00

[58] **Field of Search** .... 96/3, 77, 29 D

[56] **References Cited**

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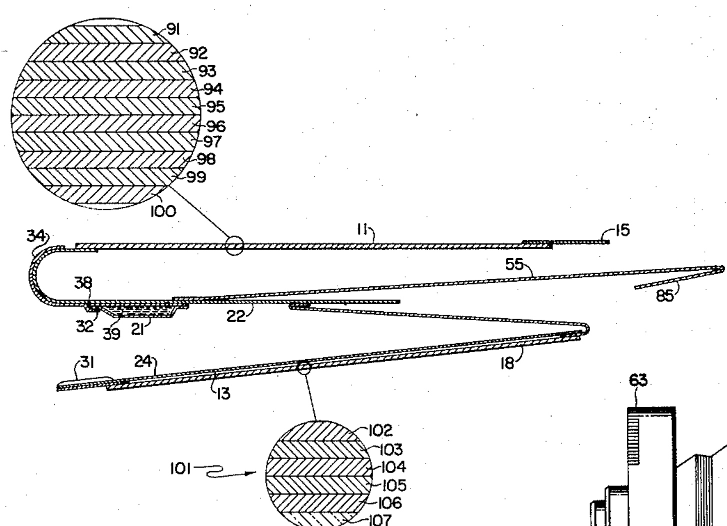
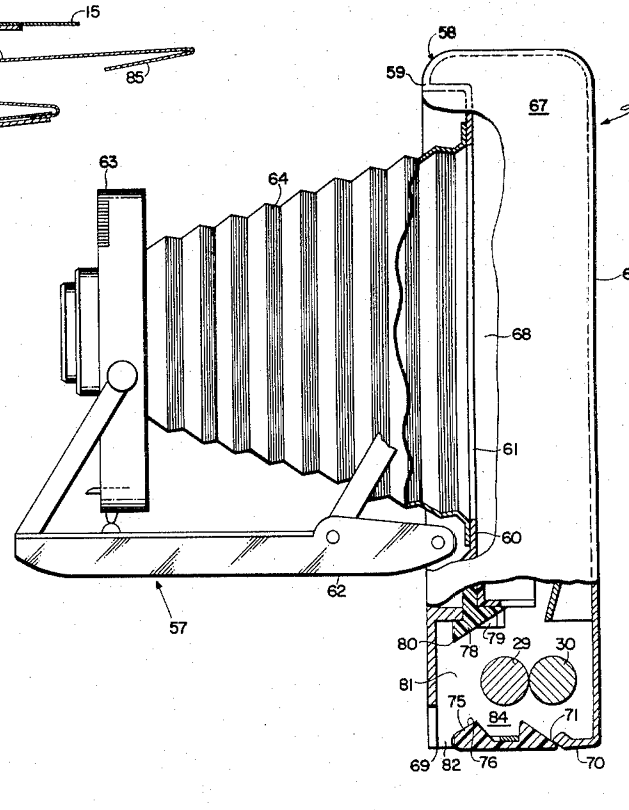
[57] **ABSTRACT**

Film assemblies in the nature of a self-developing film which comprise a photosensitive element including an opaque support carrying photosensitive silver halide having associated diffusion transfer process dye image-providing material; an image-receiving element including a transparent support carrying a diffusion transfer image-receiving layer and a reflecting layer; rupturable container means retaining a fluid processing composition for distribution between the photosensitive and the image-receiving elements; and including opacifying agent disposed in the fluid processing composition and/or integral with or as a layer on the surface of the image receiving element's reflecting layer opposite the transparent support. for processing external a camera in which the film assembly is exposed and adapted to provide a color reflection print as a function of the film unit's photoexposure.

Subsequent to exposure, the film unit is specifically adapted to be withdrawn from the camera between pressure-applying members which effect release of the fluid processing composition for production of the dye transfer image. During and subsequent to processing, formation of the color reflection print may be viewed through the image-receiving element's transparent support against the background provided by the element's reflection layer and the reflection layer, taken together with the opacifying agent, is specifically adapted to protect the photosensitive silver halide from exposure during processing in the presence of radiation incident on the viewing surface.

