June 26, 1973 P. A. LA MONACA 3,741,766

PHOTOGRAPHIC FILM UNIT FOR PRODUCING IMAGES IN COLOR

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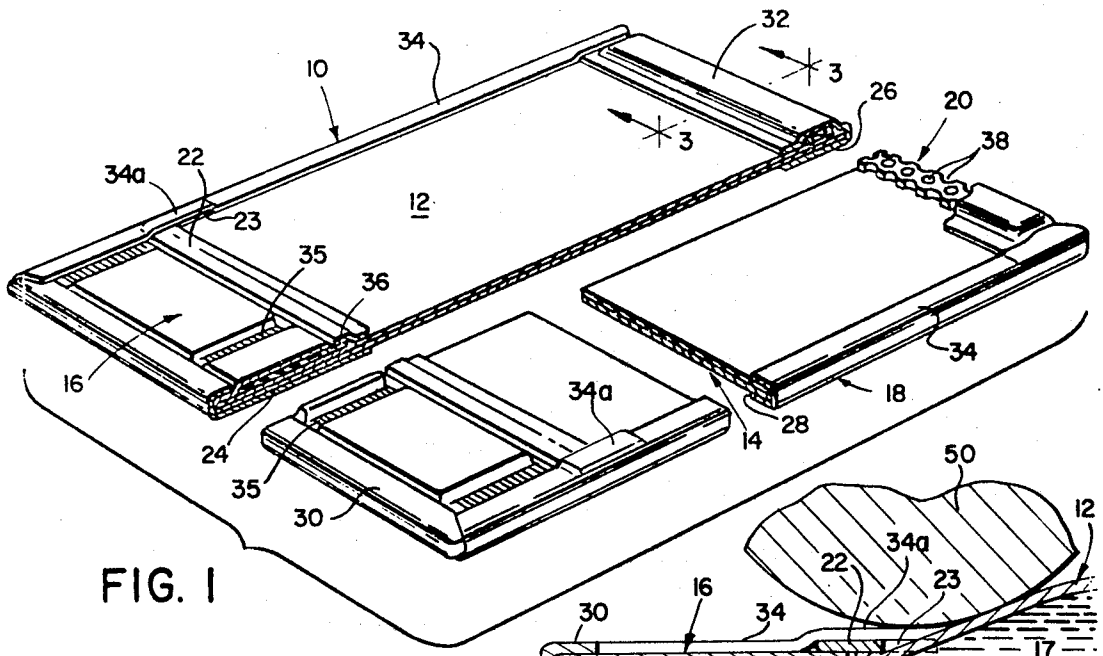


FIG. 1

FIG. 3

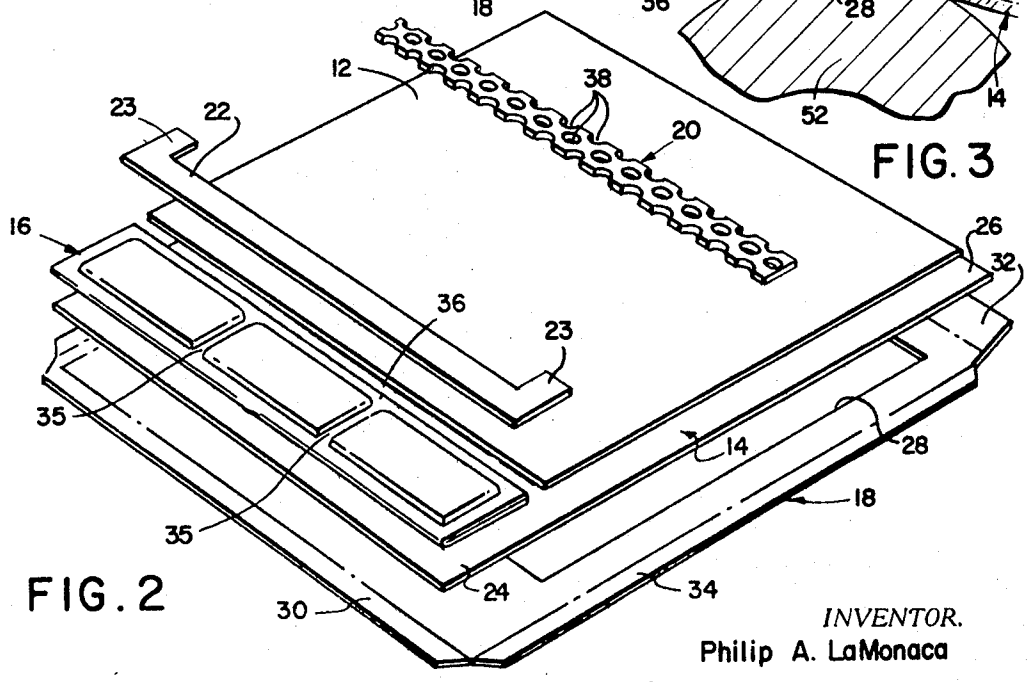


FIG. 2

INVENTOR.
Philip A. LaMonaca

BY Brown and Mikulka
and
Robert E. Corb
ATTORNEYS

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PHOTOGRAPHIC FILM UNIT FOR PRODUCING IMAGES IN COLOR

Philip A. LaMonaca, Randolph, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

