Sept. 25, 1973 J. E. CAMPBELL 3,761,269

SELF-DEVELOPING PHOTOGRAPHIC FILM UNIT WITH LIQUID TRAP AND AN ALKALI NEUTRALIZING SPACER ELEMENT

Filed Sept. 27, 1971 2 Sheets-Sheet 1

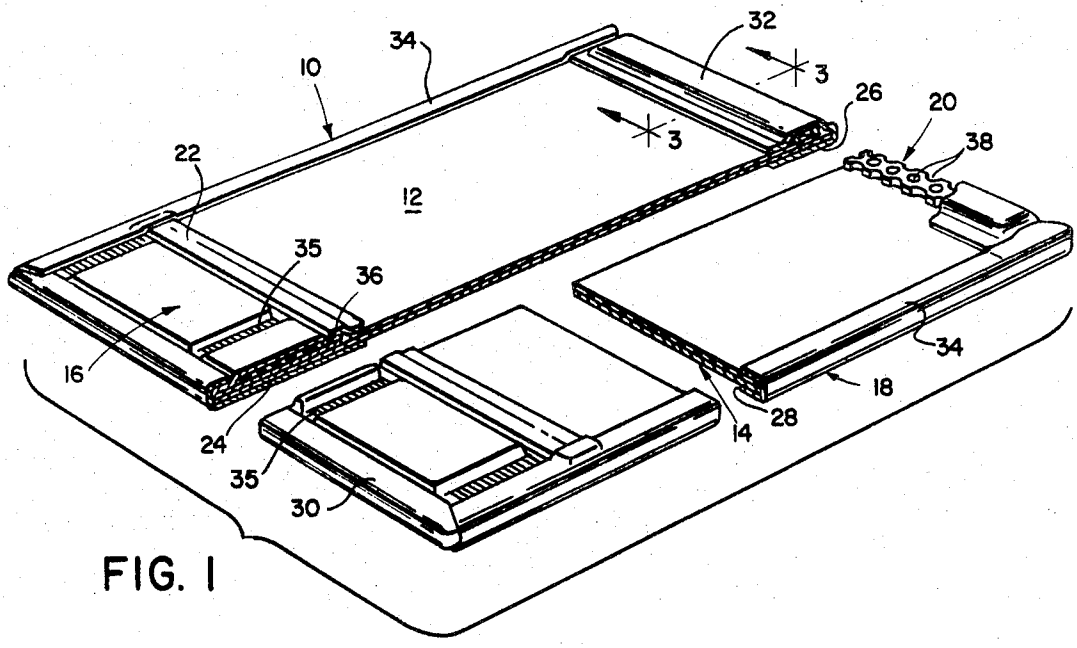


FIG. 1

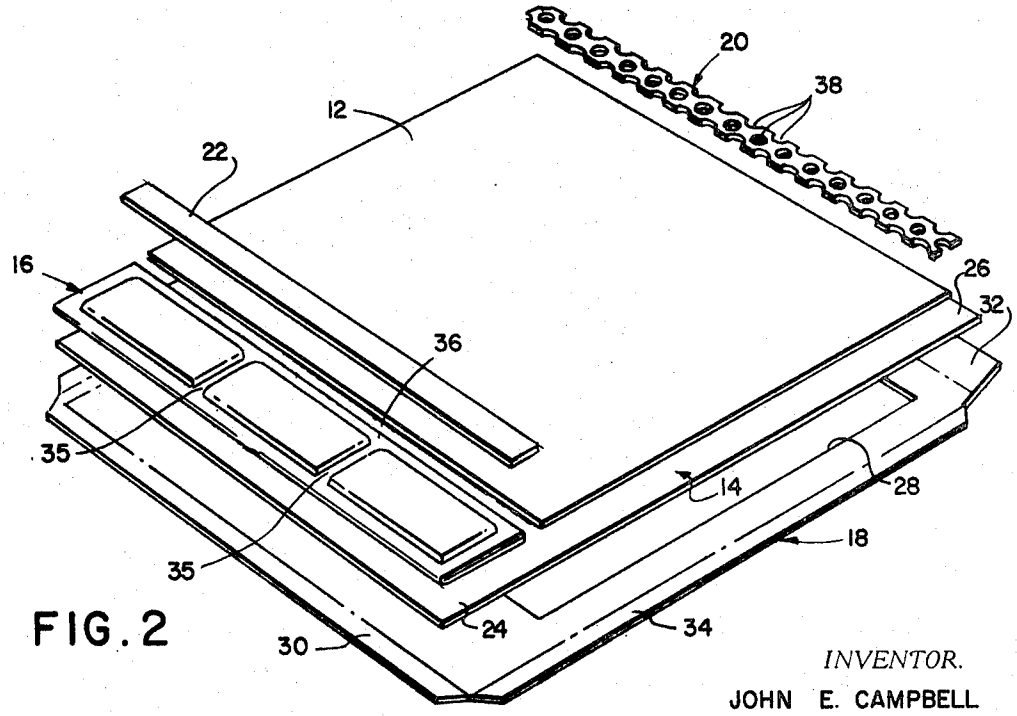


FIG. 2

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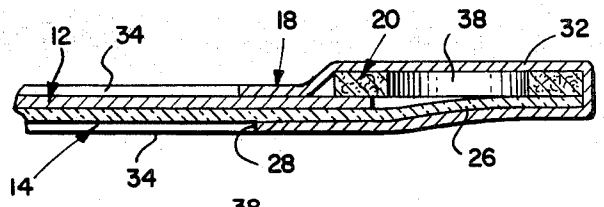


