United States Patent [19]

Chen et al.

[11] **3,833,381**

[45] **Sept. 3, 1974**

[54] **PHOTOGRAPHIC PRODUCTS INCLUDING RUPTURABLE CONTAINERS**

[75] Inventors: **Richard J. Chen,** Winchester; **Thomas P. McCole,** South Natick, both of Mass.

[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Oct. 25, 1972**

[21] Appl. No.: **300,709**

[52] **U.S. Cl.** ..... **96/76 C,** 96/77, 95/13, 222/94, 222/107

[51] **Int. Cl.** **G03c 1/48**

[58] **Field of Search** ..... 96/76 C; 95/13; 222/94, 222/107

[56] **References Cited**

UNITED STATES PATENTS

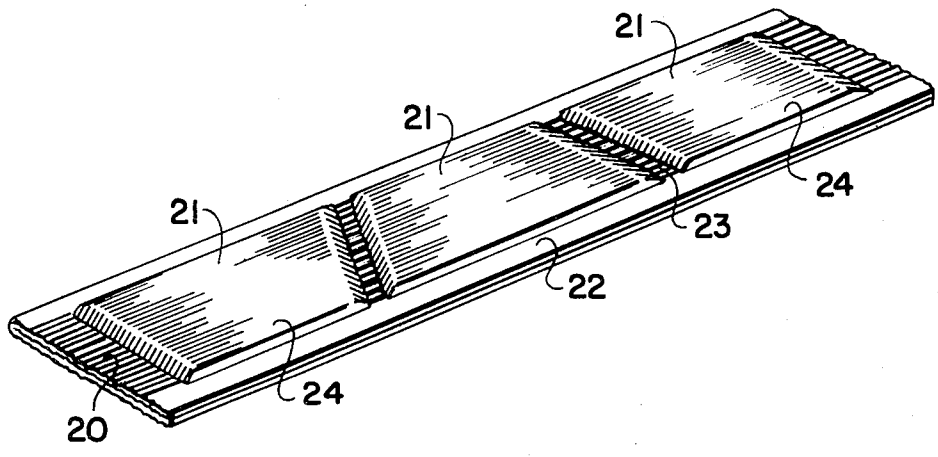
2,653,732	9/1953	Land	96/76 C
3,415,646	12/1968	Land	96/3
3,649,282	3/1972	Campbell	96/76 C
3,741,766	6/1973	Monaca	96/76 C

Primary Examiner—Ronald H. Smith
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Susan M. Cooke

[57] **ABSTRACT**

Single use rupturable containers or "pods" are disclosed for use in diffusion transfer film units. These pods are particularly adapted for use in film units providing integral negative-positive multicolor reflection prints. The rupturable containers have a plurality of fluid-retaining compartments, and the end compartments have a trapezoidal configuration effective in assisting the uniform distribution of processing fluid released by rupture of the pod.