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ABSTRACT OF THE DISCLOSURE

A photographic, self-developing film unit comprising a photosensitive layer including selectively sensitized silver halide emulsions having associated therewith dye image-forming materials, adapted to be exposed and processed to produce a color transfer image. The film unit comprises first and second rectangular sheets secured in face-to-face relation at their lateral and trailing end margins by a generally rectangular binding sheet including a medial rectangular opening surrounded by lateral and end marginal portions. The binding sheet is secured to the outer surface of one of the sheets and the lateral and end marginal portions are folded around lateral and trailing end edges of the sheet and secured to the outer surfaces of the other sheet. A container of processing liquid is attached to the leading end of one of the sheets by a binding strip secured in overlapping relation to the container and leading end margin of the sheet. The film unit is adapted to be processed by advancing it, container foremost, relative to and between a pair of juxtaposed pressure-applying members which discharge the liquid contents of the container therefrom and distribute the processing liquid in a layer between the sheets for permeation into the photosensitive layer. The external binding sheet functions to control the thickness of the layer of liquid and to provide processing liquid at the edges of the exposed area sufficient to insure complete transfer color image formation to the edges of the area in which the visible image is desired. The binding strip includes end sections extending a short distance toward the trailing end of the film unit beyond the leading edge of the opening in the binding sheet for spacing apart the pressure-applying members to insure spreading of sufficient processing liquid between the sheets in this region.

BACKGROUND OF THE INVENTION

A film unit of the type with which the present invention is concerned generally includes laminated first and second sheetlike elements and a container of processing liquid including all of the various strata and materials required to produce a positive reflection print, preferably in full color, by a diffusion transfer process. Such film units are disclosed, for example, in U.S. Pat. Nos. 3,415,644, 3,415,645, 3,415,646, 3,443,500, 3,573,925, 2,578,840, 3,589,904, 3,594,164, and 3,594,165. Such film units are also disclosed in Pat. No. 3,619,192, dated Nov. 9, 1971, which is more specifically concerned with the structural and mechanical aspects of the film unit and their functional cooperation with and relation to the processing liquid, its distribution and permeation into the various layers of the film laminate to produce an attractive, high quality image.

In general, the film unit of the invention includes rectangular first and second sheetlike elements arranged in superposed face-to-face relation, one of the sheets, preferably the first sheet, comprising a layer of a photosensitive, image-recording material having, as components thereof, selectively sensitized silver halide emulsions having associated therewith, dye image-forming materials. The film unit also includes a dyeable, polymeric layer

which may be carried on the other or second sheet in which case the second sheet functions as an image-receiving sheet, or the dyeable, polymeric layer may be supported on the same sheet as the photosensitive layer in which case the other or second sheet may function primarily to aid in the distribution of a liquid processing compositon between the sheets. The processing liquid is preferably supplied in a container such as described in U.S. Pat. No. 2,543,181 and in any of the aforementioned patents and applications. The container is formed of a rectangular blank of a fluid-impermeable sheet material folded upon itself and sealed at its margins to form a cavity which is filled with the processing liquid. The seal at a longitudinal margin of the container is adapted to become unsealed in response to the application of compressive pressure to form a discharge passage for the liquid contents of the container.

The film unit also includes a generally rectangular binding sheet having lateral and end marginal portions surrounding a generally rectangular medial opening permitting exposure of the photosensitive layer and/or viewing of a color diffusion transfer image formed within the film unit. At least one, and in some instances, both of the first and second sheets is transparent to permit exposure and image viewing, and the rectangular binding sheet is preferably secured to the transparent sheet through which the color transfer image is to be viewed in order to provide an aesthetically pleasing border surrounding the visible image. The lateral and trailing marginal portions are folded around the lateral and marginal edges of both sheets and secured to the outer surface of the other sheet to retain the superposed sheets in face-to-face relation along three sides thereof. Depending upon the particular structure of the film unit, the leading end marginal portion of the binding sheet may be secured to the rectangular margin of the container at the discharge passage and thereby function to attach the container to one of the sheets.

The film unit also includes a narrow, elongated binding strip having substantially parallel, longitudinal edges, secured in overlapping relation to a rectangular marginal portion of the container at the discharge mouth and to the leading edge portion of the sheet to which the end and marginal edges of the binding sheet are secured. The binding strip performs at least the dual functions of securing the container to one of the sheets at an edge thereof and providing a passage for conducting the processing liquid contents of the container therefrom between the superposed portion of the first and second sheets.

