United States Patent

[11] **3,615,436**

[72] Inventor **John E. Campbell**
Needham, Mass.

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[73] Assignee **Polaroid Corporation**
Cambridge, Mass.
Continuation-in-part of application Ser. No. 288,011, June 14, 1963, now abandoned, Continuation-in-part of application Ser. No. 309,968, Sept. 19, 1963, now abandoned.

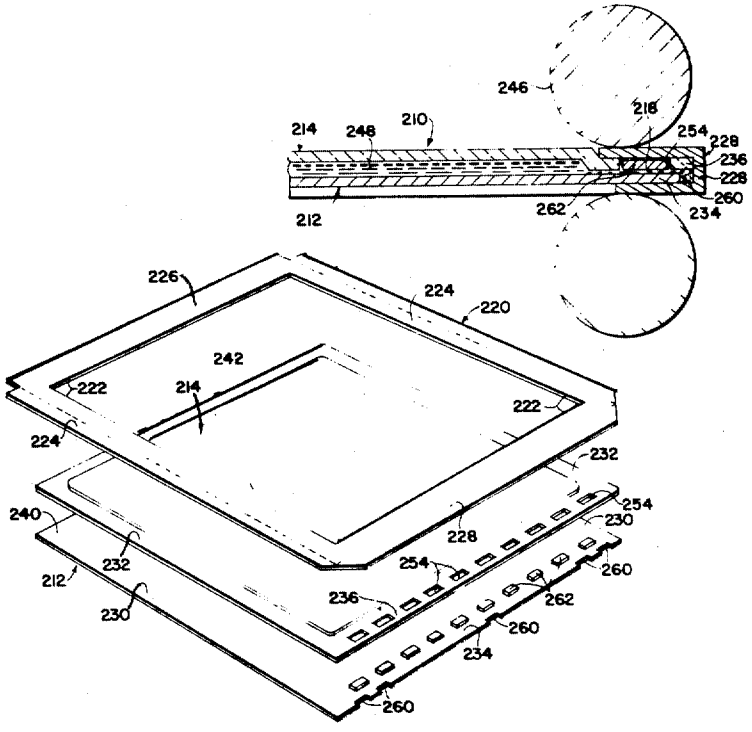
[54] **SELF-DEVELOPING PHOTOGRAPHIC PROCESS WITH LIQUID TRAP**
8 Claims, 6 Drawing Figs.

[52] **U.S. Cl.** 96/29, 96/76
[51] **Int. Cl.** G03c 5/54
[50] **Field of Search** 96/76, 29

[56] **References Cited**
UNITED STATES PATENTS
3,294,538 12/1966 Downey 96/76

Primary Examiner—Norman G. Torchin
Assistant Examiner—John L. Goodrow
Attorneys—Brown and Mikulka and Robert E. Corb

ABSTRACT: A photographic film assemblage comprising a pair of sheetlike elements, one of which includes a photosensitive area adapted to be exposed and processed by an alkaline processing liquid distributed in a layer between the two elements to form a visible transfer image. The film assemblage includes means defining a liquid trapping and retaining space near one edge of the area adapted to be exposed, for collecting and retaining excess processing liquid, and liquid permeable means impregnated with an acid located in the trapping and retaining space for neutralizing the excess processing liquid collected therein. In a preferred film structure and method, the two sheets are retained together during and subsequent to processing, one of the sheets is transparent to provide for viewing an image formed between the sheets and the liquid trapping and retaining space is located between the sheets very close to the area containing the visible image.