FIG. 3

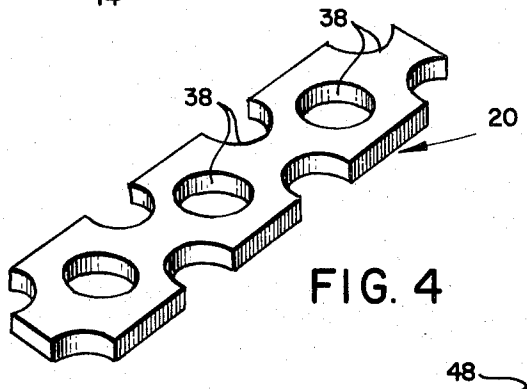


FIG. 4

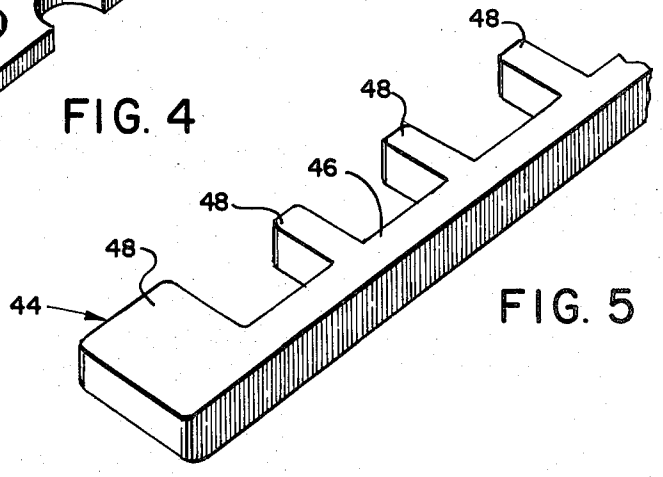


FIG. 5

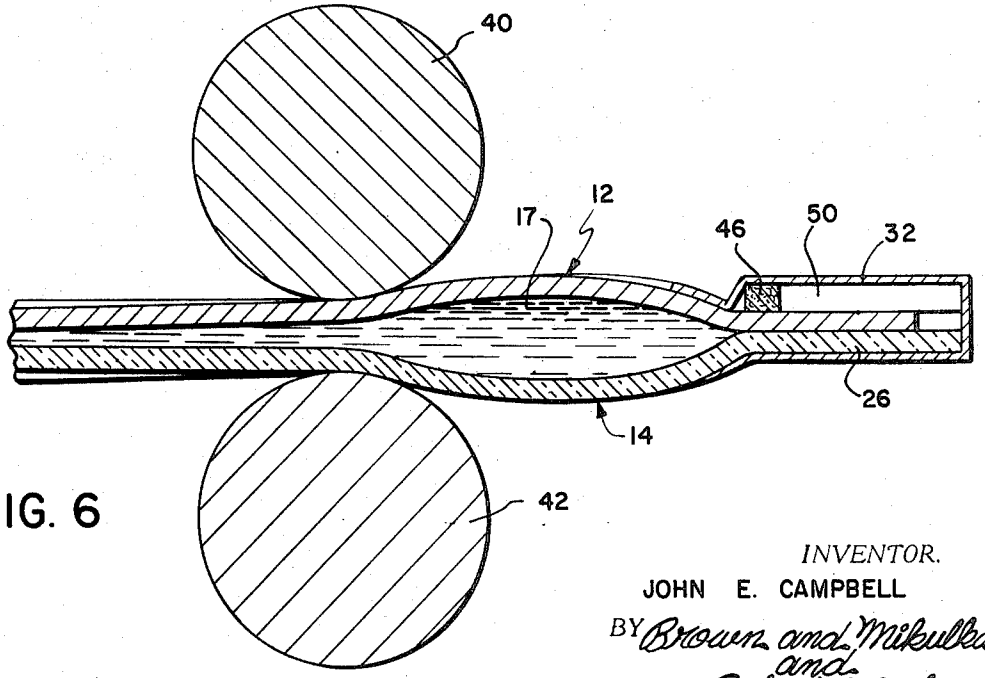


FIG. 6

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SELF-DEVELOPING PHOTOGRAPHIC FILM UNIT WITH LIQUID TRAP AND AN ALKALI NEUTRALIZING SPACER ELEMENT

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Continuation-in-part of application Ser. No. 643,273, June 2, 1967, now Patent No. 3,615,436, which is a continuation of abandoned application Ser. No. 309,968, Sept. 19, 1963, which in turn is a continuation-in-part of application Ser. No. 288,011, June 14, 1963. This application Sept. 27, 1971, Ser. No. 183,989

Int. Cl. G03c 1/48

U.S. Cl. 96—76 R 9 Claims

ABSTRACT OF THE DISCLOSURE

A photographic film assemblage comprising a pair of sheet-like elements and a layer of a photosensitive material sandwiched between the elements including an area adapted to be exposed and processed by an aqueous alkaline processing liquid spread in a layer between the two elements to form a visible transfer image. The film assemblage includes a binding sheet secured around and to the exterior of adjacent end sections of the two elements and a spacer formed of a fibrous material contained within the film assemblage between the sheet-like elements and binding sheet. The spacer is formed with gaps which cooperate with the elements and binding sheets to provide trapping spaces for collecting and retaining excess processing liquid overrun as the end portions of the two elements are moved betwen a pair of pressure-applying members which spread the processing liquid. The two sheets are retained together subsequent to processing and the liquid trapping and retaining spaces formed by the spacer element are located within the film assemblage very close to the area containing the visible image. To neutralize excess processing liquid collected in the trapping spaces and prevent migration of a alkali into the image area, the spacer itself is at least coated with citric acid on the side in contact with which the processing liquid is spread.