In the preferred embodiment of the film unit shown and described in the aforementioned patents, particularly 3,619,192, the edges of the rectangular opening in the binding sheet, i.e., the opening through which the image is viewed, are located inwardly from the corresponding edges of the binding sheet and binding strip. Thus the edges of the binding sheet, in combination, form another rectangular opening preferably larger than the opening in the binding sheet and located symmetrically with respect thereto. One of the functions of the binding sheet is to control the distribution of the processing liquid between the sheets, i.e., the thickness and extent of the layer of liquid. An important feature of the arrangement described and pointed out in greater detail in the aforementioned patents, particularly 3,619,192, is that it provides for distribution of the processing liquid outwardly beyond at least the lateral and trailing end edges of the opening (image-viewing) in the binding sheet thereby assuring the presence of processing liquid in an amount sufficient to insure complete processing and image formation to the edges of the smaller of the two openings, namely the image-viewing opening preferably formed in the binding

sheet. This occurs by virtue of the fact that this construction permits the processing liquid to spread between the sheets into the region underlying the edges of the smaller opening and thereby provide a reservoir of excess liquid available to prevent liquid starvation and to insure complete processing and color diffusion transfer image-formation in a region extending at least to the edges of the smaller opening. This problem is particularly critical in a film structure in which the photosensitive layer includes a plurality of selectively sensitized silver halide emulsions and dye image-forming materials. If any area of one of the emulsions or associated dye image-forming materials is not adequately permeated with the processing liquid, then an image defect is the possible result.

SUMMARY OF THE INVENTION

The present invention is concerned with a novel and improved film unit construction of the type described, designed to provide for distribution of processing liquid at the leading edges of the image-viewing opening sufficient to insure complete processing and image formation in this region particularly near the edges thereof.

This and other objects of the invention are achieved by providing end sections on the binding strip extending a relatively short distance toward the trailing end of the film unit for spacing apart the pressure-applying members as they pass over the film unit in the region of and slightly beyond the leading edges of the image-viewing opening and thereby provide for a greater amount of processing liquid in this region than would otherwise be provided. Thus there is assured sufficient processing liquid to completely permeate the multi-strata photosensitive layer with its selectively sensitized emulsions and associated dye-image forming materials and enable diffusion transfer of all of the transferrable image-forming material, particularly from the strata situated furthest from the layer of processing liquid.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view, partially in section, showing a film unit embodying the invention;

FIG. 2 is an exploded perspective view of the film unit of FIG. 1; and

FIG. 3 is a somewhat schematic, longitudinal, sectional view of the film unit illustrating the spreading of the processing liquid, the thickness of the materials being exaggerated for purposes of clarity of illustration.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, the preferred form of the film assemblage is designed for the production of a dye reflection print and 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. These components include first and second sheetlike elements comprising two dimensionally stable layers, at least one of which is transparent; and a multiplicity of layers supported on and between said dimensionally stable layers including a diffusion transfer process dye image-receptive layer; layers of a photoresponsive material each having associated therewith a dye image-providing material which is processing composition diffusible as a function of the photoexposure of its associated photoresponsive material to produce photographic information recordatin; and an opaque layer. One of the dimensionally stable layers constitutes a sheet or element superposed and at least coextensive with the portion of the layer of photoresponsive material supported on the other dimensionally stable layer or support sheet and constituting the first or photosensitive sheet or element. The film unit includes a rupturable container of a fluid agent including an opacifying agent adapted to be distributed between the sheetlike elements for reacting with exposed photoresponsive material for forming the image in the image-receptive layer. The opacifying agent disposed in the processing composition is adapted to cooperate with the opaque layer to prevent exposure of the photoresponsive material by radiation actinic thereto inicident on the film unit during processing in the light. Thus, the film unit of the present invention enables the production color reflection prints employing photographic diffusion transfer processing effected externally of the camera in which the film unit is subjected to exposure and in the presence of ambient radiation.

Multicolor images may be obtained using color image-forming components in the diffusion transfer process of the present invention by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing, for example, dye developers as dye-image-providing materials by employment of an integral, multilayer photosensitive element, such as is disclosed in aforementioned U.S. Pat. No. 2,983,606, wherein at least two selectively sensitized photosensitive strata, superposed on a single support, are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises an 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. Each 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 alochol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

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

The dye developers are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include 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, in a preferred embodiment, or in a separate layer behind the respective silver halide stratum. Specifically, the dye developer may, for example, be in a coating or layer behind or directly disposed in the respective silver halide stratum and such dye developer structure may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

In a preferred embodiment of the present invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order, at least two selectively sensitized silver halide emulsion strata each having dye image-providing material of predetermined image color subsequent to processing associated therewith which is soluble and diffusible, in alkali, at a first pH, as a function of the photoexposure of its associated silver halide emulsion stratum; an alkaline solution permeable opaque layer; an alkaline solution permeable polymeric layer dyeable by the dye image-providing materials; an alkaline solution permeable polymeric layer containing sufficient acidifying capacity to effect reduction, subsequent to substantial multicolor transfer dye image formation, of a processing composition having the first pH to a second pH, at which the dye image-providing material is substantially nondiffusible; and the dimensionally stable transparent layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing subsequent to photoexposure or processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion. Specifically preferred dyes comprise dyes which exhibit major spectral absorption outside of the primary regions of the spectrum to which the associated silver halide emulsion is sensitive and a spectral transmission substantially complementary to that absorption, during exposure of the emulsion, and major spectral absorption within the spectral range to which the associated silver halide emulsion is sensitive and spectral transmission substantially complementary to said absortpion, subsequent to exposure or processing of said emulsion, for example, of the type disclosed in U.S. Pat. No. 3,307,947.