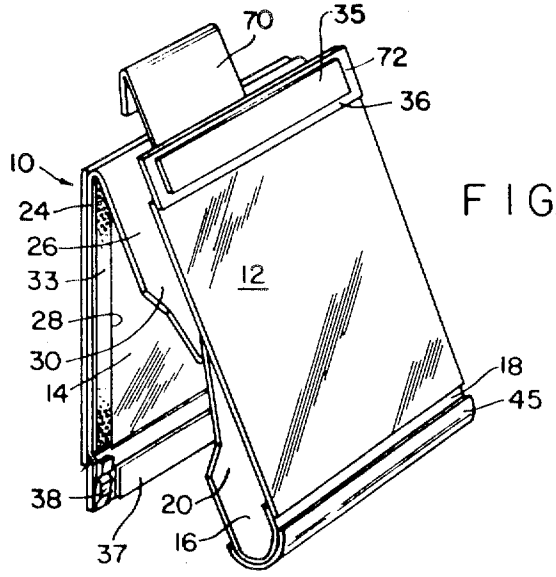


FIG. 1

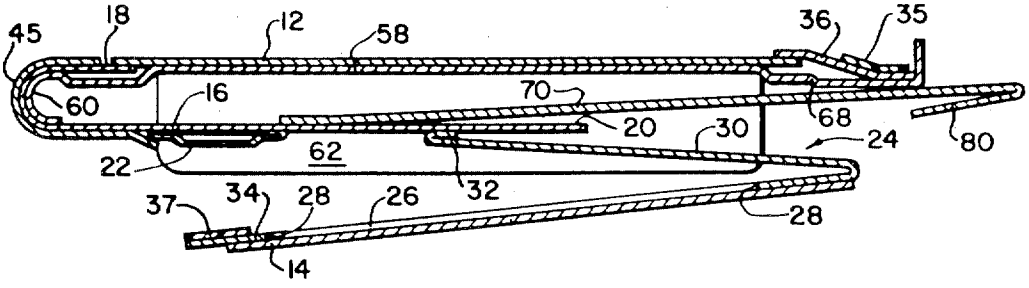


FIG. 2

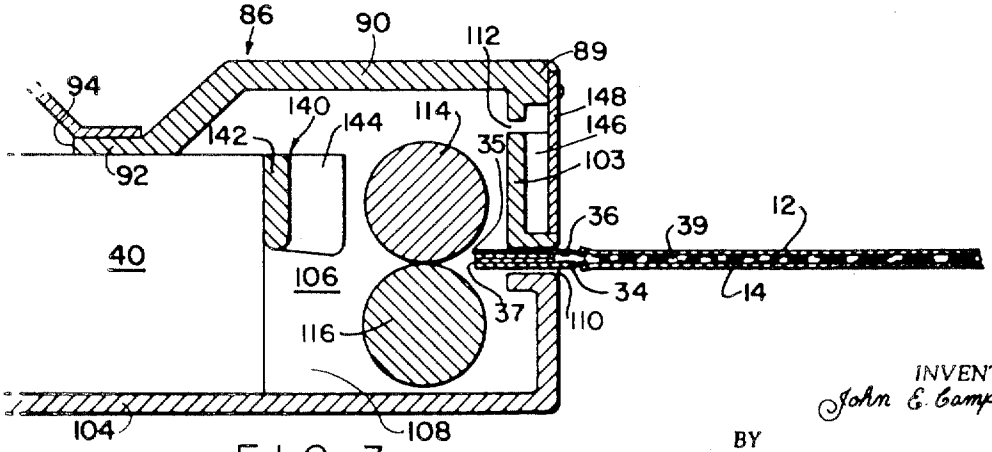


FIG. 3

INVENTOR.
John E. Campbell

BY

Brown and Mikulka
and
Robert E. Corb
ATTORNEYS

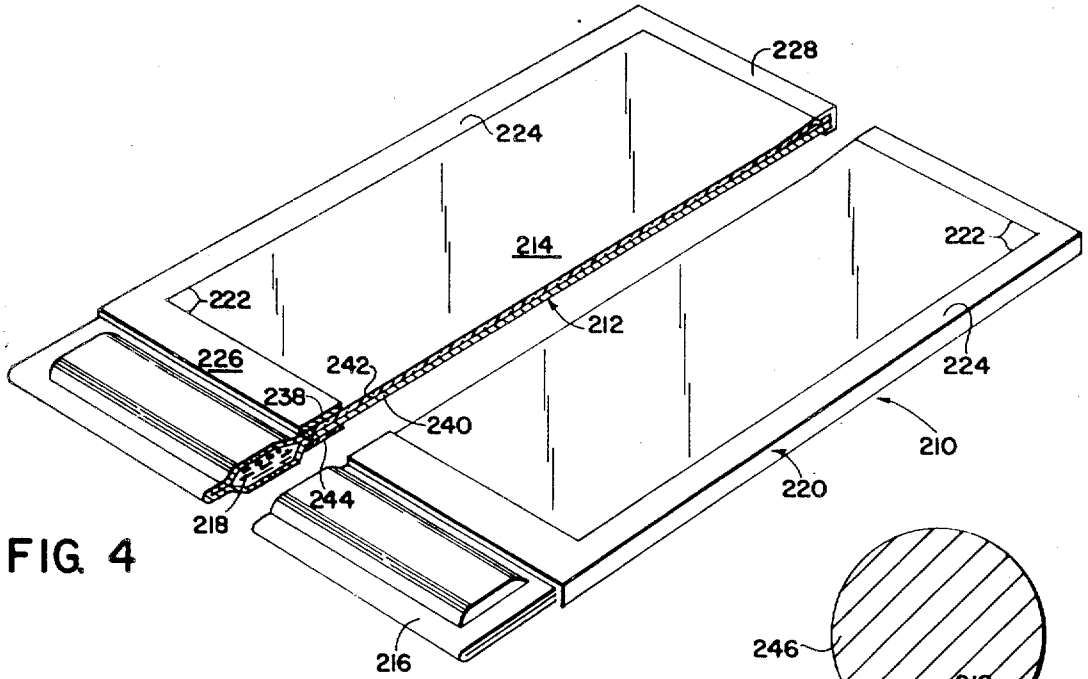


FIG. 4

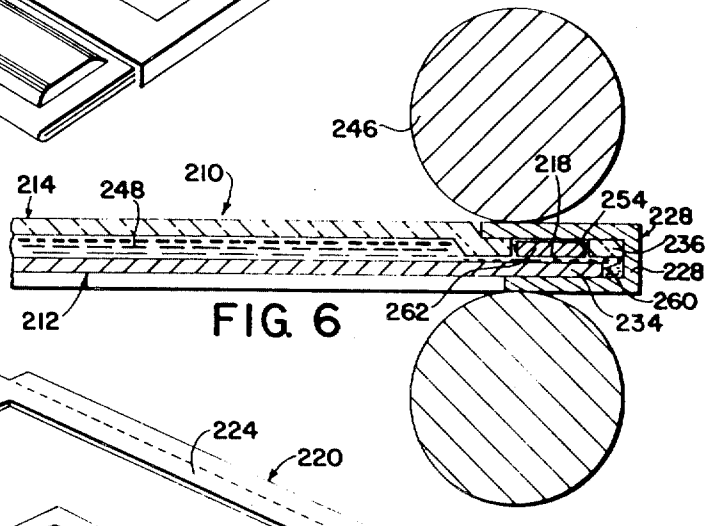


FIG. 6

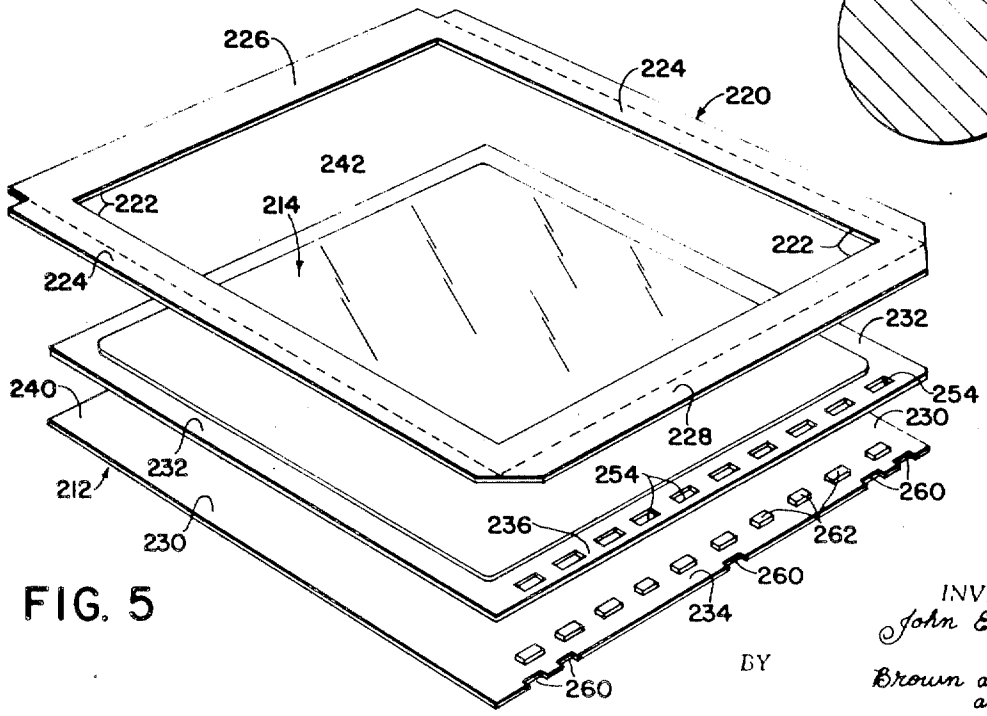


FIG. 5

INVENTOR.
John E. Campbell

BY

Brown and Mikulka
and
Robert E. Corl
ATTORNEYS

SELF-DEVELOPING PHOTOGRAPHIC PROCESS WITH LIQUID TRAP

This application is a continuation-in-part of copending applications of John E. Campbell, Ser. No. 288,011 filed June 14, 1963, and Ser. No. 309,968, filed Sept. 19, 1963, (both abandoned), the later also being a continuation-in-part of Ser. No. 288,011.

The present invention is concerned with photographic image-forming processes and film assemblages particularly adapted for employment in such processes. The film assemblages may take a variety of forms such as 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; or an assembly or pack of film units such as described in the U.S. Pat. applications of Edwin H. Land et al. Ser. Nos. 622,286, now abandoned and 627,538, filed Mar. 10, 1967, and Mar. 31, 1967, respectively. As disclosed in the aforementioned patent and applications, each film unit generally includes, in combination, a first photosensitive element including an area adapted to be exposed to form an image; a second nonphotosensitive element, preferably an image-receptive element, adapted to be superposed with the photosensitive element at least during processing of the film unit following exposure thereof; and a rupturable container releasably containing an alkaline liquid processing composition for distribution between the superposed exposed area of the photosensitive element and the print-receiving element subsequent to photoexposure of the film unit. Film assemblages of this type are intended to be employed in photographic apparatus, such as a camera, which include means for differentially exposing the photosensitive element of a film unit, and means for engaging the film unit subsequent to exposure and distributing the processing liquid between and in contact with the contiguous photosensitive and print-receiving elements of the film unit for effecting photographic diffusion transfer processing of the photoexposed film unit. Processing of a film unit thus may be effected either manually as by grasping a leader attached to the film unit and drawing the leader and film unit between a pair of pressure-applying members, or automatically by mechanical means for driving a pair of pressure-applying rolls to progressively apply compressive pressure to the film unit.

In photographic diffusion transfer processing, the photosensitive element may be first exposed and then biased into superposed relationship with a second sheet element which is usually photographically inert and aids in the controlled distribution of an aqueous alkaline processing composition. Alternatively, the two sheetlike elements may be disposed initially in superposed relation and the photosensitive medium exposed through one of the elements. The film unit includes a print-receiving stratum for supporting a visible transfer image and this stratum may be constituted by a layer on either element or an agent in the processing liquid. Processing is achieved by moving the elements in superposition relative to and between a pair of suitably opposed members such as pressure rollers or platens. Application of pressure to the rupturable fluid-filled container effects controlled rupture thereof and predetermined unidirectional release of its aqueous alkaline processing composition contents between the superposed elements adjacent the exposed area for subsequent spreading as a layer in contact with the opposed surfaces of the superposed elements. Subsequent to transfer processing in which a visible image is formed between the elements, the image-carrying area of the print-receiving element may be separated from the laminate, or the laminate may be retained intact.