15 Claims, 9 Drawing Figures





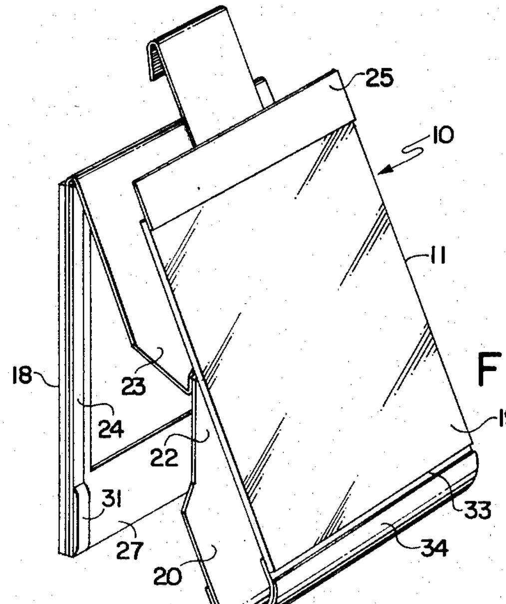


FIG. 1

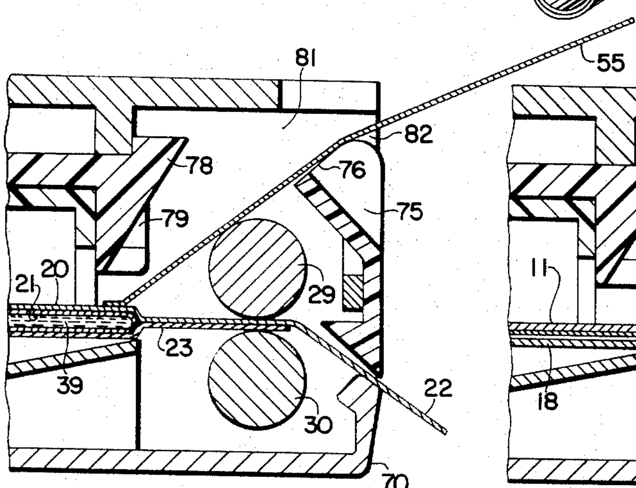


FIG. 7

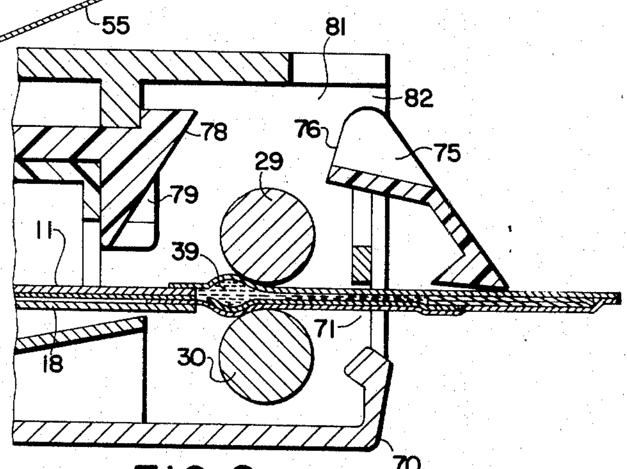


FIG. 8

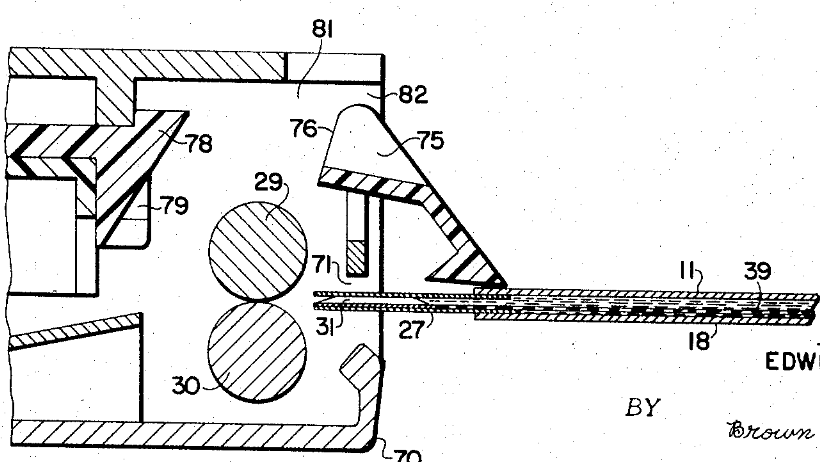


FIG. 9

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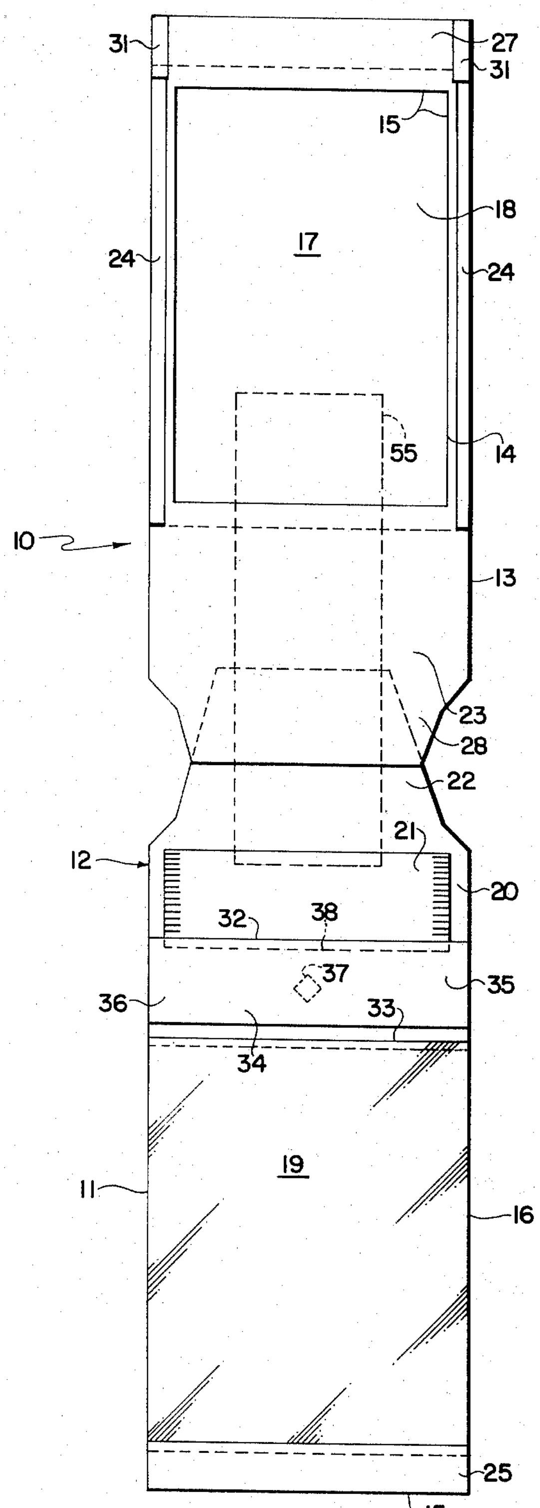

FIG. 2

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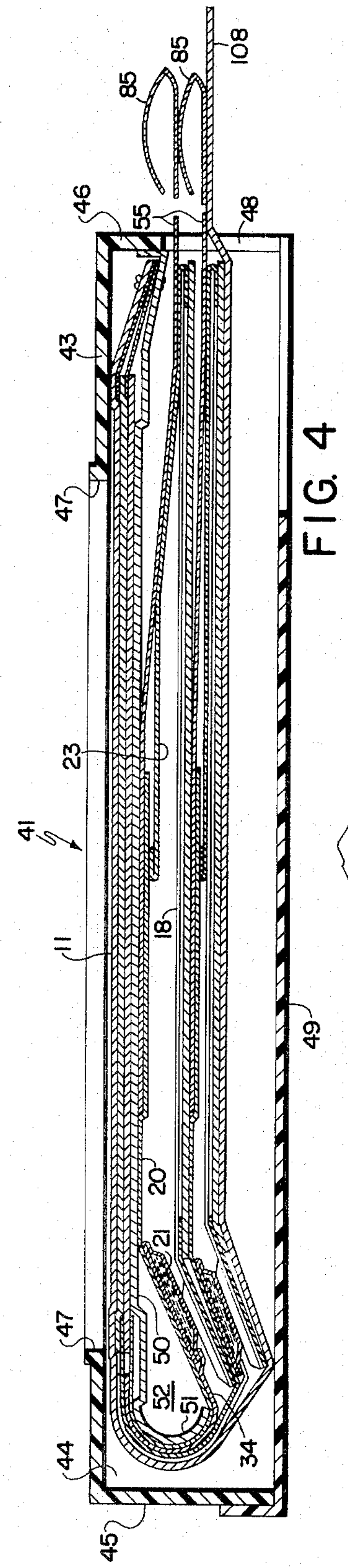