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

In such preferred embodiments of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself may be dispersed in an aqueous alkaline solution permeable polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; the alkaline solution polymeric spacer layer is transparent and about 0.1 to 0.7 mil in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mils in thickness; and the dimensionally stable transparent layer is alkaline solution impermeable and about 2 to 6 mils in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

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

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

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

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

Employment of the detailed film unit of the present in-

vention, according to the hereinafter described color diffusion transfer photographic process, is specifically adapted to provide for the production of a color transfer image accomplised by a diffusion transfer process which may include in-process adjustment of the environmental pH of the film unit, from a pH at which transfer processing is operative to a pH at which dye transfer is substantially inoperative, subsequent to substantial transfer image formation, in order to obviate the previously discussed disadvantages of the prior art products and processes. The color transfer image is thus obtained and maintained irrespective of the fact that the film unit comprises an integral laminate unit during exposure, processing and subsequent viewing, and storage of the unit. Accordingly, by means of the present invention, color transfer images and specifically multicolor images may be obtained, employing an integral laminate film unit, which exhibit desired maximum and minimum dye densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation, over an extended period of time, as compared with prior art disclosed film materials. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

Reference is now made to FIGS. 1 and 2 of the drawings wherein there is illustrated one form of a photographic self-developing film unit **10** of the type described embodying the invention, the thickness of the materials being exaggerated to facilitate understanding. Film unit **10** comprises a first or photosensitive sheetlike element **12**, a second or image-receiving sheetlike element **14** and a rupturable container **16** holding a quantity of processing liquid **17**. Sheetlike elements **12** and **14** are preferably rectangular and co-extensive with one another and are arranged in superposed face-to-face contact with at least the lateral edges of each element aligned with the lateral edges of the other.

Second sheet **14** is substantially longer than sheet **12** and includes a leading end section **24** extending beyond the leading edge of sheet **12** by a distance slightly in excess of the shorter dimension of container **16**; and a trailing end section **26** extending a relatively short distance beyond the edge of sheet **12** in a preferred embodiment of the film unit. Although sheets **12** and **14** may be separate and distinct sheets, they are preferably laminated to one another throughout substantially the entire area of their facing surfaces except for a narrow region adjacent the leading edge of sheet **12**. This provides for a more stable and easier to handle structure while eliminating the problem of air between the sheets.

Container **16** is mounted on the leading edge section **24** of sheet **14** adjacent the leading edge of sheet **12** in position to discharge its liquid contents between the photosensitive and second sheets. Container **16** is retained in place by portion of lateral edge sections **34** secured to the ends of the container and leading end section **30** of binding sheet **18** which is folded around the leading edge of sheet **14** and secured to a longitudinal edge of the container. A binding or sealing strip **22** is secured to a longitudinal marginal section of the container and the leading end margin of photosensitive sheet **12** and cooperates with the container and sheets to bridge the gap between the container and the photosensitive sheet and form a conduit for conducting the liquid from the container between the photosensitive and second sheets.

Sheets **12** and **14** are secured in face-to-face relation at their lateral and trailing end margins by a binding sheet **18** which is generally rectangular in shape and formed with a rectangular exposure opening **28** slightly smaller than sheet **12** and defining the area of the photosensitive sheet adapted to be exposed. Binding sheet **18** is preferably formed of a light opaque, white material such as, for example, a laminate including a layer of paper, a polymer, and an opaque layer such as metallic coating and/or pigment carried on or within a layer of sheet **18**. The mask or binding sheet **18** is larger than second sheet **14** and includes a leading end section **30**, a trailing end section **32**, and lateral marginal sections **34** adapted to be folded along the broken lines shown in FIG. 3. Sheet **18** is adhered to the outer surface of sheet **14** substantially over the entire area of the facing surface of the two sheets surrounding exposure opening **28**. Lateral marginal sections **34** of sheet **18** are folded around the lateral edges of sheets **12** and **14** and secured to the margins of sheet **12**. Trailing end section **32** of sheet **18** is folded around the trailing edge of sheet **14** and secured to the outer surface of photosensitive sheet **12** near the trailing edge thereof.