In order to insure that a predetermined, exposed area (to be processed) is completely covered by the aqueous alkaline processing composition in the desired layerwise thickness, it is advisable to supply an amount in excess of the minimum amount of liquid required. For this reason, some means must be provided to collect and retain excess liquid subsequent to distribution of the processing composition, in order to prevent the undesired escape of the highly caustic liquid from the laminate within and/or without the camera apparatus.

In order to prevent this processing composition overrun, it has been heretofore taught that the trailing portions of the respective sheet elements may be elongated and that a pair of spacing elements, typically comprising hard rubber or plastic, generally rectangular, projections of sufficient length to equal the necessary elongation of the respective sheet element and to provide a fluid reservoir, may be adhered to the lateral edge of, most preferably, the print-receiving sheet elements, in superposed relationship with the spacing elements separating opposed surface contact, are drawn between the pressure-applying members, during distribution of the processing composition, the spacing elements force a release in the compressive force provided by the opposed pressure-applying members. The excess processing fluid, rather than being further advanced, is thus collected and retained in the space formed between the superposed elongated trailing portions of the elements. The extent that the respective trailing edges are elongated is dependent on both the amount and the distribution of the excess fluid and must be of sufficient length to retain all excess fluid forced beyond the distal edge of the laminate area to be processed.

As will be appreciated from the preceding description, the highly caustic processing composition is present in what is, in fact, an open end of the laminate, and the only force holding the trailing edges of the laminate together, during and subsequent to processing is the adhesive capacity of the fluid composition overrun. The presence of an open trailing edge in the laminate provides the singular disadvantages in that the caustic fluid processing composition is much too accessible to discharge from the laminate, to the detriment of persons and objects with which it comes in contact and the fact that the length of the film unit, and generally film packs and cameras employing same, must be increased in size in order to accommodate the elongations necessary to retain the fluid composition overrun, with the resultant increase in their various manufacturing costs.

An object of the present invention is to provide a novel and improved film unit of the type described including a first photosensitive sheet element; a second sheet element; and a rupturable container adapted for unidirectional release of a retained aqueous alkaline processing composition for selective distribution between and in contact with opposed surfaces of said first and said second sheet elements; wherein at least one of said first and said second sheet elements includes trapping means integral the distal or trailing edge thereof and adapted to collect, retain and neutralize caustic processing composition overrun.

Excess processing liquid presents a substantial problem in a film unit of the type comprising two sheets secured at their margins in face-to-face relation and which remains intact during and subsequent to exposure and processing in which a visible image is formed between the sheets for viewing through one of the sheets. The size of such a film unit is minimized by providing space for collecting and retaining excess processing liquid in a region very close to the area in which the visible image is formed, specifically, in the narrow margin of the film unit constituting the border for the photographic print. The space within the film unit in which the excess processing liquid is collected and retained is in communication with the region between the sheets containing the visible image and may be spaced therefrom by a distance of the order of 0.1 to 0.2 inches, i.e., a few times the thickness of the sheet materials themselves. This structure, coupled with the fact that the structural integrity of the film unit (laminate) is maintained intact following processing and the print-receiving sheet containing the image is not separated from the photosensitive sheet and/or materials containing the excess processing liquid, creates a situation in which the processing liquid can readily migrate back into the image area to discolor or otherwise injure or impair the visible image, thus making it increasingly

imperative that the alkali be neutralized as well as collected and retained.

Another object of the invention is to provide a film unit and a photographic print-forming process utilizing said film unit in which the film unit is of a minimum size, is retained intact subsequent to processing, and excess processing liquid is collected, retained and neutralized in a region providing a border for the print and is located in close proximity to the visible image.

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 process involving the several steps and the relation and order of one or more of such steps with respect to each of the others 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 drawings wherein:

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

FIG. 2 is a diagrammatic sectional view taken substantially midway between the sides of a film assemblage showing one film unit with the components thereof spaced apart to more clearly illustrate the construction and arrangement of the film unit;

FIG. 3 is a fragmentary sectional view illustrating completion of the passage of the film unit between a pair of juxtaposed pressure rolls, the laminate formed by distribution of the fluid processing composition between the superposed sheet elements, and trapping or retaining and neutralizing layers on each of the opposed trailing surfaces of the superposed sheet elements;

FIG. 4 is a perspective view partially in section of another form of film unit embodying the invention;

FIG. 5 is an exploded perspective view of the film unit of FIG. 4; and

FIG. 6 is a sectional view, similar to FIG. 3, illustrating the passage of the film unit between a pair of juxtaposed pressure-applying rolls.

In accordance with the present invention, a preferred form of the film unit comprises a photosensitive sheet adapted to be exposed for producing a photographic image; a second or print-receiving sheet for carrying a positive transfer image; a rupturable container of an aqueous alkaline liquid for reacting with the exposed photosensitive sheet to produce the positive transfer image on the second sheet when distributed between the two sheets; means including a leader for coupling the two sheets and withdrawing the sheets in superposition from a film pack in which they are contained; and positive trapping means integral the trailing opposed surface of at least one of the sheets for trapping or collecting, retaining and neutralizing liquid overrun, upon superpositioning of the sheet elements and distribution of the liquid.

The trapping 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.

It has now been discovered that the aforementioned problem presented by caustic processing composition overrun, may be prevented by trapping means which comprise a permeable acid-containing absorbent layer or stratum disposed on the prospectively opposed trailing surface of at least one of the sheet elements and, thus, adapted to trap or retain and neutralize fluid processing composition upon contact therebetween. The acid-containing absorbent layer may take a variety of forms, preferably absorbent paper or a polymeric material.

As employed throughout the instant specification, the term "absorbent paper" is intended to signify the art-accepted designation for soft, loosely felted, and bibulous papers which have the property of absorbing water, solutions, or special chemicals. They are generally unsized and commonly referred to as water leaf. Among the papers included within the term are blotting, filter, matrix toweling and the base papers commonly employed for the manufacture of vegetable parchment, artificial leather, vulcanized fiber and many other analogous processed papers.

The absorbent paper employed is only limited by the fact that it possesses a permeability to the alkaline processing composition employed such that retention and neutralization by the incorporated acid is readily achieved.

As specific examples of a wide variety of permeable polymeric materials adapted for employment in the practice of the present invention, mention may be made of, for example, natural resins, such as starch, gelatin, dextrin, etc., and synthetic resins such as polyethylene oxide, polyvinyl alcohol, hydroxyethyl cellulose, and synthetic acid resins such as polyacrylic acid and those specifically mentioned hereinafter, etc.

As specific examples of acids particularly adapted for employment, mention may be made of water-soluble, relatively low molecular weight acids which exist in the solid or particulate state, within the ambient temperature range of photographic film usage, such as, for example, citric, ascorbic, sulfamic, oxalic, maleic, succinic, boric, malonic, tartaric, fumaric, etc.; corresponding anhydrides; and/or acid sols such as $(NH_4)_2HOP_4$, $NH_4H_2PO_4$, NH_4HSO_4, etc.

Of the aforementioned acids, citric acid has been found to be a preferred material, particularly for use with absorbent paper, in that it is nontoxic; soluble in water, methanol, aqueous alkaline solutions, etc. possesses a high alkali equivalent per mole; and is free from tackiness at high humidities. In addition, citric acid has been specifically found to provide synergistic effect, in combination with the absorbent paper, whereby markedly improved wetting speed is provided to the absorbent paper.

Where desired, the permeable polymeric material may contain integral acid groups such as carboxylic, sulfonic, carboxylic acid anhydride, etc., and may, in addition, also releasably retain one or more of the previously mentioned acids. As examples of such permeable polymeric acids, mention may be made of, for example, dibasic acid halfester 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 of cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic 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; etc.