This application is a continuation-in-part of my copending application, Ser. No. 643,273, filed June 2, 1967, and now U.S. Pat. No. 3,615,436 in turn a continuation of application Ser. No. 309,968, filed Sept. 19, 1963, (now abandoned) in turn a continuation-in-part of application Ser. No. 288,011, filed June 14, 1963 now abandoned.

In patent application, Ser. No. 65,084, filed Aug. 19, 1970 now Patent No. 3,672,890, and U.S. Pat. No. 3,594,-164, issued July 20, 1971, there are shown and described photographic film assemblages of the self-developing type comprising first and second sheets arranged in superposition and sandwiched therebetween, at least a layer of a photosensitive material including an area adapted to be exposed and processed to form a visible image. This area of the photosensitive material is processed following exposure to form a visible image by an aqueous alkaline processing liquid spread in a thin layer between the sheets for permeation into the photosensitive material by moving the film unit relative to and between a pair of juxtaposed, pressure applying members. The processing liquid is initially provided in a rupturable container coupled with the sheets near one edge of the area to be exposed and processed, and the quantity of liquid supplied in the container is in excess of the amount required to provide a layer of the desired area and thickness. Accordingly, means are provided near the opposite edge of the area in which the image is formed for collecting and retaining excess processing liquid overrun. These means include a binding sheet secured around and to the margins of the superposed

sheets and relatively incompressible spacer means contained within the film unit for separating facing surfaces of the sheet materials as they pass between a pair of pressure-applying members during liquid spreading in order to provide liquid trapping and retaining spaces within the film unit.