Container **16** is of the type shown in U.S. Pat. No. 2,543,181 and is formed by folding a rectangular blank of a fluid impervious sheet material medially and sealing the marginal sections of the blank to one another to form a cavity for containing processing liquid **17**. A pair of transverse regions **35** of the container are sealed together so as to divide the liquid-filled cavity into three sections and thereby obtain improved distribution of the processing liquid upon discharge thereof from the container. The seal between longitudinal marginal sections **36** of container **16** is weaker than the seals at the ends of the container so that upon the application of a predetermined compressive force to the walls of the container in the region of the liquid-filled cavity, there will be generated within the liquid hydraulic pressure sufficient to separate the longitudinal marginal sections **36** throughout the major portion of their length except in regions **35** and in the regions of the end seals, to form three discharged passages extending throughout the length of the cavity and the width of exposure opening **28**.

The most useful and advantageous film unit insofar as packaging, storing, handling, exposure, and processing are concerned, is one characterized by an integral, unitary, laminate form of structure designed so that its integrity may be maintained during and after exposure and processing; and a structure that is sturdy, has some flexibility, resists buckling and warping, remains flat particularly during exposure, and can be handled and manipulated by mechanical means without damage to produce a useful and attractive photographic print. A useful and attractive photographic print can be described as being substantially flat or planar and without a tendency to curl as the result of temperature and humidity changes; as being relatively rigid and inflexible as opposed to being limp or easily bent; as having a uniform white border surrounding a well-defined rectangular image that extends to the border; and a protective coating or covering for the image permitting the print to be handled and stored without the necessity for taking special precautions to avoid damage and deterioration. The structure and composition of components of the film unit of the invention combine to provide a film unit meeting these criteria and specially adapted, when processed, to provide a useful and attractive photographic print, preferably in full color, having the foregoing characteristcis.

In order to provide a rigid durable structure having an integity which is maintained from the time of assembly (during manufacture) to the finished print and providing a protective environment for the photosensitive medium as well as the final image, while permitting exposure of the photosensitive medium and viewing of the final image, at least one of the sheets of the film unit is formed of a transparent material. In the embodiment shown, the second or image-receiving sheet is transparent and the photosensitive medium is exposed and the final image is viewed through the image-receiving sheet

which functions to protect the image-recording medium prior to and during exposure and to protect the final image during and following formation thereof. In other embodiments of the film unit, the photosensitive sheet may be transparent depending upon the manner in which the image-recording medium is exposed and the final image is formed and viewed. The transparent image-receiving sheet may be formed of a conventional film base material such as cellulose triacetate coated on its inner surface with one or more layers such as previously described providing an appropriate environment for the formation of a diffusion transfer image.

The embodiments of the film unit illustrated and described herein are adapted to be exposed in a light-free environment such as in a camera. Processing is then initiated within the light-free environment by spreading the processing liquid between sheets **12** and **14**. In the preferred method of processing, the film unit is moved directly from the camera into the presence of radiation actinic to the photosensitive material immediately as the processing liquid is spread bewteen the sheets. In order to prevent exposure by ambient radiation, the photosensitive layer is required to be protected by opaque layers located on opposite sides of the photosensitive layer. In the preferred embodiment, one of these opaque layers, specifically, the layer located to the side (rear) of the photosensitive layer opposite transparent sheet **12** is formed during the manufacturing process, is in existence at the time of exposure and may retain its opacity subsequent to processing. The location of this opaque layer depends upon the location of the layer in which the transparent layer is formed. For example, in the embodiment in which the image-receiving layer is intermediate the photosensitive layer and the transparent support of sheet **12**, e.g., coated on the transparent film base, the opaque layer may comprise light absorbing material in the support of sheet **12** and/or a layer or layers of opaque material coated thereon between the support and photosensitive layer. Alternatively, in an embodiment in which the photo sensitive layer is located intermediate the image-receiving layer and sheet **14**, the opaque layer is formed and located (as described in detail hereinafter, between the photosensitive and image-receiving layers and is formed of a material through which the image-forming substances, i.e., dye developers, are diffusible. In both embodiments, the opaque layer also functions to prevent exposure of a film unit arranged in underlying, stacked relation with a film unit being exposed in a camera. The opaque layer is, of course, required to be formed after exposure, specifically, by distributing between the sheets an opaque liquid processing composition such as described hereinafter. If the illustrated binder sheet and strip are also opaque, as stated above, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The opaque layer or layers located between the photosensitive and image-receiving layers, however, should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric (image-receiving) layer. In general, while substantially any permeable opaque layer may be employed in the case where diffusion transfer is through the opaque layer, it is preferred that a layer be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, a layer which is aesthetically pleasing to the viewer and does not provided a background noise signal degrading, or detracting from, the information content of the image. Opaque layers particularly desirable for this purpose will be those providing a white background for viewing the transfer image, and specifically those adapted to be employed to provide background for reflection photographic prints and, especially, those layers possessing the optical properties desired for reflectance of incident radiation. The same properties are also desirable in the embodiment in which the opaque processing liquid provides the background for viewing the dye transfer image.