FIG. 4

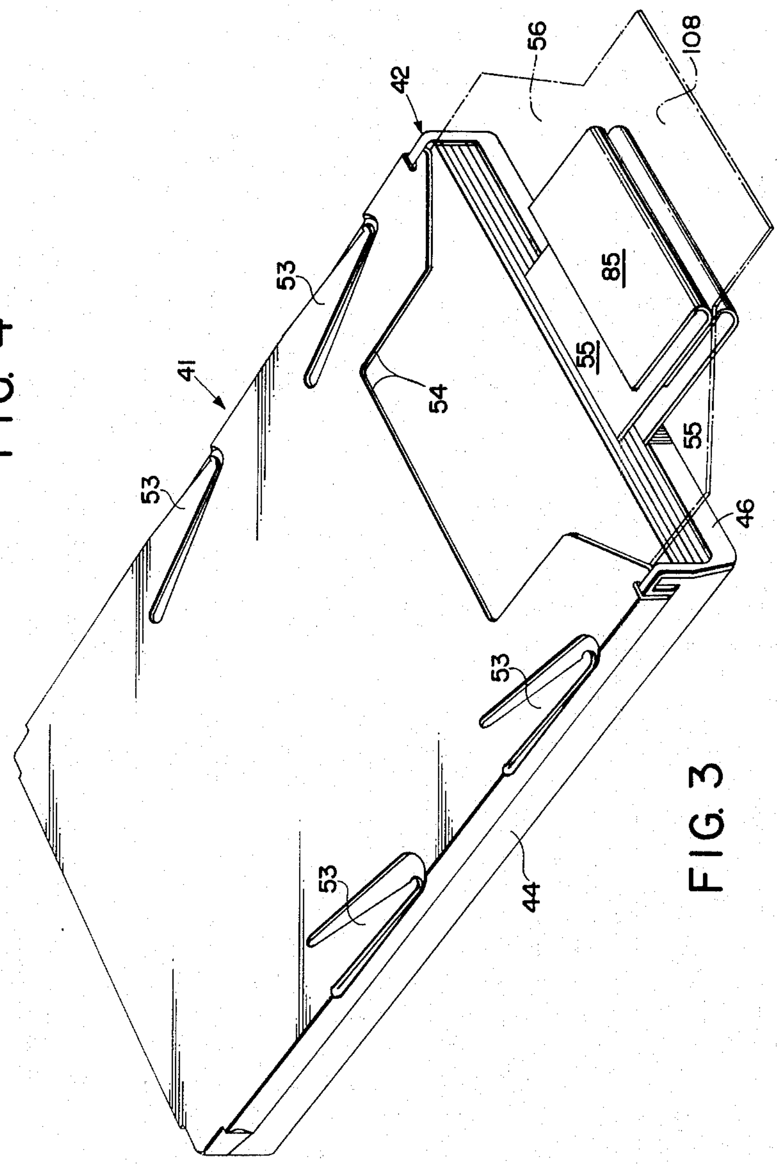

FIG. 3

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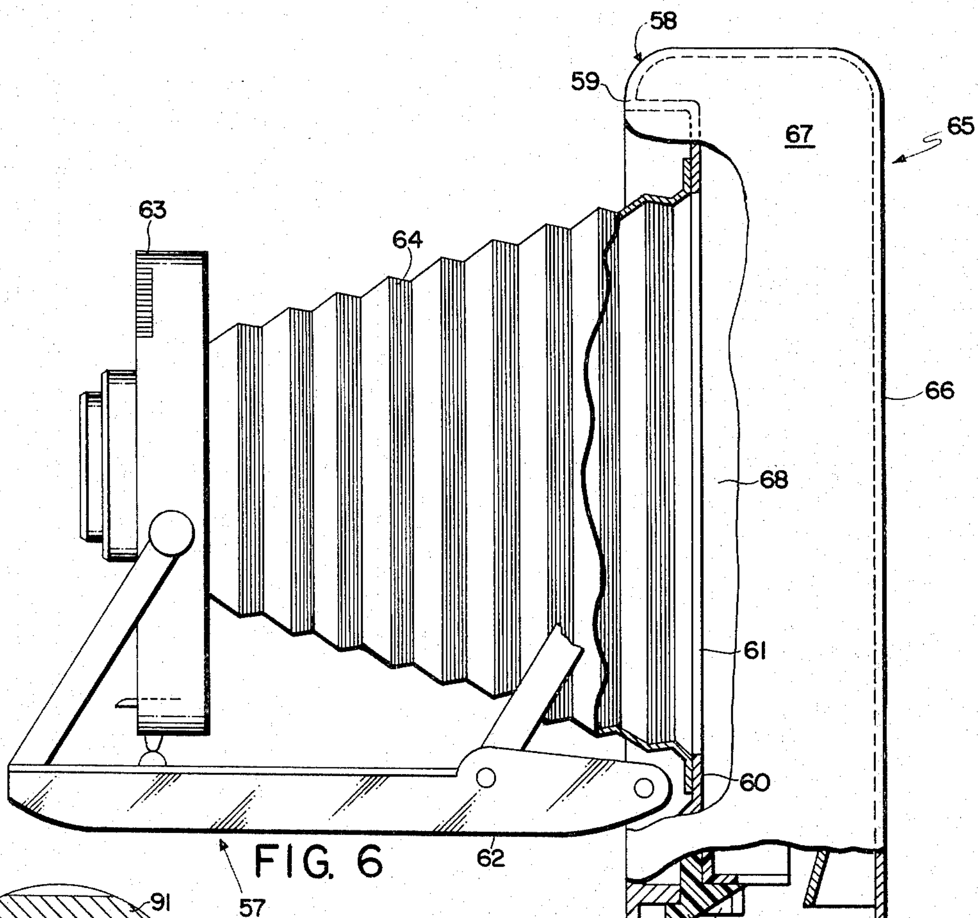

FIG. 6

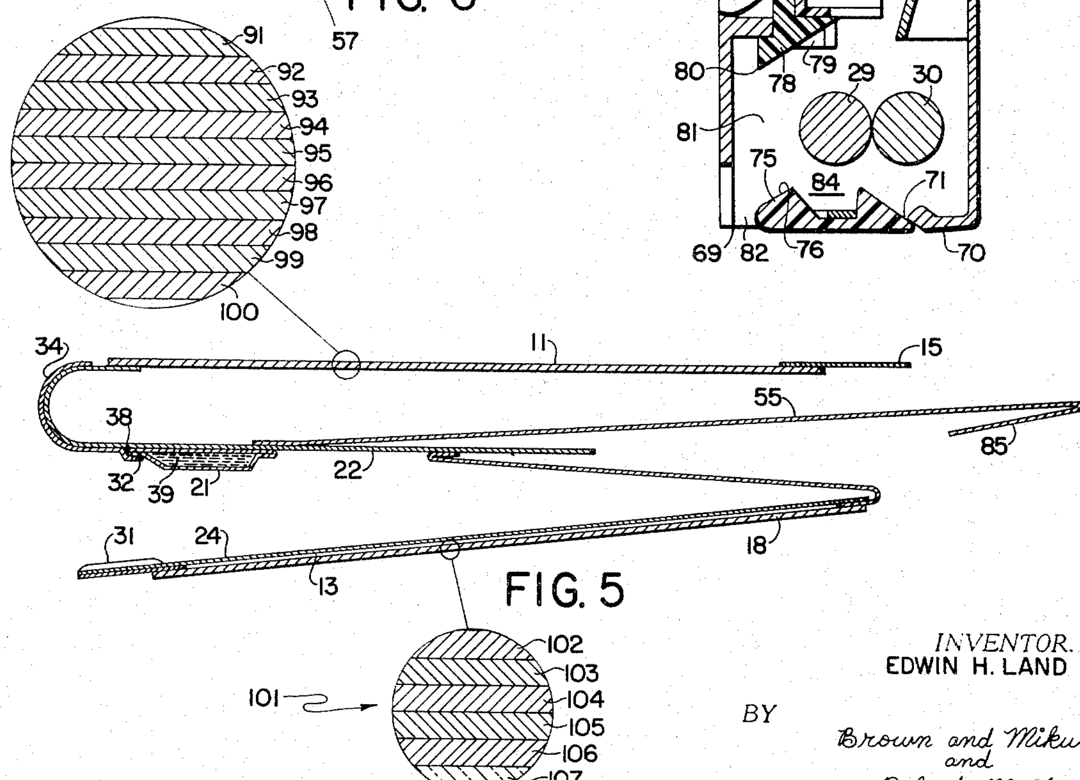

FIG. 5

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PHOTOGRAPHIC PRODUCTS COMPRISING AN OPACIFYING AGENT IN ASSOCIATION WITH A REFLECTING AGENT

BACKGROUND OF THE INVENTION

The present invention is concerned with photographic film units, particularly adapted for employment in a photographic film pack or film magazine of the type shown in U.S. Pat. No. 3,080,805, issued Mar. 12, 1963, in the name of Joel A. Hamilton, comprising 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 during withdrawal of the film unit from the container, following exposure thereof; 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, photoexposed 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 processing, 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. Pat. 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 film assembly for producing color reflection prints employing a film pack or magazine type unit. The assembly is composed of a first sheet element comprising a photosensitive structure including, in essence, an opaque support carrying a photoresponsive material, such as photosensitive silver halide crystals having associated therewith a dye image-providing material which is processing composition diffusible as a function of the photoexposure of associated photosensitive silver halide; a second sheet element comprising, in essence, a transparent support carrying, in order, a layer adapted to receive the image formed as a function of photo-exposure of the photoresponsive material and a dye image-providing material permeable visible light-reflecting layer, adapted to be superposed over the exposure surface of the photosensitive element, with the respective supports outermost, subsequent to exposure of the photoresponsive material; frangible fluid retaining means adapted to discharge processing composition retained therein between the first and second sheet elements; means including a leader for coupling the first sheet element and the second sheet element and withdrawing same in superposed relationship from the exposure apparatus; and an opacifying agent disposed integral with and or/ contiguous the surface of the reflecting layer opposite the transparent support and/or in the processing composition in a concentration effective, taken together with the reflecting layer, to prevent photoexposure of the first sheet element's photoresponsive material by radiation actinic thereto incident on the second sheet element in superposed relationship with the first sheet element's exposure surface.