In the preferred form of film unit with which the present invention is concerned, the two sheets are retained in superposition subsequent to processing and image formation one of the sheets preferably being transparent to permit viewing of the image. The excess processing liquid is trapped and retained in a space or spaces provided within the film unit and located in very close proximity to the edge of the image-containing area in order to minimize the overall size of the film unit. Thus, during processing (liquid spreading), there is formed a reservoir of a highly alkaline liquid available to migrate into the closely adjacent image-containing area and impair the visible image formed therein. My aforementioned application suggests, as a solution to this problem, the provision in the liquid trapping and retaining space or spaces of absorbent elements impregnated with an acid for absorbing and neutralizing the excess processing liquid overrun.

As previously noted, the liquid trapping and retaining space or spaces are located within the film unit within a region at one edge of the image-containing area bound by the binding sheet and that in order to minimize the size of the film unit and, in turn, the size of the container and camera in which the film unit is supplied, exposed and processed. This area is kept to a minimum, being but a very small fraction of the total area of the film unit; thus, the volume of the liquid trapping and retaining spaces is extremely limited, in turn limiting the amount of excess processing liquid that can be supplied in the container to insure complete spreading of a layer of desired thickness and extent. While the inclusion in the liquid trapping spaces of acid-impregnated, absorbing elements has proved satisfactory with regard to trapping, retaining and neutralizing excess processing liquid overrun, the absorbing element or elements themselves occupy a finite portion of the available space, e.g., 50 to 70 percent of the volume, thereby substantially reducing the quantity of liquid that the trapping and retaining spaces provided by the spacer(s) can accommodate.

An object of the present invention is to provide in a film unit structure of the type described, improved means for trapping, retaining and neutralizing excess processing liquid, characterized by more efficient utilization of the total space available, measured in terms of the quantity of processing liquid being trapped, retained and neutralized.

This and other objects of the invention are realized by providing a film unit structure including a single spacer occupying substantially the entire region of the film unit available for trapping and retaining excess liquid and formed with gaps occupying a major portion of the spacer providing liquid trapping and retaining spaces, and itself coated and impregnated with an acid for neutralizing the excess processing liquid trapped and retained in the spaces provided by the spacer.

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 drawings wherein:

FIG. 1 is a perspective view showing, partially in sec-

tion, a typical photographic film unit embodying the invention;

FIG. 2 is an exploded perspective view of the film unit in FIG. 1, illustrating details of the structure thereof;

FIG. 3 is a fragmentary, sectional view of a portion of the film unit of FIG. 1, the section being taken substantially along the line 3—3 of FIG. 1;

FIG. 4 is an enlarged fragmentary perspective view of a spacer constructed in accordance with the invention and incorporated in the film unit of FIG. 1;

FIG. 5 is a view, similar to FIG. 4, of another form of spacer embodying the invention; and

FIG. 6 is a somewhat schematic, sectional view illustrating the processing of a film unit incorporating the spacer of FIG. 5.

Reference is now made to FIGS. 1 through 3, wherein there is illustrated a typical film unit of the type embodying the invention and comprising the materials described in the aforementioned patents and applications. The film unit, designated **10**, generally includes a photosensitive or image-recording sheet **12**, a second sheet **14** and a rupturable container **16** holding a quantity of processing liquid **17**. The two sheets and processing liquid preferably include all of the materials and reagents required to produce a full-color photographic print by a process such as described in the aforementioned patents and applications and in U.S. Pats. Nos. 2,983,606, issued May 9, 1961, and 3,594,164, issued June 20, 1971. These patents describe film units adapted to produce full-color images by diffusion of a dye transfer, image-forming material to an image-receptive layer from a layer associated with a silver halide layer. These references also describe in detail the composition and arrangement of the various layers or strata which comprise the two sheet-like elements of the film unit and the composition of the aqueous alkaline liquid employed to initiate visible image formation.