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

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

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

In the embodiment in which the dye developers are transferred through a preformed opaque layer which forms the image background, the opacifying agent dispersed in the processing composition may be any of the multiplicity of such agents known in the art such as carbon black, iron oxide, titanium (III) oxide, titanium (III) hydroxide, and the like. In preference, the agent or agents should be selected which possess the maximum opacifying capacity per unit weight, is photographically nondeleterious and is substantially non-diffusible throughout the film unit subsequent to distribution. A particularly preferred agent has been found to comprise carbon black employed in a concentration effective to provide the opacity required to prevent undesired physical fogging of the emulsion formulations selected and employed by radiation transmitted through the spread processing composition. On the other hand, when the opaque processing composition provides the background for the visible dye image, it will contain the aforementioned agents designed to provide a white background and a lesser (if any) quantity of opacifying agents that do not appear white.

In the preferred form of the film unit designed to produce a full color dye transfer image in a dyeably polymeric layer, the photosensitive layer comprises a laminate including, in order, a blue-sensitive silver halide emulsion layer containing a yellow dye developer; an interlayer; a green-sensitive silver halide emulsion layer containing a magenta dye developer; an interlayer; and a red-sensitive silver halide emulsion layer containing cyan dye developer.

Subsequent to exposure, film unit **10** is processed by being passed between a pair of superposed pressure-applying member such as rollers designated **50** and **52** in FIG. 3 to apply compressive pressure to container **16** to effect rupture of longitudinal seal between portions **36** and distribution of processing the composition containing an opacifying agent and having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate transparent sheet **14** and the coextensive surface of the blue-sensitive silver halide emulsion layer. The processing composition permeates the

emulsion layers to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers 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 transfer, by diffusion, to a processing composition permeable polymeric (image-receiving) layer to provide a multicolor dye transfer image in that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising the aqueous composition transfer, by diffusion, through a permeable spacer layer and to permeable polymeric acid layer both coated on one of the two sheets, whereby the solution decreased in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image viewable through one of dimensionally stable transparent support sheets.

During processing the pressure-applying members e.g., rollers **50** and **52**, initially apply compressive pressure to the container to eject its liquid contents as a mass between the photosensitive and second sheets and then distribute the mass of liquid between the sheets toward the trailing ends thereof to form a layer of substantially uniform predetermined thickness which is continuous and at least coextensive with the area defined by exposure opening **28**. While it is desirable to provide a minimum of liquid within the container, in order to insure sufficient processing liquid to form a layer of the requisite area and thickness between the sheets, it is necessary to provide excess processing liquid in container **16**.

The film unit includes trapping means for collecting and retaining excess processing liquid overrun so that it does not escape from the film unit. In the form shown, these means comprise trapping an element **20** shown as a narrow strip of a relatively thick sheet material formed with perforations and indentations **38** which occupy a large, e.g., 45% to 55%, portion of trapping element **20**. The traping element is secured between the trailing end section **32** and the trailing end margins of sheets **12** and **14** with the perforations and indentations **38** cooperating with sheets **12**, **14** and **18** to provide spaces for collecting and retaining excess processing liquid overrun. The trapping element functions as a spacer as the trailing end portion of the film unit passes between the pressure-applying members preventing the processing liquid from being further advanced thereby in the direction of spreading.

It should be apparent that in order for proper image formation to occur throughout the visible image area defined, for example, by opening **28** in binding element **18**, the processing liquid absorbed into the photosensitive layer must be sufficient to completely permeate the layer and that this should occur throughout the entire image area in order to effect complete development of the exposed photosensitive material as well as mobilization of the dye image-forming materials required to produce a transfer image having a good color fidelity. If insufficient processing liquid is absorbed into a particular area of the photosensitive layer, then the diffusion transfer dye image formed from that area will be deficient in the dye image-forming material associated with the particular photosensitive silver halide strata located furthest from the surface against which the processing liquid is distributed for absorption by the photosensitive layer. Thus, in the example given, wherein the photosensitive layer comprises, in order, blue-, green-, and red-sensitive emulsions having associated therewith respectively, yellow, magenta, and cyan dye developers and is processed by a liquid distributed in contact with the blue-sensitive emulsion or other stratum closest thereto; insufficient processing liquid will be manifested by a lack of cyan dye in the transfer image resulting in a reddish hue in the corresponding area of the transfer image.

It will be seen from FIG. 3 as well as from the aforementioned patent and applications, particularly Pat. No. 3,619,192, that the amount of processing liquid available for permeation into any particular area is a function of the thickness of the layer of viscous processing liquid distributed in that particular area. Good color image fidelity throughout the entire visible transfer image of course is best assured if the processing liquid is distributed in a layer of uniform thickness throughout the major portion of the area in which the image is to be formed. The thickness of the layer of processing liquid and also its extent are determined by the thickness and extent of binding element **18** which determines the spacing between the medial portions of the pressure-applying members, i.e., rollers **50** and **52**, which, in turn, determine the spacing between the portions of elements **12** and **14** which contact the pressure-applying members and between which the processing liquid is distributed.