13 Claims, 3 Drawing Figures



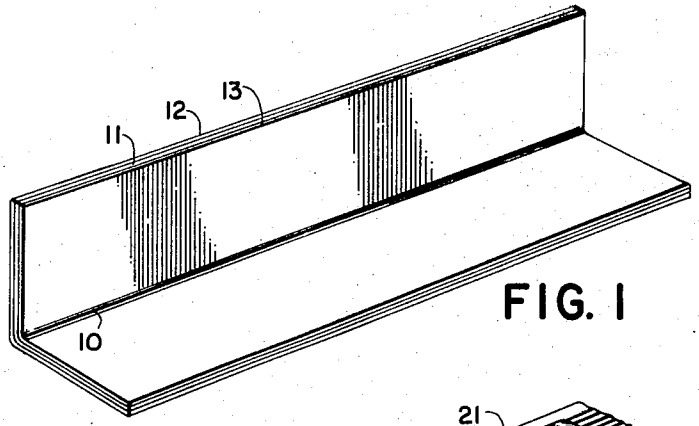


FIG. 1

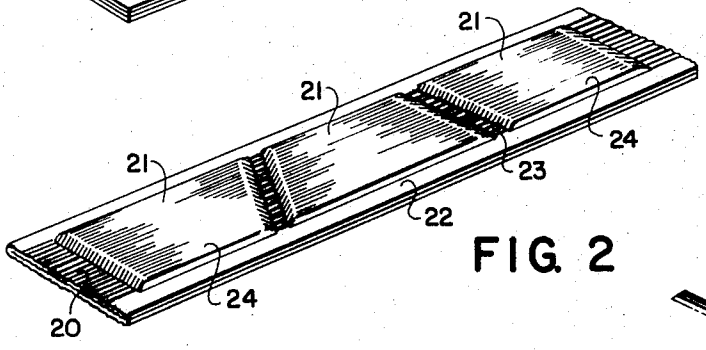


FIG. 2

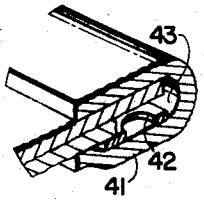


FIG. 3a

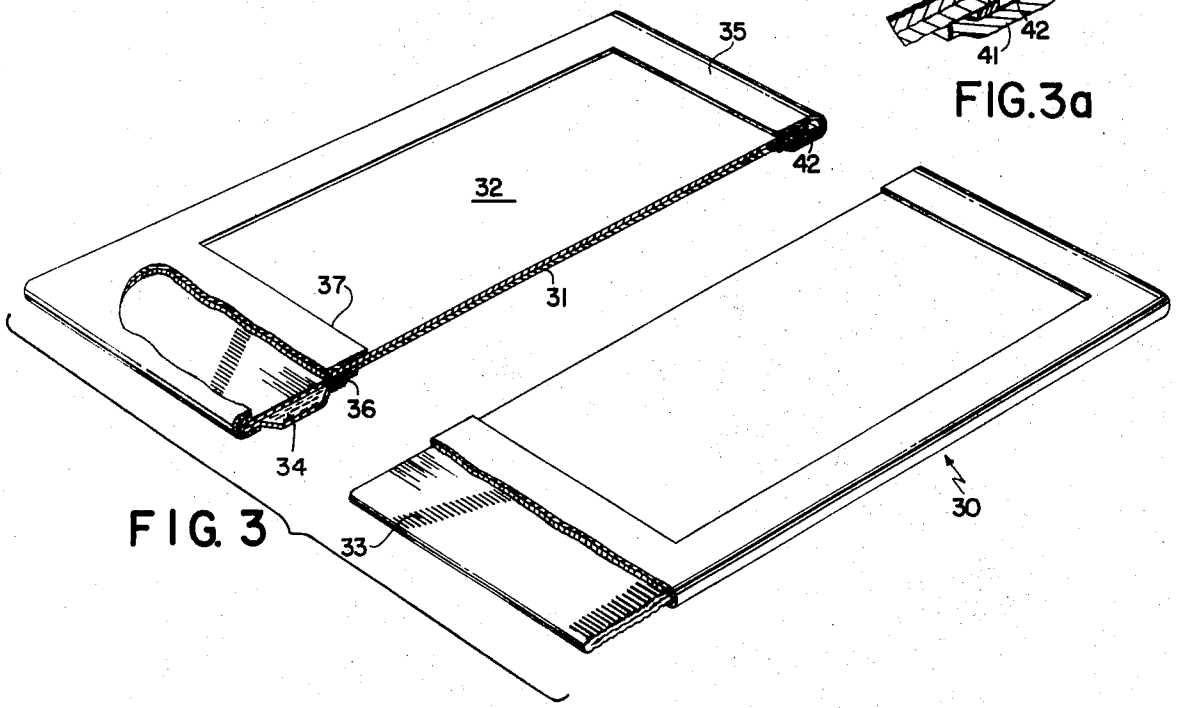


FIG. 3

PHOTOGRAPHIC PRODUCTS INCLUDING RUPTURABLE CONTAINERS

This invention relates to fluid carrying containers and, more particularly, to containers adapted to releasably retain a photographic processing composition.