As disclosed in U.S. Pat. No. 2,983,606, a preferred full-color image forming process involves the use of a photosensitive element containing a silver halide emulsion and a dye developer, that is, a dye which is a silver halide developing agent. The photosensitive element is adapted, following exposure, to be wetted by a liquid processing composition in the absence of light and then superposed with a sheet-like support element which may be utilized as an image-receiving element in a preferred embodiment. The liquid processing composition is applied to the photosensitive element as a substantially uniform layer as the photosensitive element is brought into superposed relation with the image-receiving element by moving the two elements between a pair of juxtaposed members. The liquid processing composition is introduced and spread between the two elements for permeation into the photosensitive layer to initiate development of the latent image formed therein. The dye developer is immobilized or precipitated as a consequence of the development of the latent image while in unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred by diffusion to a superposed image-receiving layer to form reversed or positive color image of the developed image.

For additional details of this process and the materials employed and the reactions involved, reference may be had to U.S. Pats. Nos. 2,983,606, 3,662,898, and 3,362,-821.

The image-receiving layer may be provided on a sheet-like support element separate from another support for the photosensitive layer in film structures such as disclosed in U.S. Pats. Nos. 3,415,644, 3,415,645, 3,414,646 and 3,473,925. Alternatively, as disclosed in U.S. Pat. No. 3,594,146, the film unit may comprise a sheet-like laminate including a dimensionally stable transparent support carrying a dyeable polymeric layer (i.e., image-receiving layer) a processing composition permeable opaque layer, and a photosensitive silver halide layer having associated therewith a dye transfer image-forming material. A film unit incorporating such a single, combination photosensitive and image-receiving element will also include another dimensionally stable sheet substantially coextensive and adapted to be superposed with the exposed area of the other (photosensitive) sheet and has, as its primary function, cooperation with the photosensitive sheet to aid in the distribution of a viscous processing liquid between the sheets.

The basic construction of the film unit **10** shown to illustrate the invention is the same regardless of the location of the image-receiving, e.g., dyeably polymer, layer. The essential distinctions will be found in the nature of the support sheets, that is, whether one or both are transparent, and composition of the various layers and strata coated thereon. For purposes of illustration, the film unit shown and described herein possesses a physical structure adapted for producing a diffusion transfer image in an image-receiving layer supported on a transparent sheet which is separate from (although it may be laminated to) the photosensitive sheet. In this particular embodiment, the photosensitive layer is exposed and the image is viewed through the second sheet **14** which, accordingly, is transparent.

In addition to photosensitive sheet **12**, second sheet **14** and container **16**, film unit **10** includes a mask or binding sheet **18**, a trapping element **20**, and a sealing strip **22**. Sheets **12** and **14** are preferably rectangular, are substantially equal in width and arranged in superposed face-to-face contact with one another with the lateral edges of the sheets substantially in alignment. 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.

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 a 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. 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**.

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 portions 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. 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.

In the processing of the film unit shown, the film unit is advanced, container foremost, relative to and between a pair of pressure-applying members shown in FIG. 6 as a pair of juxtaposed rollers **40** and **42**. The pressure-applying members, e.g., rollers **40** and **42**, 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 trapping 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.

Alternatively, another form of liquid trapping means is shown in FIGS. 5 and 6 as comprising a generally comb-shaped trapping element **44**, having a transverse section **46** approximately equal in length to the width of the sheets of the film unit and spaced teeth **48** extending from the transverse section **46**. The film unit incorporating trapping element **44** has essentially the same construction as previously described with element **44** being secured between the trailing end section **32** of sheet **18** and the trailing end margins of sheets **12** and **14** with teeth **48** extending toward the trailing end of the film unit and corporating with sheets **12**, **14** and **18** to provide spaces **50** for collecting and retaining excess processing liquid overrun. The construction and function of trapping elements **20** and **44** are similar insofar as each is formed of a relatively thick, incompressible sheet material which functions as a spacer to hold apart the pressure-applying members as the trailing end portion of the film unit passes therebetween.