The film unit is designed to be employed in photographic apparatus incorporating a pair of pressure-applying members such as rollers **50** and **52** having opposed surfaces defining a convergent passage. The surfaces of the pressure members are preferably substantially linear at least at the narrowest point in the passage so that, as in the case of cylindrical rollers, the spacing between the surfaces and, in turn, the spread thickness, is determined primarily by the thickness of binding element **18**. This is because the margins of the film unit immediately adjacent the image area where the binding element is of double thickness, constitute the thickest portion of the film unit at least in the region where the image is formed. Thus, the pressure-applying members engage the binding element adjacent the lateral edges of the image area and are spaced apart by at least the combined thickness of elements **12** nd **14** and two thicknesses of binding element **18**. This, in turn, results in a processing liquid spread thickness approximating the two thicknesses of the binding element throughout at least the major portion of the image area defined by opening **28** due to the fact that elements **12** and **14** are forced apart into contact with the pressure-pplying members (rollers **50** and **52**) as a result of hydraulic pressure generated within the processing liquid as it is being spread (see FIG. 3).

It has been found that transfer image formation problems occur at the margins of the image area where the extent of the layer of processing liquid is determined by the edges of aperture **28** and the edges of portions **32** and **34** of element **18** and binding strip **22** which also cooperate to form a rectangular opening. The problem of insufficient processing liquid to completely permeate the photosensive layer manifests itself as a discoloration (red) at the edges of the visible image and is, in part, due to the inherent stiffness of elements **12** and **14** which results in a tapering off or reduction in the depth of the space between the elements near the edges of opening **28** and the edges of the opening formed by the edges of binding element **18** and strip **22**. This problem is further aggravated by the fact that the processing liquid is not merely absorbed depthwise of the photosensitive layer but migrates laterally into the photosensitive layer beyond the actual edges of the layer of processing liquid. Thus, not only is there a gradual fall off in the amount of liquid available at the edges of the layer of liquid due to element stiffness, but the tendency for the liquid to migrate laterally into regions of the photosensitive layer (and other layers) outside of the area from which the image is formed also helps to contribute to an insufficiency of liquid near the edges of the image area.

A partial solution to this problem is suggested in the 3,619,912 patent, this being to form binding sheet **18** and opening **28** such that the lateral and trailing end edges of the binding sheet are located closer to the edges of the film unit than the corresponding edges of opening **28** through which the transfer image is viewed. By virtue of this differential width of the binding element at the lateral and trailing end edges, processing liquid is spread between the photosensitive and second elements beyond the edges of the image area defined by opening **28** thus providing extra processing liquid outside of and immediately adjacent the area in which the visible transfer image is formed. This "excess" liquid is then available to help insure complete permeation of the various layers of the laminate by processing liquid sufficient to produce a dye transfer image that is complete to the edges of the visible image area.

The same basic approach is also employed to help insure sufficient processing liquid at the leading edge of the visible image area. In the embodiment shown in detail in FIG. 3, the edge of opening **28** extends toward the trailing end of the film unit beyond the edge of binding strip **22** in order to provide for the spreading of processing liquid in the region underlying the binding element near the transverse leading edge of opening **28**.

It has been found that although helpful, offsetting of the edges may not completely solve the problem of providing sufficient processing liquid to insure transfer image formation to the edges of the visible image area. U.S. application Ser. No. 804,819, filed Mar. 6, 1969, suggests, as an answer to the problem of supplying sufficient processing liquid at the lateral edges, the use of a specially designed pressure-applying member, i.e. roller, for spreading the processing liquid. Such a roller, which engages the binding sheets at the lateral edges of opening **28**, is formed with annular grooves near its ends for receiving portions of the binding sheet at the lateral edges of opening **28** to permit additional spacing of sheets **12** and **14** in this region during spreading of the processing liquid. While such a structure incorporated in apparatus for distributing the processing liquid proves satisfactory for insuring sufficient liquid at the lateral edges of the visible image area, it does not provide a solution to the problem of providing adequate processing liquid at the leading transverse edge of opening **28**. The object of the present invention, i.e., the solution of this problem, is achieved by a novel film structure in which binding strip **22** is provided with end portions **23** which extend beyond the trailing transverse edge of strip **22** a short distance toward the trailing end of the film unit. The trailing transverse edge of strip **22** is at least equal to the width of opening **28** and portions **23** have widths which do not exceed the width of marginal sections **34** of binding sheet **18**. End portions **23** are preferably secured in face-to-face underlying relation to portions, designated **34***a*, of marginal sections **34** and function to increase the thickness of the lateral margins of the film unit in these regions. Thus, as the pressure-applying members, i.e., rollers **50** and **52**, pass beyond the trailing transverse edge of strip **22** (as shown in FIG. 3), the rolls continue to be spaced apart by the added thickness resulting from end sections **23**, thus providing for additional spacing of sheets **12** and **14** in the regions of the leading edge of the visible image area.