The described film assembly is first exposed in an apparatus such as a hand-held camera by radiation incident on the exposure surface of the first sheet element and then biased into superposed relationship with the second sheet element to permit removal from the apparatus and processing of the exposed photoresponsive material under ambient light conditions external to the exposure device. Substantially contemporaneous with the removal of the film assembly from the camera, the frangible container is ruptured, discharging its contents intermediate the opposed surfaces of the first and second sheet elements, and the leader and fluid retaining means are thereafter optionally detached from association with the remainder of the assembly.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 2 is a plan view of the film unit of FIG. 1;

FIG. 3 is a perspective view of a film pack comprising an assemblage of film units;

FIG. 4 is a longitudinal sectional view taken substantially midway between the sides of the film pack of FIG. 3;

FIG. 5 is a diagrammatic sectional view taken substantially midway between the sides of the film pack showing one film unit with the components thereof spaced apart to more clearly illustrate the construction and arrangement of the film unit;

FIG. 6 is an elevational view, partially in section, of photographic apparatus in the form of a camera for employing film units embodying the invention;

FIG. 7 is a fragmentary sectional view, similar to FIG. 6, illustrating initiation of an initial passage of one film unit between a pair of opposed pressure-applying rolls during removal of the film unit from the camera apparatus of FIG. 6, subsequent to photoexposure;

FIG. 8 is a fragmentary sectional view, similar to FIG. 7, illustrating further passage of the 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; and

FIG. 9 is a fragmentary sectional view, similar to FIG. 8, 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.

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 an opaque support carrying on one surface a photoresponsive material having associated therewith a dye image-providing material, which is processing composition diffusible as a function of the photoexposure of associated photoresponsive material adapted to be exposed by incident actinic radiation to produce photographic information recordation; a second dye image receptive sheet element comprising a transparent support carrying on one surface, in order, an image-receiving layer adapted to receive by diffusion transfer processing an image as a function of the exposure of the photoresponsive material and a dye image-providing material permeable visible light-reflecting layer, adapted to be biased into superposed relationship contiguous the exposure surface of the first photosensitive sheet element subsequent to exposure; a rupturable container containing a fluid agent for reacting with the exposed photoresponsive material for forming the image in the image-receptive layer; means including a leader for coupling the photosensitive unit and the second opaque sheet and for withdrawing the unit and the sheet in superposition from a film pack or magazine; and opacifying agent disposed integral with and/or contiguous the surface of the reflecting layer opposite the transparent support and/or in the fluid agent in a concentration effective, taken together with the reflecting layer, to prevent exposure of the first sheet element's photoresponsive material by radiation actinic thereto incident on the transparent support of the second sheet element in superposed relationship with the first sheet element in the processing mode.

The preferred form or 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 an exposure aperture therein and an opening in one end through which film assemblies can be individually withdrawn with the photosensitive and second sheet elements of each film unit in superposed relation. The photosensitive film units are positioned together within the container underlying the exposure aperture with the exposure surface of the first photosensitive sheet element uppermost and the second image-receptive sheet elements are arranged together, apart from, and behind the photosensitive elements adjacent the opening through which the film units are withdrawn so that following the exposure of the photosensitive sheet element of each film unit, the photosensitive element is moved, by drawing on the leader of the film unit, into superposition with the second element of the film unit and the film unit is then 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. The leaders of the film units and cover element extend from the pack and from the camera where the last-mentioned leader may be grasped for withdrawing the cover element from the pack and camera to allow the photosensitive elements of the pack to be exposed. After the photosensitive elements of each successive film unit is exposed, that film unit is then 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.

DETAILED DESCRIPTION OF THE DRAWINGS

Reference is now made to FIGS. **1** through **9** of the drawings wherein there are illustrated film units and an assemblage of film units in the form of a film pack. Each film unit designated **10** comprises a generally rectangular photosensitive color sheet element **11**, comprising an opaque support carrying on one surface a photosensitive silver halide layer and a second image-receptive sheet element **18** adapted to be superposed on exposure surface **19** of the element opposite the first opaque support. Photosensitive sheet element **11** possesses a first leading section **20** approximately equal in width to element **11** and provides means for mounting rupturable container **21** of processing fluid, and includes a leading end section **22.** Image-receptive sheet element **18** is approximately equal in width to element **11** and includes a tapered leading end section **23** approximately equal in dimensions to tapered end section **22** of sheet **11.** Side guides **24** are secured to the lateral edges of sheet **18** coextensive the length of element **11** whereby to provide a gap control between sheet **18** and element **11** during processing, and the lateral boundaries of the element **11** may be secured to the corresponding lateral boundaries of sheet **18** at the respective interface therebetween in any analagous manner as to facilitate retention of the processing fluid intermediate sheet **18** and element **11.**

Tapered end sections **22** and **23** cooperate to define the leading end section of film unit **10** to be advanced between the pressure-applying members as further defined hereinafter.

The length of sheets **11** and **18** is substantially equal and by virtue of this arrangement, the sheets are readily superposed in registered relation during the processing of the film unit. A trailing end section **25** of sheet **11** extends beyond the trailing edge **26** of element **11** to coact with trailing end section **27** of sheet **18** to trap any excess processing fluid which may be carried beyond the trailing ends of the photosensitive element **11** during distribution of the processing fluid. Distribution of the processing fluid, as noted, is effected by advancing sheets **11** and **18** and container **21** of processing fluid, the former in superposition, relative to and between a pair of juxtaposed pressure-applying members **29** and **30.** The pressure-applying members, e.g., opposed suitably gapped rolls, apply compressive pressure to the sheets progressively, commencing in the area of the container, to cause the ejection of the fluid contents of the container between and in contact with the opposed surfaces of the sheet **18** and element **11.** To aid in trapping of excess fluid, spacing members **31** may be provided on trailing end section **27** adjacent the margins thereof for spacing apart the pressure-applying members to provide a gap between trailing end section **25** of sheet **11** and trailing end section **27** of sheet **18** in which any excess processing fluid may be collected and retained.

As disclosed in the drawings, there may be attached to the leading edge of photosensitive laminate **16** a leader sheet **12** having a first section **20** in which the leader sheet **12** is coupled with the photosensitive laminate. First section **20** is approximately equal in width to the photosensitive laminate and provides means for mounting rupturable container **21.** As shown, leader sheet **12** includes tapered end section **22.** Image-receiving laminate **17** is shown mounted on a carrier sheet **13** having an intermediate section **14** approximately equal in width to the image-receiving laminate and having a generally rectangular opening **15** therein defining the area of the image-receiving laminate in which image formation occurs. Carrier sheet **13** includes a leading end section **23** having a tapered end portion **28** similar to tapered end section **22** and secured thereto intermediate the ends of tapered end section **22** and tapered end portion **28** of leading end section **23.** As shown, tapered end section **22** and end portion **28** cooperate to define the leading end section of the film unit which is advanced between the pressure-applying members **29** and **30.** Where desired, intermediate section **14** of carrier sheet **13** may be secured to the external surface of image-receiving laminate **17** so that portions of the intermediate section bordering on opening **15** may provide a mask for defining image area.