The acid-containing layer preferably should contain at least sufficient acid potential and permeability to effect a reduction in the pH of the fluid overrun from a pH of about 12 to 14 to a pH preferably about 5 to 8 upon contact therebetween.

The fluid contents of the rupturable container are preferably adapted to effect the formation of a transfer image on a print-receiving sheet **14** by means of photographic diffusion transfer processing. For details concerning the composition of the fluid and materials useful for the photosensitive and print-receiving sheets and the processes performed by such materials, reference may be had to U.S. Pat. No. 2,543,181, issued Feb. 27, 1951 and U.S. Pat. No. 2,662,822, issued Dec. 15, 1953, in the name of Edwin H. Land, and U.S. Pat. No. 2,983,606, issued May 9, 1961, in the name of Howard G. Rogers.

As disclosed in the above-identified patents the fluid processing composition comprises at least an aqueous solution of an alkaline compound, for example, diethylamine sodium hydroxide or sodium carbonate. As the liquid processing composition is to be applied to a photosensitive layer such as a silver halide emulsion by being spread thereon, preferably in a relatively thin uniform layer, it preferably also 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. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether which is inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature.

For employment in silver transfer processes of the type disclosed in the aforementioned U.S. Pat. Nos. 2,543,181 and 2,662,822, the processing composition will generally possess a pH of about 12 or more and may additionally contain a silver halide developing agent such as hydroquinone, etc., and a silver halide complexing agent such as sodium thiosulfate, etc.

For employment in color transfer processes of the type disclosed in the aforementioned U.S. Pat. No. 2,983,606, the processing composition may additionally contain one or more auxiliary or accelerating silver halide developing agents and/or one or more onium compounds and particularly quarternary ammonium compounds.

It will be apparent that the relative proportions of the agents of the developer composition set forth may be altered to suit the requirements of the operator. Thus, the herein described developing compositions may be modified by various and sundry substitutions. When desirable, the compositions may include, for example, components such as restrainers, accelerators, antifoggants, etc. Similarly, the concentrations of components may be varied over a wide range and when desirable one or more may be disposed in a sheet element, prior to the exposure of the emulsion, for solubilization upon contact with the distributed aqueous alkaline processing medium.

It will be understood that both the amount of absorbent paper or polymer and acid employed will be predetermined relative to the absorbent capacity of the selected paper or polymer, the neutralizing capacity of the selected acid, the amount of processing composition overrun, the alkalinity of the overrun fluid, and the concentration of overrun solvent.

It will be recognized that, as desired, the trapping means may extend, in whole or in part, in continuous or discontinuous fashion, lengthwise the trailing edge or edges retaining same and that the acid compounds may be present in either and/or both absorbent strata when each trailing edge contains an absorbent stratum.

A preferred form of film unit embodying the invention is adapted to be exposed and processed in a camera for producing a positive photographic transfer print, and is preferably enclosed in a light-proof container or magazine together with similar film units which allows the film units to be sequentially exposed. The photosensitive sheets of the film units are positioned together within the container underlying an exposure aperture and the second sheets are arranged together apart from and behind the photosensitive elements adjacent an opening through which the film units are withdrawn so that following the exposure of the photosensitive 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 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 unit 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 sheets of the pack to be exposed. After the photosensitive sheet 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.

Reference is now made to FIGS. 1 through 3 of the drawings wherein there is illustrated a film unit, designated **10**, comprising a generally rectangular photosensitive sheet **12** and a second or print-receiving sheet **14**. Both of these sheets comprise a support which is opaque to light actinic to the photosensitive material of the photosensitive sheet. This photosensitive material comprises a layer of any of the conventional photographic recording media, gelatino silver halide emulsions being the preferred material, carried on a light-opaque flexible sheet such as paper, organic plastics and the like. The second or print-receiving sheet may merely serve to aid in the distribution of a processing fluid in contact with the photosensitive layer or, in the preferred form of film unit, comprises means for supporting a transfer image formed, for example, by a silver halide diffusion-transfer reversal process. Attached to the leading edge of photosensitive sheet **12** is a leader sheet **16** having a first section **18** at which leader sheet **16** is coupled with the photosensitive sheet. First section **18** is approximately equal in width to the photosensitive sheet and provides means for mounting a rupturable container **22** of processing fluid. Leader sheet **16** also includes a tapered end section **20**. Second sheet **14** is mounted on a carrier sheet **24** having an intermediate section **26** approximately equal in width to second sheet **14** and having a generally rectangular opening **28** therein defining the area of the second sheet in which image formation occurs. Second sheet **14** is secured to intermediate section **26** so that the portions of the intermediate section bordering on opening **28** provide a mask for defining the image area and cooperating in spreading of the processing fluid. Side guides **33** are secured to the lateral edges of carrier sheet **24** and extend the length of second sheet **14** whereby to provide a gap between sheet **12** and sheet **14** and retention of the processing fluid intermediate side guides **33** upon formation of the laminate. Carrier sheet **24** includes a leading end section **30** having a tapered end portion **32** similar to tapered end section **20** and secured thereto intermediate the ends of tapered end section **20** and tapered end portion **32** of leading end section **30**. Tapered end section **20** and end portion **32** cooperate to define the leading end section of the film unit which is advanced between the pressure-applying members.

The length of leader sheet **16** between the leading edge of photosensitive sheet **12** and the point of attachment of the leader sheet to carrier sheet **24** is substantially equal to the length of carrier sheet **24** between its point of attachment to the leader sheet and the leading edge of second sheet **14**. It is by virtue of this arrangement that the photosensitive and second sheets are superposed in registered relation during the processing of the film unit. A trailer sheet **36** is provided secured to the trailing edge of photosensitive sheet **12** and possesses acid-containing absorbent paper layer **35** coated on its surface for contact upon superpositioning with acid-containing absorbent paper or polymer layer **37** coated on the trailing surface of trailing end section **34** of carrier sheet **24**, which extends beyond the trailing edge of the second sheet, to trap, retain and neutralize any excess processing fluid which may be carried beyond the trailing ends of the photosensitive and second sheets during distribution of the processing fluid.

As previously mentioned, the amount of acid employed is generally equivalent to the amount of alkali destined to be

neutralized. For example, two layers of 32 pound absorbent paper, sold commercially by Regal Paper Corporation, Regalville, New Jersey, mounted on an extruded polyethylene support 1.5 mils. in thickness, were coated with a solution comprising 43.0 grams of citric acid, 46.0 cc. of methanol, and 11.0 cc. of water, to provide a concentration in the absorbent paper of 0.04 and 0.3 milli-equivalents of acid per square inch, respectively. Subsequent to drying, the composite structures were calendered to 6.3 and 4.3 mils., respectively. A strip of each composite structure approximately three-fourth by 3¾ inches was then adhered to the trailer sheet of each of the photosensitive sheet materials and the trailing end section of each of the print-receiving materials commercially available from Polaroid Corporation, Cambridge, Massachusetts, under the trade designations of Types 107 and 108. The thus-formed film units were processed in film packs, utilizing frangible containers retaining Types 107 and 108 processing compositions, as detailed herein, to provide the advantageous results previously set forth.

As further examples of preferred compositions for deposition as strata 35 and 37 mention may be made of:

1. 672grams of starch 500 grams of sulfamic acid 3000 cc. of water 420 cc. of Teflon T-30 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for an aqueous dispersion containing approximately 60 percent polytetrafluoroethylene, by weight)
2. 5 grams of Polyox (trade name of Union Carbide Corporation, New York, New York, for polyethylene oxide) 16 grams of sulfamic acid 100 cc. of water 10 cc. of Teflon T-30
3. 5 grams of PVA 72-05 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for a polyvinyl alcohol) 10 grams of sulfamic acid 5 grams of citric acid 100 cc. of water 10 cc. of Teflon T-30
4. 672 grams of starch 500 grams of NH_4HSO_4 3000 cc. of water 420 cc. of Teflon T-30
5. 672 grams of starch 500 grams of citric acid 3000 cc. of water 420 cc. of Teflon T-30

The amount of acid employed is generally equivalent to the amount of alkali destined to be neutralized. In general, the deposition of a 3 mil. (0.003 of an inch) coating of the aforementioned compositions on prospectively opposed trailer sheet 36 and approximately ¾×3⅜ inches is totally effective where the above-identified commercial components are employed.