In an alternative embodiment, end portions **23** may be narrower than marginal sections **34** so that the edges of the end portions and the edges of marginal sections **34** are offset from one another. Also, depending upon the method of assembly, end portions **23** may be secured to the outer surfaces of marginal sections **34** rather than between the marginal sections and the lateral margins of sheet **12** as shown in FIG. 1.

It will be apparent from the foregoing that the invention provides a simple and inexpensive solution to the serious problem of achieving complete visible image formation adjacent the leading edge of the visible dye transfer image by insuring the distribution of sufficient processing liquid by virtue of the novel structure of a component of the film unit itself.

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

What is claimed is:

1. A photographic film unit for producing a diffusion transfer process color image comprising, in combination:

a laminate including a pair of dimensionally stable layers at least one of which is transparent and a plurality of layers therebetween including a photosensitive layer comprising at least two selectively sensitized silver halide strata each having associated therewith a diffusion transfer process dye image-forming material, and an image-receptive layer adapted to receive said diffusion transfer process dye image-forming materials diffusing thereto, said laminate being substantially rectangular and having lateral and leading and trailing end edges;

a generally rectangular binding sheet secured to the outer face of said transparent dimensionally stable layer having lateral and trailing edge portions folded around the lateral and trailing edges of said laminate and secured to the lateral and trailing end margins of the other of said dimensionally stable layers, said binding sheet being formed with a rectangular opening defining the boundaries of a dye transfer image visible through said transparent layer;

a rupturable container of a liquid processing composition for initiating development of photoexposed silver halide and diffusion transfer of dye image-forming materials, solubilized by said processing composition to said image-receptive layer upon distribution of said processing composition as a layer between layers of said laminate and permeation of at least said liquid processing composition into said photosensitive layer; and

means for securing said container to said laminate adjacent the leading edge thereof in position to discharge the liquid contents of said container between layers of said laminate in response to the application of compressive pressure to said container, the last-mentioned means including a second binding sheet secured in overlapping relation to a transverse portion of said container and the outer face of the leading transverse edge portion of said other dimensionally stable layer;

said second binding sheet having a substantially linear trailing edge arranged substantially parallel with the leading transverse edge of said opening in the first-mentioned binding sheet and at least equal in length to the transverse dimension of said opening, and including end sections extending a relatively short distance toward the trailing end of said film unit in face-to-face contact with said lateral margins of said first-mentioned binding sheet.

2. A photographic film unit as defined in claim **1** wherein said end sections of said second binding sheet are engaged between said lateral margins of said first-mentioned binding sheet and said other dimensionally stable layer.

3. A photographic film unit as defined in claim **2** wherein said trailing edge of said second binding sheet is offset with respect to said leading transverse edge of said opening toward the leading end of said film unit.

4. A photographic film unit as defined in claim **1** wherein said image-receptive layer is located between said photosensitive layer and said transparent dimensionally stable layer and the weakest bond between any layers of said film unit is located intermediate said photosensitive

and image-receptive layers to provide for delamination of said laminate by and in response to distribution of said processing liquid from said container between said photosensitive and image-receptive layers.

5. A photographic film unit as defined in claim 1 wherein each of said selectively sensitized silver halide strata process predominant spectral sensitivity in a separate region of the visible spectrum and the dye image-forming material associated with each of said silver halide strata is adapted to provide a dye transfer image having a spectra absorption range, subsequent to processing, substantially complementary to the predominant sensitivity range of its associated silver halide stratum.

6. A photographic film unit as defined in claim 5 wherein said liquid processing composition comprises an aqueous alkaline composition and said laminate includes a layer for converting the pH of said liquid processing composition, subsequent to substantial diffusion of dye image-forming materials to said image-receptive layer, from an initial pH to a second pH at which the dye transfer image provided by the dye image-forming material exhibits increased stability.

7. A photographic film unit as defined in claim 6 wherein said photosensitive layer includes, as essential strata, a red-sensitive silver halide emulsion stratum having associated therewith a diffusion transfer process cyan dye image-forming material, a green-sensitive silver halide emulsion stratum having associated therewith a diffusion transfer process magenta dye image-forming material, and a blue-sensitive silver halide emulsion stratum having associated therewith a diffusion transfer process yellow dye image-forming material.

8. A photographic film unit as defined in claim 1 wherein said laminate includes an opaque layer comprising a visible light reflecting material dispersed in a polymeric material permeable to said processing liquid solubilized dye image-forming materials, located intermediate said photosensitive and image-receptive layers, and the weakest bond between any adjcent layers of said film unit is located intermediate said photosensitive layer and said dimensionally stable layer located to the side of said photosensitive layer opposite said image receptive layer to provide for delamination by and in response to distribution of said processing liquid between said photosensitive layer and the last-mentioned dimensionally stable layer.

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NORMAN G. TORCHIN, Primary Examiner

R. L. SCHILLING, Assistant Examiner

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