The length of leader sheet **12** between the leading edge of photosensitive laminate **16** and the point of attachment of leader sheet **12** to carrier sheet **13** is substantially equal to the length of carrier sheet **13** between its point of attachment to the leader sheet and the leading edge of image-receiving laminate **17.** By virtue of this arrangement, photosensitive laminate **16** and image-receptive laminate **17** are superposed in registered relation during processing of film unit **10.** As shown, a trailer sheet **25** is provided secured to the trailing edge of photosensitive laminate **16** for cooperation with the opposed trailing end section **27** of carrier sheet **13** to trap excess processing fluid which may be transported beyond the trailing ends of the photosensitive and image-receptive laminates during distribution of processing composition.

The rupturable container is of the type shown and described in U.S. Pat. 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 **32** 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 **21** is mounted on sheet **11** with the longitudinal marginal seal directed toward the leading edge **33** of element **11.** Bib sheet **34** is secured to sheet **11** at lateral edges **35** and **36,** center area **37,** trailing edge **38** of container **21,** and leading edge **33** of element **11,** and facilitates restricted unidirectional flow of fluid contents **39** upon compressive rupture of container **21.** Edge **40** of bib sheet **34** extends beneath leading edge **33** of element **11.** Thus, the flow of fluid contents **39** from container **21** is directed beneath bib sheet **34** and distributed intermediate element **11** and sheet **18.**

For details concerning the composition of the fluid and materials useful in forming the color image, reference may be had to the aforementioned U.S. Pats.

A film pack or assemblage of film units **10** is shown in FIGS. **3** and **4** of the drawings. This film pack, designated **41**, comprises a generally parallelepiped-shaped container or box **42** for holding and enclosing a plurality of film units **10**. Container **42** is shown as comprising two sections, including a forward section having a forward wall **43**, side walls **44**, a trailing end wall **45**, and a leading end wall **46**. 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** comprises only a partial wall, i.e., it does not extend rearwardly to the same extent as the side walls, which cooperates with the rear section of the container to provide a passage **48** at the leading end of the container through which film units **10** carried by the container are withdrawn. The rear section of the container comprises a rear wall **49** secured to side walls **44** and formed preferably of a resilient sheet metal.

The arrangement of each film unit within container **41** is illustrated in FIGS. **1** and **5**; and the arrangement of a plurality of film units (two are shown) is illustrated in FIG. **4**. Each film unit is arranged with the photosensitive and second sheets in overlying relation with the photosensitive layer of element **11** facing outward and with the reflecting layer of image-receptive sheet **18** which is superposed therewith, during processing, facing inwardly in the same direction. Leading end section **20** of sheet **11** is folded or curved adjacent the leading edge **33** of element **11** intermediate that edge and container **21**, and leading end section **23** of sheet **18** is similarly folded adjacent the leading edge of the sheet so that leading portions of leading end sections **20** and **23** interconnect sheet **11** and **18** in the stated spacial arrangement upon superpositioning of the sheets; and trailing end section **25** of sheet **11** is disposed adjacent, respectively, trailing end section **27** of sheet **18**. The film pack is provided with a generally flat, rectangular pressure plate **50** located intermediate sheet **11** and the other portions of the film unit for supporting element **11** against the inner surface of forward wall **43** in position for exposure through aperture **47**. Pressure plate **50** includes a rolled end section **51** around which extends the curved portion of sheet **16**. Rolled end section **51** is provided for guiding photosensitive element **11** around the end of the pressure plate in a manner to be described hereinafter. The major portion of first section **20** of sheet **11** rupturable container **21** mounted thereon, tapered section **22** and the leading tapered end section **23** of sheet **18** are located behind pressure plate **50** between the latter and sheet **18**. Pressure plate **50** is provided with lateral flanges **52** disposed adjacent side walls **44** of the container. Rear wall **49** of the housing is provided with springs **53** formed from the rear wall and biased inwardly for engaging lateral flanges **52** and biasing pressure plate **50** toward forward wall **43** to retain element **11** in position for exposure. Rear wall **49** is also provided with a U-shaped opening or enlarged notch **54** in the end portion thereof adjacent opening **48** the purpose of opening **48** to be further described hereinafter.

The means for withdrawing each film unit **10** from container **41** with element **11** and sheet **18** in superposition and advancing tapered end sections **22** and **23** between a pair of pressure-applying members comprises a relatively narrow elongated leader **55** secured at the trailing end of the leader to tapered end section **22** of sheet **11** preceding the point of attachment of the tapered end section **22** to tapered end portion **23** of sheet **18**. Leader **55** is of substantially uniform width throughout its length. The areas of adherence of leader **55** to tapered end section **22** 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 **22**, to prevent shearing. The adhesive bond is such that the application of a suitable shearing force to leader **55**, effective by applying tension to the leader in a direction at an angle from the plane of tapered end section **22**, causes leader **55** to disengage from contact with tapered end section **22**. 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 **55** and tapered end section **22** diverges sufficiently (as shown in FIG. **7**), 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 **22**.

Leader **55** extends from container **41** through opening **48** therein and, when drawn from the container, advances element **11** around rolled end section **51** of pressure plate **50** into superposition with a second sheet **18** and then advances the two sheets in superposition within the container towards opening **48**. As leader **55** commences to advance towards opening **48**, tapered end section **22** of sheet **11** is required to commence rolling upon itself toward the opening in response to movement of tapered end section **22** of sheet **11** toward the same opening. It is for this reason that section **22** and portion **23** are tapered, since this provides for the weakest portion of end portion **22** in the area where the end portion is required to commence rolling. Means may also be provided for preventing movement of elements underlying the foremost element **11** as the latter is moved from exposure position around the end of the pressure plate.

Film pack **41** is provided with means for initially sealing aperture **47** against the admission of light until the pack has been loaded into the camera in which it is to be employed. This light-sealing means comprises a cover sheet **56** (double) of a light-impervious material located between the foremost photosensitive sheet and forward wall **43** across opening **47**. Cover sheet **56** extends around the curved end of the pressure plate behind the latter to a position against rear wall **49** with the leading end of the cover sheet located adjacent passage **48**. An elongated leader section **108**, similar to leader **55**, provides means for withdrawing cover sheet **56** from container **41** after the container has been loaded into a camera.

The film units incorporating the invention and comprising film pack **41** are adapted to be employed in photo-graphic apparatus such as a hand-held camera **57**, illustrated in FIGS. **6** through **9** 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 element **11** 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**, the former comprising an image-reversing optical system adapted to rectify geometric transfer image reversal which is resultant from exposure and processing of the film unit by reason of the unit's structural parameters. 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 or film pack adaptor 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 loading 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 **58**. 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 the leaders 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 of film unit **10** between pressure-applying rolls **29** and **30** in response to withdrawal movement of leader **55** past roll **29** to the front thereof and through opening **71**. In the form shown in FIG. **6**, 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 **55**. A guide plate **78**, approximately equal in length to the width of leader **55**, including facing end sections **79** spaced from one another by a distance slightly greater than the width of leader **55**, 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 curved, where desired. Guide bar **75**, facing end sections **79**, and guide plate **78** 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 **55**, so that the leader may be moved through passage **81**. It will be noted that tapered end section **22**, at the leading edge thereof, is wider than leader **55** so that tapered end section **22** is unable to enter passage **81**. Facing surfaces **79** of guide plate **78** function to guide tapered end section **22** of the film unit 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 leaders **55** and leader **108** 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 the leaders displacing them forwardly so that they extend 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 **55** is withdrawn from the camera through opening **71**, the tapered end section 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 withdrawal passage **71**, in the lower end wall **70** of the camera housing, is at least equal in width to the width of the film unit, whereas passage **81** need be of a width only sufficient to allow the passage of leaders **55**. It is desirable to allow only one leader at a time to project from the camera where the leader may be grasped; and this is desirable to prevent the operator from accidentally pulling the wrong leader, or pulling more than one leader at a time. For this purpose, end wall **70** is provided with a recess, designated **84**, adjacent passage **81** for holding the leading end sections of leaders **55.** The leading end sections, designated **85**, of leaders **55**, are folded back upon themselves and each leading end section is detachably adhered to the leader of the preceding film unit, with the leading end section **85** of the first (to be exposed) film unit being attached to leader **56.** The folded leading end sections **85** of leaders **55** are contained within recess **84** which is provided with a deplaceable guide bar element **75.** As leader **56** or a leader **55** is withdrawn through opening **71**, the the leader is attached to the tapered end section and results in separation of the leader at these areas.