Where it is desired to increase the dimensional stability of either trailer sheet 36 and/or the trailing end section 34, of carrier sheet 24, a suitable polymeric coating may be applied to either or both surfaces of sheet 36 or section 34, for example, a polyethylene coating of approximately 0.5 mil., in order to provide a base adequate in terms of stability and curl characteristics. In addition, trailer sheet 36 and/or end section 34 may have appropriate subcoats, such as a polyvinyl alcohol/cellulose nitrate subcoat, where it is desired to provide additional adhesion between the section to be coated and the permeable acid-coating polymeric layer mounted thereon.

Distribution of the processing fluid, as noted, is effected by advancing the photosensitive and second sheets and container of processing fluid in superposition relative to and between a pair of juxtaposed pressure-applying members. The members 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 the sheets and the spreading of the fluid in a layer between and in contact with the sheets. To aid in trapping of excess fluid, spacing members 38 are provided on trailing end section 34 adjacent the margins thereof for spacing apart the pressure-applying members to provide a gap between trailing end section 34 and trailer sheet 36 in which any excess processing fluid may be collected for trapping and neutralization upon contact with acid containing absorbent layers 35 and 37.

The rupturable container is of the type shown and described in U.S. Pat. No. 2,543,181, issued Feb. 27, 1951, in the name of Edwin H. Land, and comprises 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 their longitudinal and end margins to form a cavity in which the processing fluid is contained. The longitudinal marginal seal 41 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 22 is mounted on first section 18 of leader sheet 16 with this longitudinal marginal seal directed toward the leading edge 43 of the photosensitive sheet. Bib sheet 45 is secured to leader sheet 16 at lateral edges 47 and 51, center area 53, and to lateral edge 49 of container 22, and facilitates restricted unidirectional flow of fluid contents 39 upon compressive rupture of container 22.

The arrangement of a film unit for exposure (within a container not shown) is illustrated in FIGS. 1 and 2, the film unit being arranged with the photosensitive and second sheets in overlying relation with the photosensitive surface of the photosensitive sheet facing outward and with the surface of the print-receiving sheet which is superposed therewith, during processing, facing inwardly in the same direction. Leader sheet 16 is folded or curved adjacent the leading edge of photosensitive sheet 12 intermediate that edge and carrier sheet 24 is similarly folded adjacent the leading edge of second sheet 14 so that the portions of the leader sheet and carrier sheet which connect the photosensitive and second sheets lie therebetween; and the leading and trailing ends of the photosensitive sheet are disposed adjacent, respectively, the trailing and leading ends of the second sheet. The film pack, of which the film unit is a component, is provided with a generally flat, rectangular pressure plate 58 located intermediate photosensitive sheet 12 and the other portions of the film unit for supporting the photosensitive sheet against the inner surface of the forward wall of the container in position for exposure through an aperture therein. Pressure plate 58 includes a rolled end section 60 around which extends the curved portion of leader sheet 16. Rolled end section 60 is provided for guiding photosensitive sheet 12 around the end of the pressure plate in a manner to be described hereinafter. The major portion of first section 18 of leader sheet 16, rupturable container 22 mounted thereon, tapered section 20 and the leading end section 30 of carrier sheet 24 are located behind pressure plate 58 between the latter and second sheet 14. Pressure plate 58 is provided with lateral flanges 62 disposed adjacent the sidewalls of the container and are engaged by springs for biasing pressure plate 58 forwardly to retain the photosensitive sheet in position for exposure.

The means for withdrawing each film unit 10 from the film pack container with the photosensitive and print-receiving sheets 12 and 14 in superposition and advancing tapered end section 20 between a pair of pressure-applying members comprises a relatively narrow elongated leader 70 secured at the trailing end of the leader to tapered end section 20 intermediate first section 18 and the point of attachment of the tapered end section to tapered end portion 32. Leader 70 is of substantially uniform width throughout its length. The areas of adherence of leader 70 to tapered end section 20 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 20, to prevent shearing. The adhesive bond is such that the application of a suitable shearing force to leader 20, effected by applying tension to the leader in a direction at an angle from the plane of tapered end section 20, causes leader 70 to disengage from contact with tapered end section 20. 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 move-

ment of leader 70 and tapered end section 20 diverges sufficiently 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 20.

The film units incorporating the invention and comprising a film pack are adapted to be employed in photographic apparatus such as a hand-held camera 86, a portion of which is illustrated in FIG. 3 of the drawings. Camera 86 comprises a housing including a forward wall 90 with a recessed or reentrant section 92 and an aperture 94 in the reentrant section for transmitting light for exposing the photosensitive sheet of a film unit positioned for exposure within the camera. The camera housing includes a rear wall 104 and sidewalls 106 cooperating to provide a chamber 108 to the rear of forward wall 90 for containing a film pack, generally designated 40, in position for exposure within chamber 108.

Camera 86 includes a pair of juxtaposed pressure-applying members in the form of pressure-applying rolls 114 and 116 mounted within chamber 108 adjacent film withdrawal passage 110. Pressure-applying rolls 124 and 116 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 110. In the arrangement of the pressure-applying rolls shown in the drawings, both rolls are mounted on a section (rear) of the housing 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 89 and 103 cooperate to define an opening 112 between (forward and rear) housing sections through which the leaders extend from the camera housing.

Camera 86 includes means for guiding tapered end section 20 of film unit 10 between pressure-applying rolls 114 and 116 in response to withdrawal movement of leader 70 past roll 114 to the front thereof and through opening 112. In the form shown in FIG. 3 these guide means comprise a guide bar 142 and two guide members 144. Guide bar 130 and guide members 134, and the guide members of guide means 140 may comprise a single element or three separate elements. Guide means 140 is mounted on a forward section of the camera housing adjacent forward roll 114 with the rearmost surfaces of guide members 144 disposed approximately in a plane tangent to the surfaces of rolls 114 and 116. The spacing between the facing surfaces of guide members 144 is slightly greater than the width of leader 70 but less than the narrowest portion of tapered end section 20 so that leader 70 may pass between guide members 144 while tapered end section 20 is supported on and guided by members 144 between the pressure-applying rolls. The intermediate section another and roll 114 to define what may be termed a passage through which leader 70 is guided to the front of roll 114 and through opening 112.

Film withdrawal passage 110, in the lower end wall of the camera housing, is at least equal in width to the width of the film unit, whereas opening 112 need be of a width only sufficient to allow the passage of leader 70. 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 103 is provided with a recess, designated 146, adjacent passage 112 for holding the leading end sections of leaders 70. The leading end sections, designated 80, of leader 70, 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 80 of the first (to be exposed) film unit being attached to leader 78. The folded leading end sections 80 of leaders 70 are contained within recess 146 which is provided with a resilient cover element 148. As leader 78 or a leader 70 is withdrawn through opening 112, the leading end section 80 of the next succeeding leader 70 is unfolded and withdrawn from recess 146 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 146 in position to be engaged and withdrawn.

In the operation of the film unit of the invention, leader 70 is pulled from the camera advancing tapered end section 20 and tapered end portion 32 between pressure-applying rolls 114 and 116 to a position at which leader 70 extends from its point of attachment to tapered end section 20 at almost a right angle from the plane of the tapered end section 20 projects through passage 110 a sufficient distance to permit the tapered end section to be grasped, and the application of a continued pulling force on leader 70 results in the exertion of a shearing force to leader 70 at the areas where the leader is attached to the tapered end section and results in separation of the leader at these areas.