In the photographic processes identified hereinafter, it is often necessary to apply a thin layer of fluid or liquid material over a fairly large surface area. For example, a photosensitive film may be processed by the surface application of a liquid layer containing a silver halide developing composition. Such processing fluids if left in contact with air generally possess a limited shelf life, due in part to degradation of their active components by environmental conditions. Suitable protective containers for releasably retaining them have thus been proposed and patented.

One object of the present invention is to provide a novel container for releasably retaining fluid materials.

Another object is to provide a novel rupturable container releasably retaining a photographic processing composition, said container being so constructed as to assist in more uniformly distributing said processing composition.

A still further object is to provide a photographic film unit including a rupturable container which carries viscous fluid for processing said film unit, said fluid being released from said container upon application of compressive force.

Other objects 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 of a sheet of material partly fabricated for use according to the present invention;

FIG. 2 is a perspective view of one form of fluid container constructed according to the present invention; and

FIG. 3 is a perspective view, partially in section, of a film unit constructed according to the present invention.

Containers useful in releasably retaining photographic processing fluids are disclosed in U.S. Pat. Nos. 2,543,181; 2,634,886 and 2,653,732 among others. Such containers generally comprise a multilayered rectangular blank folded in half longitudinally and secured along the margins of the three unfolded sides to form a central storage cavity. Fluid release is preferentially effected at only the unfolded longitudinal margin by securing its edges less tightly than those on the two side margins. When this rupturable margin is placed adjacent to one side of the surface to be covered by the fluid and the container is compressed, rupture occurs and the fluid contents are released for application over the adjacent surface area.

Such a container is often incorporated in rolls of photographic film which may be stored so that the container stands on end. Unless the container contents are redistributed before rupture, more fluid is released from the end of the cavity where it has accumulated during storage. Since a layer of uniform thickness is required for processing, fluid released from this end region must be extended out further than that released from other parts of the container. Since the area being processed is generally rectangular in shape, coverage of the corners of the sheet is insured by providing the container with more fluid than would be needed if a "square" distribution front had been generated.

U.S. Pat. No. 2,750,075 discloses a rupturable container which is subdivided along its length into smaller rectangular chambers. With such a multichambered container, excess fluid cannot accumulate in one section and areas of retarded rupture on the fluid releasing margin are more uniformly distributed along its length. Upon rupture a plurality of smaller tongue shaped streams are emitted, one from each compartment. These streams merge to form a more linear front and thus provide more uniform coverage than that obtained above. But a problem still remains, since the tongue shaped streams released from the compartments at either end of the container cannot be linearized by contact with another stream further out. Their curved shape is thus retained along the sides of the fluid front so that one or both outer corners of the area to be covered may not be reached or adequately supplied with fluid.

The present invention provides a rupturable, fluid-carrying container which is configured to aid in uniformly distributing said fluid over a predetermined area using a smaller quantity of said fluid than would otherwise be used.

The container of the present invention may be formed from two substantially rectangular blanks secured together along their outer margins or from a folded blank similarly secured. One longitudinal margin is less tightly secured than the others to provide a preferential site for rupture and fluid release when the container is compressed; this longitudinal margin is hereinafter referred to as the front or fluid-releasing seal or margin. The container is subdivided into a plurality of compartments substantially equal in volume as by securing the container walls together in transverse strips which extend from one longitudinal margin to the other. At least the compartments at either end of the container are trapezoidally shaped, a container side or end seal and a transverse wall partition or seal forming the non-parallel legs of a trapezoid. The transverse wall partition forming each end compartment is slanted from the back seal to the front seal such that the length of the front seal of the end compartment is shorter than the back seal of said end compartment. As explained below, this difference in rupturable margin length and the slant of the transverse partitions produce a jetting effect following container rupture, forcing fluid toward the outer corners of the area being covered.