Application of withdrawing force on tapered end section **22**, advancing element **11**, second sheet **18** and container **21** between pressure-applying rolls **29** and **30** to the position shown in FIG. **8** provides rupture of the longitudinal marginal seal **32** of container **21** and unidirectional release of fluid processing composition **39** between and in contact with opposed leading end section **85** of the next succeeding leader **55** is unfolded and withdrawn from recess **84** where the leading end section may be grasped for pulling the leader from the camera. By virtue of this arrangement, only one leader at a time extends outside of recess **84** in position to be engaged and withdrawn.

In the operation of the film unit of the invention, leader **55** is pulled from the camera advancing tapered end section **22** and tapered end portion **23** between pressure-applying rolls **29** and **30** to the position shown in FIG. **7** at which leader **55** extends from its point of attachment to tapered end section **22** at almost a right angle from the plane of the tapered end section. At this position, the leading end of tapered end section **22** 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 **55** results in the exertion of a shearing force to leader **55** at the areas where it is secured to the surfaces of photosensitive element **11** and image-receptive element **16.**

Continued withdrawing force on film unit **10** between pressure-applying rolls **29** and **30** to the position shown in FIG. **9** provides interengagement under pressure between sheet **18** and exposure surface **19** of photosensitive element **11**, and sheet **18** will be maintained in superposed relationship with element **11** during and subsequent to processing external camera **57**, although optionally subject to separation, and the resultant dye transfer image viewed in image-receiving layer **104** during and subsequent to its formation through transparent support **107.**

Where desired trailing end section **27** of sheet **18** and trailing end section **25** of sheet **11**, for example, may be secured together by positive engaging means adapted to insure retention of processing composition overrun disposed intermediate the sections thus preventing escape external the film unit boundaries.

The positive engaging means employed should be simple and inexpensive to fabricate, so that it does not add appreciably to the cost of the film unit, and it should be easy to assemble and employ in order to contribute in a practical manner to the efficient operation of the film unit, and film pack and camera employing same. As examples of such engaging or lock closure means, mention may be made of moisture sensitive adhesives activatable upon contact with the fluid processing composition; self-adhering adhesives coated on the trailing prospectively opposed surface of each sheet element; and engaging members such as shaped, extruded plastic interlocking elements having a pluality of, preferably resilient, interlocking tongues and grooves mounted on the distal opposed surfaces of each sheet element; a male engaging member mounted on the distal surface of one sheet element and a female engaging member mounted on the distal prospectively opposed surface of the other sheet element and may comprise, respectively, tongue and groove or ball and socket construction, and preferably possesses at least one resilient component member adapted for frictional retention upon engagement with the second member; a plurality of polymeric hooks, for example, nylon hooks, positioned on the trailing edge of one sheet element and a plurality of filamentary loops on the trailing edge of the second sheet element such as the closure materials sold by Velcro Corporation, Manchester, N.H. etc.

It will be recognized that, as desired, the engaging means may extend, in whole or in part, in continuous or discontinuous fashion, lengthwise the trailing edge of edges retaining same.

In a preferred embodiment of the present invention, the means for interposing the processing composition selected intermediate the reception layer and the silver halide layer comprises a rupturable container retaining a processing composition comprising the solvent and pH concentrations required fixedly positioned and extending transverse a leading edge section of the sheet elements to effect, upon application of compressive pressure, discharge of the processing composition intermediate the reception layer and the photosensitive silver halide layer next adjacent. In such embodiment the opacifying agent is preferably disposed within the processing composition, as retained in the rupturable container, for distribution as a component of such composition intermediate the reception and silver halide layers, subsequent to selective exposure of the film unit.

Multicolor images may be obtained using color image-forming components in the diffusion transfer process of the present invention by several techniques. On 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 opaque support carrying a red-sensitive silver halide stratum, a green-sensitive silver halide stratum and a blue-sensitive silver halide stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide stratum, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide strata. Each set of silver halide strata and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate sepectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

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

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

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

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

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

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

In such preferred embodiment of the invention, the silver halide strata comprises photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution 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 dyeable polymeric layer is transparent and about 0.25 to 0.4 mil. in thickness; and each of the dimensionally stable opaque and transparent layers are alkaline solution impermeable 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 the preferred embodiment of the present inventions's film unit for the production of a multicolor transfer image, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable opaque layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the opaque layer and the magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing that the relative order of such units may be varied in accordance with the desires of the operator.

Referring to FIG. **5** there is shown a diagrammatic enlarged cross-sectional view of sheet elements **11** and **18** constructed in accordance with the present invention. The film unit is shown to specifically comprise with respect to sheet element **11** a photosensitive laminate **90** including, in order, dimensionally stable opaque layer **91**, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer **92**; red-sensitive silver halide emulsion layer **93**; interlayer **94**; magenta dye developer layer **95**; green-sensitive silver halide emulsion layer **96**; interlayer **97**; yellow dye developer layer **98**; blue-sensitive silver halide emulsion layer **99**; auxiliary layer **100**, which may contain an auxiliary silver halide developing agent. Image-receptive sheet laminate **101** is shown to comprise, in order, opaque layer **102**; reflection layer **103**; image-receiving layer **104**; spacer layer **105**; neutralizing layer **106**; and dimensionally stable transparent layer **107**, preferably an actinic radiation transmissive flexible sheet material.

The fluid contents of the container preferably comprise an aqueous alkaline solution having a pH and solvent concentration at which the dye developers are soluble and diffusible and contains an opacifying agent preferably in a quantity sufficient, upon distribution, effective to provide a layer exhibiting optical transmission density $> \sim 6.0$ to prevent exposure of photosensitive silver halide emulsion layers **93**, **96** and **99** by actinic radiation incident on dimensionally stable transparent layer **107** during processing in the presence of such radiation and to afford immediate viewing of dye image formation in image-receiving layer **104** during and subsequent to dye transfer image formation. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of laminate are appropriately protected from incident radiation, at one major surface of the opaque layer **102** and at the remaining major surface by the dimensionally stable opaque layer **91.**

The selected reflecting agent providing reflecting layer **103** should be one providing image formed in the dyeable polymeric layer. In general, while substantially any reflecting agent may be employed, it is preferred that a reflecting agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable reflecting agents will comprise pigments providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially those agents possessing the optical properties desired for reflection of incident radiation.

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

A particularly preferred reflecting agent comprises titanium dioxide due to its highly effective reflection properties. In general, in such preferred embodiment, titanium dioxide will be present in a concentration effective to provide a percent reflectance of $> \sim 85$ will be coated at a coverage of $> \sim 200$ to $\sim 1{,}000^{+}$ mgs./ft.^{2} to provide the reflecting layer.