Continued application of withdrawing force on tapered end section 20, advancing photosensitive sheet 12, second sheet 14 and container 22 between pressure-applying rolls 114 and 116 provides rupture of the longitudinal marginal seal 41 of container 22 and unidirectional release of fluid processing composition 39 between and in contact with opposed surfaces of photosensitive sheet 12 and sheet 14.

Continued withdrawing force on tapered end section 20 between pressure-applying rolls 114 and 116 to the position shown in FIG. 3 provides distribution of excess processing composition 39 between and in contact with acid-containing absorbent layer 35 on trailer sheet 36 and acid-containing absorbent layer 37 mounted on the trailing surface of carrier sheet 24, whereat the solvent of the excess processing composition permeates the absorbent layer and is retained therein and the acid components of layers 35 and 37 neutralize the processing composition overrun.

As will be recognized from the foregoing disclosure, where desired, layers 35 and/or 37 may also be incorporated in roll film units. For example, such roll film units may comprise a type wherein a continuous sheet element contains a plurality of photosensitive areas adapted to be sequentially exposed and individually transfer processed to provide a sequential plurality of transfer images to a contiguous sheet element possessing a plurality of image-receptive areas, by means of compressive pressure application to individual rupturable containers, adapted for unidirectional release and distribution of a retained processing composition sufficient for single frame processing, as detailed hereinbefore. For employment in roll films of this type, a separate acid-containing absorbent layer may be mounted on the prospectively opposed trailing edge surface adjacent each of the plurality of photosensitive and/or image-receptive areas distal to the rupturable container adapted to process the photographic frame immediately preceding the acid-containing absorbent layer or layers.

Reference is now made to FIGS. 4 and 5 of the drawings wherein there is illustrated another form of photographic film unit constructed in accordance with the invention and comprising all of the materials required to produce a photographic print including a pair of sheets secured at their margins in face-to-face relation and a liquid processing agent; and a method of processing the film unit with a viscous liquid processing agent. The film unit generally comprises a photosensitive sheet and a second sheet secured in face-to-face relation at the edges of the sheets by essentially fluidtight binding means and a collapsible container of alkaline processing liquid secured at one edge of the sheets so as to discharge its contents between the sheets when compressive pressure is applied to the container. The film unit of the invention is adapted to be employed in and the process of the invention is adapted to be performed by a self-developing camera of the type in which a completely, self-contained film unit is ex-

posed and then processed by moving it between a pair of pressure-applying members. The components of the film unit are assembled together to form an integral structure and the integrity of this structure is maintained during exposure and processing, thereby making it unnecessary to store, handle and/or move separately, individual elements of the film unit and minimizing the complexity of the structure required to contain and manipulate the film unit to effect exposure and processing thereof. The film unit structure is attractive, includes a minimum of simple and easily assembled components, is of a minimum size in relation to image size, includes the processing liquid and means for promoting and facilitating spreading of the liquid in a layer of predetermined depth and extent and collecting, retaining and neutralizing excess processing liquid, is inexpensive and functions reliably well, and is of the type described in the copending U.S. Pat. application of E. H. Land et al., Ser. No. 627,538, filed Mar. 31, 1967. The sheets of the film unit are secured to one another to form an essentially sealed structure and during processing, the viscous liquid is spread from the leading end of the film unit between the sheets toward the trailing end thereof to form a layer between the sheets while excess processing liquid is trapped and retained within the film unit at the trailing end thereof in such close proximity to the finished image that unless it were neutralized, it might impair, discolor or otherwise damage the finished image.

The film unit, designated **210**, comprises two separate, flexible sheetlike elements including a first or image-recording sheet including a layer containing a photosensitive image-recording material and second or image-receptive sheet for aiding in the distribution of a viscous liquid processing agent as a layer in contact with an exposed area of the photosensitive material and for acting as a support for a transfer image formed by diffusion of image-forming substances from the photosensitive material-containing layer through the layer of processing liquid to the second sheet. At least one of the sheets, preferably the second sheet, is transparent to provide for exposure of the photosensitive while the sheets are in superposition and viewing of the image formed against the inner surface of the second sheet. This construction enables the two sheets to be secured to one another at their margins to form an integral unit, the integrity of which is established prior to loading into a camera, is maintained throughout exposure and processing and can be maintained subsequent to processing. The processing liquid includes, in addition to the reagents required to produce a diffusion transfer image, a thickening or film-forming agent provided to aid in the formation of a layer or film of the liquid between sheets and an opacifying agent for masking a visible (negative) image formed in the photosensitive layer and providing a background for the diffusion transfer (positive) image formed against the inner surface of the transparent second sheet.

Film unit **210** and method employing the film unit are adapted to the performance of a number of different image-forming processes and particularly to the production of a positive photographic print preferably in full color. The preferred embodiment of the film unit **210** includes all of the materials and reagents required to produce a full color photographic print by a process such as disclosed in the aforementioned U.S. Pat. No. 2,983,606. **Film unit** 210 **comprises a photosensitive or image-recording sheet** 212 **a second or image-receiving sheet** 214 **and a rupturable container** 216 **holding a quantity of processing liquid** 218. **Sheets** 212 **and** 214 **are preferably rectangular and coextensive with one another and are arranged in superposed face-to-face contact with at least one edge of each sheet aligned with an edge of the other. The two sheets are retained in superposed relation by a binding element** 220 **in the form of a rectangular sheet larger than either of the photosensitive or image-receiving sheets and secured to the two sheets at the margins thereof. Binding element** 220 **is in the general form of a frame having a large rectangular opening** 222 **defining the extent of the image produced in the film unit, surrounded by lateral edge portions** 224 **and end portions** 226 **and** 228. **Sheet** 212 **includes lateral marginal portions** 230 **and an end marginal portion** 234 **and sheet** 214 **includes lateral marginal portions** 223 **and an end marginal portion** 236 **with the lateral and end marginal portions of the two sheets being located in face-to-face contact, preferably with the edges thereof in alignment. The lateral edge portions** 224 **and end portion** 226 **of binding element** 220 **are secured around and to, respectively, lateral marginal portions** 230 **and** 232 **of sheets** 212 **and** 214 **and end marginal portions** 234 **and** 236 **of the sheets effectively binding the two sheets to one another along three sides thereof. In a preferred form of film unit adapted to produce a reflection print surrounded by a white border and viewed against a white background, at least binding element** 220 **is formed of an opaque, white material and container** 216 **may also include a white outer coating to provide a more aesthetically pleasing product.**

Container **216** is of the type shown in the aforementioned U.S. Pat. No. 2,543,181, and includes a cavity for containing processing liquid **218**, and longitudinal marginal sections **238** which open to form a discharge mouth at least equal in length to the length of the cavity and the width of opening **222** through which processing liquid **218** is discharged. Container **216** is attached to the sheets at the edges thereof opposite end portions **234** and **236**, preferably with the longitudinal edge of the container butted against the edges of the sheets and with the discharge passage of the container aligned with the facing surfaces of the sheets. Sheets **212** and **214** include, respectively, end marginal portions **240** and **242** and the means for coupling the container to the sheets include end portion **228** of binding element **220** secured to end marginal portion **242** of sheet **214** and longitudinal marginal sections **238** of the container so as to bridge the container and sheet **214**; and a strip **244** secured to end marginal portion **240** of sheet **212** and the other longitudinal marginal section **238** of the container to bridge the gap between the container and sheet **212**. The binding element and strip **244** cooperate to provide a liquidtight seal between the marginal sections of the container defining the discharge mouth thereof and sheets **212** and **214**; and form a conduit for conducting the liquid from the container between the sheets at end marginal portions **240** and **242** thereof.