As previously noted, the processing liquid functions to initiate the image-forming process including development of the latent image in the photosensitive layer or layers. A typical example of a liquid processing composition suitable for incorporation in container **16** for use in combination with sheet materials of the type disclosed, for example, in U.S. Pat. Nos. 2,983,606 and 3,594,164, is as follows:

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

Film units of the type embodying the present invention are designed to remain intact following distribution of the processing liquid between sheets **12** and **14**, i.e., the sheets are retained in superposed relation and so that the transfer image is viewed through one of the sheets depending upon the location of the image-receiving, e.g., dyeable polymer, layer. In the film unit and processing disclosed in U.S. Pat. No. 2,983,606, the dye transfer image is formed in a layer carried by second sheet **14** so that the second sheet is necessarily transparent and the processing liquid includes an opacifying agent for masking the image formed in the photosensitive layer and providing a suitable background for viewing the positive image. A suitable opacifying agent for this purpose is titanium dioxide and in the example of the formulation of the processing composition given above, may be provided in the amount of 40.0 grams. The opacifying agent performs an additional function and that is cooperating to prevent exposure of the photosensitive layer during image formation in the presence of ambient light, thus permitting the film unit to be advanced between the pressure-applying members directly into the light thus making it necessary to provide a processing chamber within the camera in which the film unit is exposed. Additional opacity may be obtained by providing another opacifying agent such as carbon black in the concentration of about one part of carbon black to 500 parts titanium dioxide.

In the form of the film unit described in U.S. Pat. No. 3,594,164 and the process performed thereby in which both the photosensitive and image-receiving layers are carried on the same support with the image-receiving layers being closest the support, i.e., sheet **12**, the image is viewed through sheet **12** which, accordingly, is transparent. In this example, the photosensitive layer is preferably exposed through second sheet **14** which is also transparent and in order to permit image formation in the presence of ambient light, the processing composition of the foregoing example may include an opacifying agent, specifically carbon black, in the amount of 6.4 grams.

For additional details and example of liquid processing compositions adapted for incorporation in container **16**, as well as the composition and arrangement of the various layers and strata of the film unit, U.S. Pat. Nos. 2,983,606, 3,594,164, and 3,594,165.

In the preferred form of the film unit, the liquid trapping spaces defined by openings or recesses **38** in trapping element **20** or the teeth of comb-shaped trapping element **44** 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 a typical

film unit of this type, for example, this separation may be of the order of 1/16 inch or less. This close proximity and the fact that the film unit is maintained intact, i.e., the sheets are not separated following processing, makes it possible for the alkali in the excess processing liquid to migrate from the trapping spaces in which it is collected and retained, into the image area where it may discolor, damage, or otherwise detract from the attractiveness and appearance of the image. As previously noted in the aforementioned application Ser. No. 643,273, this problem may be solved by providing acid-impregnated absorbent elements within the liquid trapping spaces. However, the volume occupied by the absorbent elements detracts from the volume of the available trapping space and, in many instances, may leave insufficient room to collect and retain all of the excess processing liquid.

In accordance with the present invention, this problem is solved by the novel expedient of coating and/or impregnating the trapping element itself with the neutralizing acid. By way of example, the liquid trapping element **20** illustrated in detail in FIG. 4 is formed of a fibrous sheet material, specifically an absorbent paper board sold by Riegel Paper Corporation under the trademark "Foldcote." The paper fold has a thickness of approximately 0.010 inch and is coated on one side with a citric acid solution having a typical formulation as follows:

Citric acid	grams	43
Methanol	cc	46
Water	cc	11

The citric acid solution is applied by conventional coating methods such as, for example, a roll coater in conjunction with a Meyer rod and then dried to provide an acid content of the order of 22 to 26 pounds per sq. ft. of the paper area. The coating process may be performed in two operations, each comprising liquid application and drying steps. It has been found that the major portion of the acid content of the paper board is absorbed thereby, while a lesser proportion remains on the paper board as a surface coating and it is this surface which is located facing second sheet **14**. The opposite or uncoated surface is intended to remain free of acid so as not to interfere with the adherence of that surface to the trailing end section **32** of sheet **18** during the assembly process.