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

Where desired, reflecting agent pigment may thus be distributed in whole or in part within a processing composition permeable polymeric matrix such as gelatin and/or any other such polymeric matrixes as are specifically denoted throughout the specification as suitable for employment as a matrix binder and may be distributed in one or more of the film unit layers which may be separated or contiguous, opposite the image-receiving layer from the transparent support, provided that its distribution and concentration is effective to provide the denoted post processing masking function.

the opacifying agent selected should be one exhibiting maximum spectral absorption of radiation at the wavelengths to which the film unit's photosensitive silver halide layer or layers are sensitive and should be substantially immobile or nondiffusible during performance of its radiation filtration function, in order to maintain and enhance the optical integrity of the dispersion as a radiation filter unit functioning in accordance with the present invention, and to prevent its diffusion into and localized concentration within the reflection and/or image-receiving layer thereby decreasing the efficiency of the reflecting pigment dispersion as a background against which image formation may be immediately viewed, during and subsequent to the initial stages in the diffusion transfer processing of the film unit. Commensurate with the spectral sensitivity range of the associated silver halide layer or layers, the opacifying agent selected may comprise one or more filter materials possessing absorption complementary to such silver halide layers in order to provide effective protection against physical fog providing radiation during processing and the selected agents should be those exhibiting major spectral absorption during transfer image formation and will be preferably selected for employment in the minimum concentration necessary to provide an optical transmission density $> \sim 6.0$, at wavelengths at which the silver halide layer is maximally responsive.

As examples of opacifying agents adapted for employment in the practice of the present invention, mention may be made of opacifying pigments and opacifying dyes and mixtures of such dyes and/or pigments preferably dyes and pigments of black coloration and most preferably black pigments such as carbon black, iron oxide, titanium (III) oxide, titanium (III) hydroxide, and the like.

Preferred opacifying agent or agents will possess the maximum opacifying capacity per unit weight, be photographically nondelterious and substantially nondiffusible during and subsequent to distribution of the processing composition which may contain the same. A particularly preferred opacifying agent has been found to comprise carbon black due to its highly efficient absorption characteristics. In general, a processing composition particularly desired for employment in the letter identified embodiment will contain carbon black in a concentration effective, e.g., about 3 to 6 grams of carbon black dispersed in 100 cc. of water, to prevent transmission, through the distributed stratum comprising the composition, of in excess of 95 percent of the actinic radiation incident on the stratum.

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

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

In the performance of a diffusion transfer multicolor process employing film unit **10**, the unit is exposed to radiation, actinic to photosensitive laminate **90**, incident on the laminate's exposure surface.

Subsequent to exposure, film unit **10** is processed by being passed through opposed suitably gapped rolls **29** and **30** in order to apply compressive pressure to frangible container **21** and to effect rupture of longitudinal seal **32** and distribution of alkaline processing composition **39**, optionally possessing an inorganic opacifying pigment and a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible as a function of the point-to-point degree of exposure of red-sensitive silver halide emulsion layer **93**, green-sensitive silver halide emulsion layer **96** and blue-sensitive silver halide emulsion layer **99**, respectively, intermediate auxiliary layer **100** and image-receiving laminate **101**.

Alkaline processing composition **39** permeates emulsion layers **93, 96** and **99** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **92, 95** and **98**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to dyeable polymeric layer **104** to provide a multicolor dye transfer image to that layer which is viewable against the background provided by the reflecting layer **103** masking cyan, magenta and yellow dye developer remaining associated with blue-sensitive emulsion layer **99**, green-sensitive emulsion layer **96** and red-sensitive emulsion layer **93**. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline processing composition **39** transfer, by diffusion, through permeable polymeric reception layer **104**, permeable spacer layer **105** to polymeric neutralizing layer **106** whereby the environmental pH of the system decreases as a function of neutralization to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially nondiffusible to thereby provide a stable multicolor dye transfer image.

The alkaline solution component of the processing composition, positioned intermediate the photosensitive element and the image-receiving layer, thus permeates the emulsions to initiate development of the latent images contained therein. The respective associated dye developers are mobilized in unexposed areas as a consequence of the development of the latent images. This mobilization is apparently, at least in part, due to a change in the solubility characteristics of dye developer upon oxidation and especially as regards to solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsions, the associated dye developer is diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image.

Subsequent to distribution of processing composition **39**, leading end sections **20** and **23** including container **31** may be manually dissociated from the remainder of the film unit, as described above.

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

Photosensitive sheet elements similar to that shown in the drawings may be prepared, for example, by coating, in succession, on a gelatin subbed, 5 mil. opaque cellulose triacetate film base, the following layers:

1. a layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl-α-methyl]-ethylamino)-5,8-dihydroxy-anthraquinone dispersed in gelatin and coated at a coverage of about 80 mgs./ft.^{2} of dye and about 100 mgs./ft.^{2} of gelatin;
2. a red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 225 mgs./ft.^{2} of silver and about 50 mgs./ft.^{2} of gelatin;
3. A layer of the acrylic latex sold by Rohm and Haas Co., Philadelphia, Penna., U.S.A., under the trade designation AC–61 and polyacrylamide coated at a coverage of about 150 mgs./ft.^{2} of AC–61 and about 5 mgs/ft.^{2} of polyacrylamide;
4. a layer of magenta dye developer 2-(p-[β-hydroquinonylethyl]-phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of 70 mgs./ft.^{2} of dye and about 120 mgs./ft.^{2} of gelatin;
5. a green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 120 mgs./ft.^{2} of silver and 60 mgs./ft.^{2} of gelatin;
6. a layer comprising the acrylic latex sold by Rohm and Haas Co. under the trade designation B–15 and polyacrylamide coated at a coverage of about 100 mgs./ft.^{2} of B–15 and about 10 mgs./ft.^{2} of polyacrylamide;
7. a layer of the yellow dye developer 4-(p-[β-hydroquinonylethyl]-phenylazo)-3-(N,n-hexylcarbox-amido)-1-phenyl-5-pyrazolone and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 50 mgs./ft.^{2} of dye, about 15 mgs./ft.^{2} of auxiliary developer and 50 mgs./ft.^{2} of gelatin;
8. a blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 75 mgs./ft.^{2} of silver and about 75 mgs./ft.^{2} of gelatin; and

9. a layer of gelatin coated at a coverage of about 50 mgs./ft.^{2} of gelatin.

Image-receiving sheet elements may be constructed by coating a transparent 5 mil. cellulose triacetate film base, in succession, with the following illustrative layers:

1. a 7:3 mixture, by weight, of polyethylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1,400 mgs./ft.^{2}, to provide a polymeric acid layer;
2. a graft copolymer of acrylamide and diacetone acylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mgs./ft.^{2}, to provide a polymeric spacer layer;
3. a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of about 900 mgs./ft.^{2} and including about 20 mgs./ft.^{2} phenyl mercapto tetrazole, to provide a polymeric image-receiving layer; and
4. a layer of titanium dioxide coated at a coverage >~600 mgs./ft.^{2} titanium dioxide and ~ 150 mgs./ft.^{2} gelatin to provide a polymeric reflecting layer approximately 0.15 mil. thick.

The two components thus prepared may then be assembled together in the film unit form shown in the drawing employing rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising:

Water	100 cc.
Potassium hydroxide	11.2 gms.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250]	3.4 gms.
N-phenethyl-α-picolinium bromide	1.5 gms.
Benzotriazole	1.0 gm.
Titanium dioxide	40.0 gms.
Carbon black	6.0 gms.

such that, upon application of compressive pressure to a container, its contents may be distributed, upon rupture of the container's marginal seal, between the reflecting layer and next adjacent gelatin layer.

The photosensitive composite film units may be exposed and processed by passage of the exposed film units through appropriate pressure-applying members, such as suitably gapped, opposed rolls, to effect rupture of the container and distribution of its contents. During processing, the multicolor dye transfer image formation may be viewed through the transparent cellulose triacetate layer against the titanium dioxide reflecting layer backgroun. Multicolor dye transfer image formation will be found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation, with a period of approximately 90 seconds. The image formation may be immediately viewed upon distribution of the processing composition by reason of the protection against incident radiation afforded the photosensitive silver halide emulsion layers by the composition's optical transmission density of >~6.0 density units and against the titanium dioxide's effective reflective background.