A rupturable container so designed is especially useful in carrying photographic processing compositions. A latent image formed upon exposure of a photosensitive sheet to actinic radiation may be developed by rupturing the container and distributing its contents between the photosensitive sheet and another superposed sheet, both sheets being generally rectangular in dimension and aligned next to the fluid releasing margin. When the container is positioned so that its contents are adapted to flow between these sheets, rupture and

fluid release may be accomplished, e.g., by passing the entire film unit, container end first, between a pair of pressure applying members. Upon compression, fluid is forced toward the fluid releasing margin, the fluid stored in the trapezoidal end compartments being forced from the wider back seal toward the narrower front seal on the fluid releasing side. This constriction places additional pressure on the end compartments so that their fluid contents jet forth, spreading out and to the sides of the area being covered as directed by the outwardly slanted transverse partitions. This directional, jetting effect has been found to substantially reduce the incidence of fluid not reaching an outer corner of the area intended to be covered; in addition since less fluid is required for complete coverage, the accumulation of excess fluid at the end of the processed area is minimized. If an image-receiving layer is included, the processing composition will facilitate transfer of image-forming substances such as those found in silver halide diffusion transfer processes wherein a latent image is developed at the photosensitive sheet and a positive print of this image is produced at the image-receiving layer.

A preferred embodiment of the container comprises a thin, deformable rectangular blank of several layers, folded medially, as illustrated at **10** in FIG. **1.** The container walls preferably possess a thin layer, **11,** of material impervious to the processing fluid such as a metal foil of lead, aluminum, etc., approximately 0.001 of an inch thick. Surrounding this layer may be an outer layer, **12,** of sheet material such as kraft paper to limit deformation of container walls. A preferred composition for the innermost layer, **13,** is polyvinyl chloride or a similar thermoplastic resin inert to the processing fluid and its vapors.

The various layers comprising a container wall are laminated together by such means as heat, pressure or adhesive. The resultant sheet of material is folded medially and at least its unfolded edges are also secured together, as at **20** and **22** in FIG. **2,** to provide a fluid retaining container. To effect a directional flow of fluid upon container rupture, the unfolded longitudinal margin, **22,** is more weakly secured than the other margins. This may be accomplished by positioning a thin strip of a second thermoplastic material between the opposing container walls to form a weaker seal. The container is also subdivided along its length into a plurality of compartments **21** of substantially equal volume, the walls being secured together by transverse seals, such as **23,** which extend from one longitudinal margin to the other. The transverse seals forming the trapezoidally shaped end compartments, such as **24,** slant outward toward the fluid releasing margin, i.e., from the back seal to the front seal. When the container is divided into three compartments as shown in FIG. **2,** these transverse strips intercept the longitudinal margins at an angle of 10°–15° from a line perpendicular to the front seal. For additional strength both the transverse seals and the side seals may be ribbed. The transverse seals are of sufficient strength to resist rupture when the container is compressed and may have substantially the same strength as the end seals.

The rupturable container of this invention is particularly adapted for utilization in a film unit such as that shown in FIG. **3.** Film unit **30** comprises a photosensitive or image-recording sheet, **31,** a second or image-receiving sheet, **32,** and a rupturable container, **33,** holding a quantity of processing fluid, **34.** Sheets **31** and **32** are rectangular and may be coextensive with one another, being arranged next to the container in superposed face-to-face contact with at least their lateral edges aligned. These sheets and the container fit within a frame or mask **35,** arranged on a sheet **32** and extending over the edges of both sheets and the adjacent container to bind them together, the frame's rectangular opening defining the area of the image produced in the film unit. The longitudinal fluid releasing margin of container **33** is aligned with the facing surfaces of sheets **31** and **32** as to eject its fluid contents between them. It is held in place by a strip of material, **36,** extending along its fluid releasing margin and the adjacent margin of sheet **32** and within the overlying edge of frame **35.** Strip **36** cooperates with the folded under side portions of frame **35** to retain released fluid within the film unit.

Since the processing fluid must remain within the confines of frame **35** throughout processing, it is necessary to minimize the amount of excess fluid accumulated at the opposite or trailing end of the film unit. Any fluid advanced beyond the image area **32** may be stored within a trap area, **43,** formed by the folded over portion, **41,** of the trailing end of mask **35.** An elongated rectangular spacing element, **42,** is located within trap area **43,** extending along its length, to aid in retaining any excess fluid. Formed of porous material that is substantially imcompressible, spacing element **42** maintains separation between sheet **32** and folded over mask portion **41** after compression to provide a trapping space for excess fluid both within and without its pores.