The most useful and advantageous film unit insofar as packaging, storing, handling, exposure and processing are concerned, is one characterized by an integral, unitary structure constructed so that its integrity may be maintained during and after exposure and processing; and a structure that is sturdy, has some flexibility and can be handled and manipulated by mechanical means without damage to producing 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 meeting these criteria, and together with the steps involved in the process of the invention, are specially adapted to provide a useful and attractive photographic print, preferably in full color, having the foregoing characteristics.

In order to provide a rigid durable structure having an integrity 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 both the image-recording medium and the final image. 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 providing an appropriate environment for the formation of a diffusion transfer image.

The embodiment of the film unit illustrated and described herein is adapted to be exposed and processed to produce a multicolor dye transfer image in a dyeable polymeric layer located between a transparent film on which the dyeable polymeric layer is supported and an opaque layer located between the image and the photosensitive medium. This opaque layer comprises the liquid contents **218** of container **216** provided in sufficient quantity to form a layer of predetermined thickness, e.g., of the order of .004 inch, when distributed uniformly between the sheets over an area at least coextensive with opening **222** in binding element **220**. The quantity of liquid **218** supplied in the container is preferably slightly in excess of the minimum quantity required to form a layer of the desired thickness and extent, thereby making it necessary to provide means for collecting and retaining excess processing liquid.

The opacifying agent in the processing liquid is selected for its suitability as a background for viewing the dye-transfer image formed in the dyeable polymeric layer as well as for its opaque property. Another factor considered in the selection of the opacifying agent is the requirement that it does not interfere with the formation and color integrity of the dye-transfer image in the image-receiving sheet and that the agent be aesthetically pleasing and does not provide a "noisy" background that may degrade the image or detract from the information content thereof. Opacifying agents particularly desirable for incorporation in the liquid processing composition are those providing a white background for viewing the transfer image and particularly those compositions conventionally employed to provide a background for photographic reflection prints and having optical properties particularly suited for the reflection of incident radiation. As examples of suitable opacifying agents, mention may be made of 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. An opacifying agent especially preferred because of its high reflection properties is titanium dioxide and where it is desired to increase the opaqueness of the processing composition containing, for example, titanium dioxide, beyond that ordinarily obtained, an additional opacifying agent such as carbon black may be added in a concentration of about one part carbon black to 100–500 parts titanium dioxide. A liquid processing composition suitable for incorporation in container **216** for use in combination with sheet materials of the type disclosed in the foregoing example is as follows:

water	100 cc.
Potassium hydroxide	11.2 grams
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4 grams
N-benzyl-α-picolinium bromide	1.5 grams
Benzotriazole	1.0 grams
Titanium dioxide 40.0 grams	

Subsequent to exposure, film unit **210** is processed, as illustrated in FIG. **6** of the drawings, by moving the film unit with container **216** foremost relative to and between a pair of juxtaposed members for applying compressive pressure first to the container to eject the fluid contents of the container between the photosensitive and image-recording sheets **212** and **214** and then spread processing liquid **218** in a uniform, thin layer between the sheets over an area at least coextensive with opening **222** in binding element **220**. Preferred means for spreading the processing liquid in a thin layer of uniform predetermined thickness comprise a pair of cylindrical rolls **246** mounted in juxtaposition for rotation about axes located in a common plane and biased toward one another and/or mounted a fixed maximum distance apart so as to apply compressive pressure to the container and elements of the film unit during movement thereof between the rolls. During movement of the film unit between rolls **246**, compressive pressure is initially applied to container **216** generating hydraulic pressure in liquid **218** effecting the rupture of the bond between longitudinal marginal sections **238** of the container and the discharge of liquid **218** in the form of an elongated mass between sheets **212** and **214** at end marginal portions **240** and **242** thereof. Continued movement of the film unit relative to and between spread rolls **246** causes advancement of the mass of liquid between the sheets toward the opposite end thereof and spreading of the liquid as a thin layer **248** of predetermined thickness between and in contact with the facing surfaces of the sheets. A number of expedients are possible for controlling the thickness of the layer of processing liquid distributed between sheets including means in the processing apparatus for appropriately gapping or spacing apart spread rolls **246** and/or components of the film unit capable of performing this function. The film unit illustrated in the drawings is adapted to be employed with cylindrical rolls with the thickness of the liquid layer **248** being controlled by components of the film unit itself. The spacing between spread rolls **246** and hence the thickness of the layer of processing liquid is determined by the thickness of the film unit at the lateral margins thereof. This thickness is in turn a function of the thickness of the photosensitive and second sheets **212** and **214** and the thickness of lateral edge portions **224** of binding element **220**. Since the photosensitive and second sheets are of substantially uniform thickness throughout, the thickness of layer **248** of processing liquid is determined by the thickness of binding element **220** and is approximately twice the thickness of the binding element. In a typical film unit, for example, the binding element may have a thickness of the order of 0.002 inch and provide for spreading of the processing liquid in a layer having an initial depth of the order of 0.004 inch.

To insure spreading of the processing liquid to the edges of the area defined by opening **222** in the binding element and formation of a transfer image extending to the edges of this image-receiving sheet **214** is embossed at its margins to displace marginal portions **232**, **236** and **242** out of the plane of the medial portion of sheet **214** toward sheet **212** by a distance or depth approximating the thickness of binding element **220**, or one-half of the desired initial thickness of the layer of processing liquid. This construction provides for the formation of a layer of processing liquid extending substantially to the lateral edges of opening **222** in the binding element. To further insure the formation of a layer of processing liquid extending at least to the lateral edges of the opening in the binding element, the edge sections of lateral edge portions **224** and end portion **228** secured to marginal portions **232** and end portion **236** of sheet **214** are wider than the sections of lateral edge portions **224** and end portion **228** secured to marginal portions **230** and end portion **234** of sheet **212**. Strip **244** is also narrower than end portion **226** and as a result of this construction, during spreading of the processing liquid between sheets **212** and **214**, the inner surfaces of the sheets will be spaced apart in lateral and end regions extending outside of the edges of opening **222** allowing processing liquid to enter these regions and provide a reservoir of liquid for effecting image formation within the region of the exposed image-recording medium immediately adjacent the lateral and end edges of opening **222**. The processing liquid is initially spread in a layer having a depth approximately twice the thickness of the binding element and calculated to provide aqueous liquid sufficient to permeate the layer containing the photosensitive medium and effect formation of a diffusion transfer image. As the liquid permeates the photosensitive layer and is absorbed

and/or dissipated by sheets **212** and **214**, the thickness of layer **248** is reduced and the film-forming agent becomes increasingly solid to provide a dimensionally stable opaque layer providing a background for the transfer image and tending to adhere the sheets to one another to preserve the integrity of the film unit structure. The depth of embossing of image-receiving sheet **214** approximates the final thickness of layer **248** to provide an integral laminated assembly of substantially uniform thickness throughout in which layer **248** and the image extend to the edges of opening **222** in binding element **220**.

While it is desirable, in a film unit of the type embodying the invention, to limit the processing liquid provided in the container as closely as possible to the precise amount required to provide a layer of the desired depth over the region between the sheets defined by opening **222** in binding element **220**, in order to insure distribution of the liquid in a layer of uniform predetermined depth over the entire exposed region to the trailing end thereof and allow some tolerance in the manufacture and filling of the container as well as the depth of the layer of liquid, it is usually necessary to provide some excess processing liquid. This makes it necessary to provide for collecting and retaining the excess processing liquid within the film unit at the trailing end thereof so the liquid does not escape and contaminate the apparatus, e.g., camera, in which the film unit is processed. Collection and retention of the processing liquid is accomplished by providing spaces within the film unit in which the processing liquid cannot be squeezed by the pressure-applying members employed to spread the liquid.