Following coating with the acid, the paper board is perforated to remove approximately 50 percent of the sheet material and cut to size and shape as shown in FIG. 4. The comb-shaped trapping element **33** may be formed in a similar manner, i.e., impregnating a suitable absorbent, fibrous sheet material with a citric acid solution and then employing conventional cutting methods to form the trapping elements.

While citric acid is the preferred material, other relatively low molecular weight acids may be used. These include acids which are water soluble and exist in the solid or particulate state within the ambient temperature range of photographic film useage such as, for example, ascorbic, sulfamic, oxalic, maleric, succinic, boric, mallonic, tartaric, and fumaric. For examples of other materials suitable for this purpose and the reasons for suggesting citric acid as the preferred material, reference may be had to other applicant's aforementioned application of which this is a continuation-in-part.

It will be seen from the foregoing that the present invention provides an alkali-neutralizing, excess liquid trap having the advantages of greater capacity and consisting of a single element rather than multiplicity of elements. These advantages are coupled and contribute to ease of manufacture, fabrication, and assembly, as well as reduced cost, and constitute a substantial improvement over the prior art.

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

What is claimed is:

1. In a photographic film assemblage adapted to be exposed and processed to produce a visible photographic image and to remain intact after processing and image formation, said film assemblage comprising a pair of support layers, at least one of which is transparent, secured in superposed relation; at least a layer therebetween including a photosensitive material capable of recording an image when exposed to actinic radiation and having an area adapted to be exposed and processed; a collapsible container of an alkaline liquid processing composition adapted to be spread in a layer of predetermined thickness between said support layers in contact with said area of said photosensitive material by the progressive application of pressure to said film unit affected by movement thereof relative to and between a pair of pressure-applying members and capable, when so spread, of reacting with said photosensitive material to produce a visible image in said area between said support layers, the quantity of said liquid contained in said container being greater than the amount required to form a layer of said predetermined thickness between said support layers in contact with said area; and sheet-like binding means secured to said support layers adjacent an edge of the area adapted to be exposed and processed for securing said support layers in superposed relation;

a spacer element contained within said film unit between sections of binding means outside of and immediately adjacent said area, extending from side to side of said area and toward the end of said film unit and formed of a fibrous material sufficiently rigid to resist compression and space apart at least portions of said binding means during movement thereof between a pair of pressure-applying members;

said spacer element being formed with a multiplicity of gaps cooperating with at least portions of said binding means to provide spaces within said film unit defined in part by said gaps and communicating with the region between said support layers in which said liquid is spread and an image is formed for trapping and retaining excess processing liquid overrun;

the improvement wherein said spacer element includes an acid for neutralizing said processing liquid trapped in said spaces upon contact with said liquid.

2. A photographic film unit as defined in claim **1** wherein said gaps in said spacer element occupy on the order of 35 to 55 percent of the area of said element.

3. A photographic film unit as defined in claim **2** wherein said gaps are in the form of through holes and edge indentations in said spacer element.

4. A photographic film unit as defined in claim **1** wherein said liquid includes water and said spacer element is permeable to water.

5. A photographic film unit as defined in claim **4** wherein at least one side of said spacer element is impregnated with said acid.

6. A photographic film unit as defined in claim **1** wherein one of said support layers includes an edge portion extending beyond the edge of the other of said support layers adjacent said edge of said areas, said binding means including sheet material folded around an edge of said one support layer to form two sections secured to the outer surfaces of said support layers adjacent said edges thereof, and said spacer element is engaged between said edge portion of said one support layer and said section of said sheet material secured to said other support layer.

7 .A photographic film unit as defined in claim **6** wherein said spacer element overlaps a portion of said other support layer adjacent said edge thereof.

8. A photographic film unit as defined in claim **6** wherein said spacer element is attached to the last-mentioned section of said material.

9. A photographic film unit as defined in claim 8 wherein said spacer element is coated with said acid only on the surface thereof facing said edge portion of said one support layer.

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96—29 R