Container rupture and the spreading of released fluid may be carried out by passing the film unit between suitably gapped pressure applying members, such as a pair of cylindrical rollers. When a film unit is advanced between these rollers, container end first, the resulting compressive force generates hydraulic pressure rupturing the container along its more weakly secured fluid releasing margin or front seal **22.** The fluid is discharged and spread between sheets **31** and **32** as the sheets pass between the rollers. The greater hydraulic pressure upon the shorter front seal portions of the two end compartments **24** precipitates rupture and fluid release at these locations while their outwardly slanted wall partitions force released fluid toward the sides and far corners of the sheets being covered. The rupturable container of this invention thus minimizes the incidence of fluid not reaching an outer corner. Furthermore, this highly desirable result is achieved using smaller total quantities of processing fluid, this minimizing the amount of excess fluid to be accumulated in the trap **43.**

The rupturable containers or "pods" provided by this invention are useful in the performance of a number of diffusion transfer image-forming processes. These containers are particularly useful in the production of a positive photographic print, preferably in full color, produced by a diffusion transfer process in which a photographic image-recording medium including a photosensitive material such as silver halide is exposed to form an image (latent) therein and is treated by wetting with a liquid processing agent to develop the image in the image-recording medium, form an imagewise distribution of transferable image-providing substances and transfer the image-providing substances by diffu-

sion to an image-receptive stratum in which they are immobilized to form a visible positive image. The film unit employed in the process may comprise materials for producing a black-and-white print according to a process such as disclosed in the U.S. Pat. of Edwin H. Land, No. 2,543,181, granted Feb. 27, 1951, and No. 2,662,822, granted Dec. 15, 1953; or it may include all of the materials and reagents required to produce a full color photographic print by a process such as disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961, in the name of Howard G. Rogers. This patent discloses a photosensitive element including a silver halide emulsion and a dye developer, that is, a dye which is a silver halide developing agent; a second or image-receiving element including an image-receiving layer of a dyeable material; and a processing liquid in which the dye developer is soluble. The photosensitive and image-receiving elements are superposed with the emulsion and image-receiving layers in face-to-face relation and the processing liquid is distributed in a uniform layer between and in contact therewith for permeation into the photosensitive layer where it initiates development of exposed silver halide. The dye developer is immobilized or precipitated in exposed areas as a consequence of development while in unexposed areas and partially exposed areas of the emulsion, the dye developer remains unreacted and diffusible thereby providing an imagewise distribution of unoxidized dye developer which is transferred, at least in part, by diffusion to the image-receiving layer without altering the imagewise distribution of the dye developer, to form a reversed or positive color image of the developed latent image in the emulsion.

Diffusion transfer film units in which the rupturable container provided by this invention may be utilized generally include two sheet-like elements in superposed relationship or adapted to be brought into superposed relationship, with the discharge or front seal **22** so positioned that the released processing fluid is distributed between predetermined surfaces. The film may be of roll film type, pack film type or individual film units (as in FIG. **3**). The photosensitive and image-receiving layers may be carried on separate supports or on a common support; in the latter instance, the second sheet-like element may serve as a spreader sheet to assist in spreading the fluid. Details of such film structures are well known; for illustrative examples, reference may be made, for example, to U.S. Pat. Nos. 2,543,181; 3,080,805; 3,415,644 and 3,594,164.

Film units of the type shown in FIG. **3** 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; 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. (Film units of this type are described in detail for example, in U.S. Pat. No. 3,415,644.) 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. (Film units of this type are described, for example, in U.S. Pat. No. 3,594,164.)

The embodiment of the film unit illustrated in FIG. **3** is one of the type shown in U.S. Pat. No. 3,415,644 and 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 a light-reflecting layer located between the image and the photosensitive layers. This light-reflecting layer comprises a solidified layer of the fluid contents **34** of container **33**, the fluid being distributed in sufficient quantity to form such a layer. In order to insure that the quantity of fluid supplied in the container is at least sufficient to form a layer of the desired minimum thickness and extent, the processing liquid is provided in a quantity slightly in excess of the minimum amount required. The processing fluid contained in container **33** comprises an aqueous alkaline solution having a pH at which the dye developers are soluble and diffusible and contains a light-reflecting agent in a quantity sufficient to mask the developed silver halide layers and immobilized dye developers subsequent to processing. Also present for a film-forming viscosity increasing agent or agents to facilitate rupture of the container and distribution of the liquid processing composition and help in maintaining the layer of processing composition as a structurally stable layer tending to bind the sheets to one another.