In a preferred form of film unit shown in the drawings, liquid trapping and retaining spaces are defined by the openings in the trailing end marginal portions of either or both of the sheets underlying end portion **228** of binding element **220**. In the form shown in FIGS. **4** through **6**, openings **254** are provided in end marginal portion **236** of sheet **214** for collecting and retaining excess processing liquid as it is spread toward the trailing edge of the film unit beyond the trailing edge of opening **222**. Thus, as shown in FIG. **6**, the advancing mass of processing liquid **218** separates the trailing end marginal portions of the sheets sufficiently to enable the excess processing liquid to enter opening **254** while the thickness of sheet **214** precludes compression of the trapped liquid so that there is little or no force tending to eject the liquid from the film unit. Retention of the processing liquid within the film unit is further assured by virtue of end portion **228** of binding element **220** which is secured to the outer surfaces of end marginal portions **234** and **236** of sheets **212** and **214**, respectively, and particularly in the regions of sheet **214** surrounding openings **254**. As rolls **246** pass over the end marginal portions of the sheets and openings **254**, the rolls are spaced apart by the remaining sections of sheet **214** so that spaces defined by the binding element, sheet **212** and the edges of openings **254** are provided for trapping and retaining the excess processing liquid.

Binding element **220** and strip **244** are preferably formed of a substantially liquid-impermeable material which, in one form, e.g., a polymeric film, waterproof paper or the like, is also essentially impermeable to gas. It is important in order to facilitate spreading of the processing liquid to exclude as much as possible of the air from between the sheets ahead of the mass of liquid during spreading thereof; and since there may be some air between the sheets, it is also necessary to provide for venting or otherwise expelling the air from between the sheets without inhibiting the spreading of the processing liquid while at the same time preventing the processing liquid from escaping between sheets. Escape of the processing liquid from between the sheets is effectively prevented by the provision of trapping spaces and a liquidtight retaining element secured to the outer surfaces of the sheets; and, since any air trapped between the sheets at the trailing end thereof may tend to become compressed during spreading of the processing liquid and may thereafter expand toward the leading end of the film unit causing separation of the sheets and damage to the visible image formed between the sheets, the film unit is provided with means for venting air in such a way as not inhibit the release or escape of air, while at the same time preventing the processing liquid from escaping from the film unit. A preferred means for venting the film unit is to provide regions in which end portion **228** of binding element **220** is not adhered to end marginal portion **234** of photosensitive sheet **212** toward the leading end of the film unit to the edge of opening **222** in the binding element and provide a path for air to escape from the film unit during spreading of the processing liquid. To facilitate the escape of air between the trailing edge of sheet **212** and binding element **220** and to provide additional liquid trapping space, notches **260** are formed in the trailing edge portion of sheet **212** underlying unsealed regions **258** and communicating therewith. The construction of the film unit and of the pressure-applying member, e.g., rolls **246**, employed to spread the processing liquid are such that any air between the sheets is advanced ahead of the mass of processing liquid and is ejected from the film unit at the trailing end thereof by passing through notches **260** between end marginal portion **234** and binding element **220**, and as excess processing liquid advances ahead of spread rolls **246**, it moves behind the air into the spaces defined by openings **254** and notches **260** (as shown in FIG. **6**) wherein the excess processing liquid is trapped. Escape of the processing liquid via the same route is prevented by the pressure-applying members (rolls **246**) which, at this stage of the process, engage and compress end portion **228** of binding element **220** against the surface of sheets **212** and **214**, effectively sealing the unadhered regions designated **258** so that the processing liquid is unable to flow between the binding element and the outer surfaces of the sheets.

The liquid trapping spaces defined by openings **254** are in direct communication with the region between the sheets in which the visible image is formed and are in very close proximity to this region. In the example given, this separation may be of the order of one-sixteenth inch or less, i.e. approximately 15 times the maximum thickness (0.004 inch) of the layer of liquid spread between the sheets. This close proximity and the fact that the film unit is maintained intact, i.e. the sheets are not separated following processing, enables the alkali in the excess processing liquid to migrate from the spaces from which it is collected and retained into the image area where it may discolor, damage or otherwise detract from the appearance and attractiveness of the image. In accordance with the invention, liquid-permeable layers or elements **262**, formed of a suitable absorbent paper or polymer impregnated with an acid as heretofore described, are provided in the liquid trapping spaces defined by openings **254** between binding element **220** and marginal portion **234** of sheet **212**. Additional liquid trapping and retaining space may be provided by enlarging notches **260** or by providing openings in end marginal portion **234** of sheet **212** corresponding to and aligned with openings **254** in end marginal portion **236** of sheet **214**. In such a construction, additional liquid-permeable, acid-impregnated layers may be provided in the additional trapping spaces or the thickness (and alkali neutralizing potential) of elements **262** may be correspondingly increased.

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

What is claimed is:

1. In a photographic film assemblage adapted to be exposed and processed to produce a visible photographic image and to remain intact during and after exposure and processing, said film assemblage comprising a first sheet having an area including a photosensitive material capable of recording an image when exposed to actinic light, a second, transparent sheet secured in face-to-face relation with said first sheet at the margins of said area; a collapsible container of alkaline liquid

processing composition capable, when spread in a layer between and in contact with said exposed area and superposed portions of said second sheet, of reacting with said photosensitive material to produce an image between said sheets visible through said second sheet, said liquid being contained in said container in a quantity in excess of that required to form said image when spread in contact with said area, the improvement comprising, in combination:

binding means secured to the margins of said sheets for retaining said sheets in face-to-face relation;

at least one of said sheets including marginal portions closely adjacent the edge of said area opposite said container cooperating with said binding means to provide spaces for collecting and retaining excess processing liquid, said spaces being located closely adjacent and in direct communication with the region between said area of said first sheet and said second sheet; and

a quantity of absorbent material permeable to said processing liquid and containing an acid for neutralizing said processing liquid upon contact therebetween, located within said spaces.

2. A photographic film assemblage as defined in claim 1 wherein said processing liquid includes an opacifying agent capable, when spread between said first and second sheets, of forming an opaque layer for masking a visible image formed in said photosensitive material in said area of said first sheet.

3. A photographic film assemblage as defined in claim 1, wherein said binding means include a strip of a substantially liquid impermeable sheet material secured to the outer surfaces of said sheets at marginal portions there of in the region of said opposite edge of said area and said impermeable strip cooperates with recesses formed in said marginal portions of at least one of said sheets to provide said liquid-retaining spaces.

4. A photographic film assemblage as defined in claim 1, wherein said absorbent material comprises a layer of absorbent paper containing an acid.

5. A photographic film assemblage as defined in claim 1, wherein said absorbent material comprises an alkaline solution-permeable layer of a coatable, film-forming polymer containing an acid.

6. The method of producing a photographic print utilizing a photographic film assemblage comprising:

superposing a photosensitive sheet with a second transparent sheet;

securing said sheets to one another at the margins of an area of said photosensitive sheet adapted to be exposed by binding means secured to the margins of said sheets;

exposing said area of said photosensitive sheet through said second sheet to form an image in said photosensitive sheet;

introducing an aqueous alkaline processing liquid between said sheets at one edge of said area and spreading said liquid as a layer between said sheets in contact with said area toward the opposite edge thereof;

reacting said liquid with said exposed photosensitive sheet in said area to form an image visible through said second sheet;

collecting and retaining excess processing liquid within said film assemblage in a space defined by said binding means located closely adjacent and in direct communication with said region between said area and said second sheet at said opposite edge of said area;

retaining said film assemblage intact with said sheets in superposition; and

contacting said excess processing liquid retained in said space with an acid contained in said space to neutralize said alkaline processing liquid and prevent deterioration of said visible image formed between said sheets in the vicinity of said space.

7. A photographic method as defined in claim 6, wherein said processing liquid includes an opacifying agent, said opacifying agent is distributed between said photosensitive sheet and said second sheet to form an opaque layer capable of masking a visible image formed in said photosensitive sheet and the first-mentioned visible image is formed between said opaque layer and said second sheet.

8. A photographic method as defined in claim 6, wherein said excess processing liquid is collected and retained in a space separated from said region by a distance less than 15 times the maximum thickness of said layer of liquid spread between said sheets.

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