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

Neutralizing means, for example, a polymeric acid layer of the type discussed above will be incorporated, as stated, in the film unit of the present invention, to provide reduction of the alkalinity of the processing solution from a pH at which the dyes are 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 reflectively of the dye transfer image. In such instance, the neutralizing layer may comprise particulate acid reacting reagent disposed within the film unit or a polymeric acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mils. in thickness, positioned intermediate the transparent support and image-receiving layer, and/or the Opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer, for example, approximately 0.1 to 0.7 mil. in thickness, next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

Specifically, the film units may employ the presence of a polymeric acid layer such as, for example, of the type set forth in U. S. Pat. No. 3,362,819 which, most preferably, includes the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the image-receiving layer.

As set forth in the last-mentioned patent, the polymeric acid layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, retained in the polymer layer. In the preferred embodiments disclosed, the polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters 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 receiving 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 receiving 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 receiving layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the polymer layer may be effected by mixing acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only an acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthayl 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 dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

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

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1,000, preferably of about 1,000 to 50,000, possessing a degree of acetalation within about 10 to 30 percent, 10 to 30 percent, 20 to 80 percent, and 10 tp 40 percent, 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.

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

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

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

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

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

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

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

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

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

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

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

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

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

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

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

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

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

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

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

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, and that any one or more of the described layers may comprise a composite of two or more strata of the same, or different, components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

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

I claim:

1. A photographic film unit for the production of a color photographic reflection print by diffusion transfer processing and adapted to be processed subsequent to photo-exposure by passage intermediate a pair of juxtaposed pressure-applying members, which film unit comprises first and second sheet elements affixed transverse a leading end section, said first sheet comprising an opaque support carrying on one surface photosensitive silver halide having associated therewith a diffusion transfer process dye image-providing material, said second sheet comprising a transparent support carrying on one surface, in order, a diffusion transfer image-receiving layer and a dye image-providing material permeable reflecting layer, at least one of said first and second sheets additionally carrying on the surface of said sheet intermediate the leading edge of said first sheet and said second sheet rupturable container means retaining a fluid processing composition for distribution intermediate said first and second sheets upon application of pressure to said container means, said second sheet adapted to be superposed contiguous the surface of said first sheet with said photosensitive silver halide and said reflecting layer intermediate said opaque and said transparent supports and an opacifying agent disposed integral with said reflecting layer or as a layer on the surface of said reflecting layer opposite said transparent support or in said fluid processing composition.

2. A photographic film unit as defined in claim 1 wherein the trailing end section of said rupturable container is spaced from the leading edge section of said photosensitive silver halide on said first sheet and said container is adapted to release said fluid processing composition at said trailing end upon application of compressive pressure to said container, said film unit additionally including a sheet extending transverse and affixed each lateral edge section of said first sheet pos-

sessing a leading edge section affixed overlying said trailing end section of said container and a trailing edge section of said sheet affixed contiguous said leading edge section of said photosensitive element providing thereby a conduit for transfer of said fluid processing composition from said container to said photosensitive element.

3. A photographic film unit as defined in claim **1** wherein said first sheet element includes a trailing end section extending rearward of the trailing edge of said photosensitive element adapted to be maintained in superposed relationship with the trailing edge section of said second sheet during processing of said film unit to retain, intermediate said opposed trailing edge sections, processing composition extruded at the trailing edge of said photosensitive element.

4. A photographic film unit as defined in claim **3** including a sheet element affixed at its trailing end section to a leading end section of one of said first and second sheet elements.

5. A photographic film unit as defined in claim **1** wherein said opacifying agent is disposed in a layer carried on said second sheet contiguous the surface of said reflecting layer opposite said transparent support.

6. A photographic film unit as defined in claim **1** wherein said reflecting layer comprises titanium dioxide disposed in a polymeric matrix permeable to processing composition solubilized dye image-providing material.

7. A photographic film unit as defined in claim **1** wherein said opacifying agent is carbon black.

8. A photographic film unit as defined in claim **1** wherein said fluid processing composition possesses a first pH at which the dye image-providing material is processing composition diffusible as a function of its associated photo-sensitive silver halide's exposure to incident actinic radiation and including means for converting, subsequent to substantial diffusion of solubilized dye image-providing material to said diffusion transfer image-receiving layer, the pH of the film from said first pH to a second pH at which a dye transfer image provided by said dye image-providing material exhibits increased stability.

9. A photographic film unit as defined in claim **8** wherein said dye image-providing material comprises a dye which is a silver halide developing agent soluble and diffusible in an aqueous alkaline processing composition at the first pH and substantially nondiffusible at a second pH lower than the first pH and said means for converting said pH of said film unit are adapted to reduce said processing composition from said first pH to said second pH subsequent to substantial dye transfer image formation.

10. A photographic film unit as defined in claim **1** including, carried on said opaque support, at least two selectively sensitized silver halide layers each having a dye image-providing material adapted to provide dye image predetermined color as a function of the photoexposure of its silver halide layer.

11. A photographic film unit as defined in claim **10** wherein each of the selectively sensitized silver halide emulsion layers possesses predominant spectral sensitivity to separate regions of the spectrum and the dye image-providing material associated with each of said silver halide emulsion layers is adapted to provide a dye transfer image possessing a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity image of its associated emulsion layer.

12. A photographic film unit as defined in claim **11** wherein the reflecting layer includes an inorganic light-reflecting pigment.

13. A photographic film unit as defined in claim **8** wherein said fluid processing composition is an aqueous alkaline composition and said means for converting the pH of said film unit comprise an acidic polymeric layer disposed intermediate said transparent support and image-receiving layer or said opaque support and said photosensitive silver halide.

14. A photographic film unit as defined in claim **13** wherein said first sheet includes, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque support; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of the cyan, magenta, and yellow dyes being silver halide developing agents and being soluble and diffusible, in alkali, at a first pH; said second sheet includes an alkaline solution permeable layer comprising titanium dioxide; an alkaline solution permeable and dyeable polymeric layer; an acidic polymeric layer adapted to effect reduction of a processing composition having the first pH at which the cyan, magenta and yellow dyes are soluble and diffusible to a second pH at which the dyes are substantially nondiffusible; and a dimensionally stable alkaline solution impermeable transparent support; and said rupturable container means retain an aqueous alkaline processing composition having the first pH and containing substantially uniformly disposed therein carbon black substantially nondiffusible from said processing composition, said carbon black taken together with said titanium dioxide present in a quantity sufficient, upon distribution of the aqueous alkaline processing composition possessing the first pH as a layer intermediate the titanium dioxide layer and the blue-sensitive silver halide emulsion layer, to prevent exposure of said silver halide emulsion layers by radiation incident on said transparent support.

15. A photographic film unit as defined in claim **14** wherein said carbon black is disposed, prior to distribution of said processing composition, in an alkaline solution permeable layer contiguous the surface of said titanium dioxide layer opposite said transparent support.

* * * * *

Disclaimer

3,778,271.—*Edwin H. Land*, Cambridge, Mass. PHOTOGRAPHIC PRODUCTS COMPRISING AN OPACIFYING AGENT IN ASSOCIATION WITH A REFLECTING AGENT. Patent dated Dec. 11, 1973. Disclaimer filed May 7, 1973, by the assignee, *Polaroid Corporation.*

Hereby disclaims the portion of the term of the patent subsequent to Dec. 10, 1985.

[*Official Gazette November 19, 1974.*]