If the film unit is to be processed outside of a camera, an opacification system of the type described in U.S. Pat. No. 3,647,437 may be provided. In a particularly useful embodiment, the light-reflecting agent, together with suitable optical filter agents, will be present in the layer of fluid spread between the transparent image-receiving sheet and the opaque image-recording sheet in a concentration sufficient to prevent further exposure of the image-recording medium by actinic radiation transmitted by the transparent image-receiving sheet. Because the silver halide emulsion or emulsions comprising the image-recording strata are thus protected against exposure by incident actinic radiation at one major surface by the opaque processing composition and at the remaining major surface by the opaque support sheet, it is possible to process the film unit subsequent to distribution of the liquid processing composition in he presence of actinic radiation and thereby eliminate the need to provide a processing chamber within the camera and/or make it possible to withdraw the film unit from the camera almost immediately following distribution of the processing liquid. Binding element **35**, strip **36**, and the material comprising container **33** are also formed of a material opaque to actinic radiation to prevent exposure of the light-recording medium by light entering the laminated assembly at the edges thereof. The light-reflecting agent is selected for its suitability as a background for viewing the dye image formed in the image-receiving layer as well as for its masking and opacifying properties. Light-reflecting 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 radia-

tion. An opacifying agent especially preferred because of its highly reflective properties is titanium dioxide.

As is now well known and illustrated, for example, in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example sodium hydroxide, potassium hydroxide, and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. 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 are capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 1,000 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature. In a particularly useful embodiment, the processing fluid includes a colloidal silica in addition to the film-forming polymer such as hydroxyethyl cellulose or sodium carboxymethyl cellulose; such processing compositions are disclosed and claimed in the copending application of Edwin H. Land, Ser. No. 247,025 filed Apr. 24, 1972, reference to which may be made for further details of such processing compositions. The processing composition is typically applied in a layer having a thickness of the order of about 0.003 to 0.004 inch which is reduced as the solvent, i.e., water, is absorbed to a thickness of the order of about 0.002 inch.

In the most preferred embodiments of film units such as that shown in FIG. **3,** photosensitive and image-receiving elements **31** and **32** are temporarily laminated together, and spreading of the processing fluid effects delamination between predetermined layers. Reference may be made to U.S. Pat. No. 3,625,281 and 3,625,282, as well as to the copending application of Edwin H. Land, Ser. No. 247,023, filed Apr. 24, 1972, for details of such temporary lamination. Distribution of the processing fluid is facilitated by such a prelamination since there is little or substantially no air between the sheets to interfere with liquid distribution.

By way of summary, this invention provides novel rupturable containers releasably holding a processing composition in a plurality of chambers. At least the end chambers have a trapezoidal configuration, and are formed by a transverse seal slanting from the back seal to the front seal. The angle of this transverse seal **23** best suited to facilitate distribution of the fluid may be readily determined and will vary with the dimensions of the area to be covered. In the embodiment shown in FIG. **3,** the film unit will have an overall dimension of approximately 4.25 by 3.5 inches with an image area approximately 3.14 inches square. In such an embodiment, the angle of the slanted transverse seals may be about 10° to 15° from a line perpendicular to the front seal. The container is formed of a fluid-impervious sheet material, preferably a laminate including a layer or layers providing liquid and gas impermeability with an inner layer or stratum of a thermoplastic material which can be adhered to itself to seal the container by the external application of heat and pressure to the walls of the container. The container is formed by folding a rectangular blank of the sheet material medially and applying heat and pressure to the marginal sections of the blank to seal them to one another to form a cavity for containing processing liquid **34.** The seal **22** between longitudinal sections of the container is weaker than the end seals **20** and the transverse seals **22;** the latter seals may be corrugated to increase the seal strength, so that upon the application of a predetermined compressive force to the walls of the container in the region of the liquid-filled cavities, there will be generated within the liquid hydraulic pressure sufficient to separate longitudinal marginal sections through the major portion of their length to form the desired discharge passages.

It should be noted and appreciated that the novel container of the invention results in distribution or spreading of the mass of processing liquid along a substantially linear front parallel with the end edges of the area defined by opening **22,** at least during the latter stages of the liquid distribution and until the front has passed the end edge of the image area furthest from container **33,** thus insuring that the liquid covers the entire area to be treated. It will be apparent that because the liquid has advanced along a linear front parallel with the edge of the area, only a relatively small excess of processing liquid is required to assure complete coverage of the area, and there is little overrun constituting waste liquid that is required to be collected and retained within the film unit.

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

What is claimed is:

1. A rupturable, fluid releasing container comprising a pair of substantially rectangular opposing walls at least one wall being flexible, said walls being secured together along all four margins to enclose a fluid retaining cavity, one longitudinal margin being less tightly secured than other margins to provide a predetermined margin for rupture and fluid release upon compression of said container, the container cavity being partitioned lengthwise into a plurality of substantially equivolumed compartments, at least the compartment at each end of said cavity being trapezoidally shaped with the shorter of the parallel sides thereof forming part of said less tightly secured longitudinal margin, each of said cavities containing a photographic processing fluid.

2. A container as defined in claim **1** wherein said cavity partitions are formed by securing the container's opposing walls together in transverse strips extending from one longitudinal margin to the other, said partitions for each said end compartment forming an angle of about 10°–15° from a line perpendicular with the longitudinal margins.

3. A container as defined in claim **1** wherein said walls are formed of a fluid-impervious laminate including an inner layer of a thermoplastic polymeric material substantially impervious to said processing fluid.

4. A container as defined in claim 3 wherein said inner wall comprises polyvinyl chloride.

5. A container as defined in claim 1 wherein said fluid retaining cavity is divided into three compartments.

6. A container as defined in claim 3 wherein a thin strip of a second thermoplastic material is positioned between the opposed walls forming said less tightly secured longitudinal margin.

7. A photographic product for forming a diffusion transfer image comprising a photosensitive element having a photosensitive layer carried on a support, a second sheet-like element in superposed relation with said photosensitive element or adapted to be brought into superposed relation with said photosensitive element, an image-receiving layer positioned between said photosensitive element support and said second sheet-like element when said photosensitive element and said second sheet-like element are in superposed relation, and a rupturable, fluid releasing container as defined in claim 1, said rupturable container being positioned so that upon compression of said container said fluid will be released for distribution between predetermined layers of said superposed elements to develop said photosensitive layer and provide a diffusion transfer image at said image-receiving layer.

8. A photographic product as defined in claim 7 wherein said photosensitive element is a multicolor photosensitive element including dye developers as the imageforming materials.

9. A photographic product as defined in claim 8 wherein said image-receiving layer is positioned between said photosensitive layer and said photosensitive element support and all layers of said photosensitive element between said image-receiving layer and said support are transparent, said photosensitive element and said second sheet-like element being held in registered, superposed relationship.

10. A photographic product as defined in claim 8 wherein said second sheet-like element is transparent and said image-receiving layer is positioned on said second sheet-like element, said photosensitive element and said second sheet-like element being held in registered, superposed relationship.

11. A photographic product as defined in claim 10, including binding means extending around the edges of said superposed elements, said binding means aiding in retaining and distributing said processing composition following rupture of said container.

12. A photographic product as defined in claim 11 wherein said container is a container as defined in claim 2.

13. A photographic product for forming a diffusion transfer image comprising a photosensitive element having a photosensitive layer carried on a support, a second sheet-like element having an image-receiving layer carried on a support, said photosensitive element and said second sheet-like element in superposed relation or adapted to be brought into superposed relation with said supports outermost, and a rupturable, fluid releasing container as defined in claim 1 being positioned to that upon compression of said container said fluid will be released for distribution between predetermined layers of said superposed elements to develop said photosensitive layer and provide a diffusion transfer image at said image-receiving layer.

* * * * *