

Aug. 5, 1958

E. H. LAND

2,846,309

PHOTOGRAPHIC PRODUCTS

Filed July 17, 1952

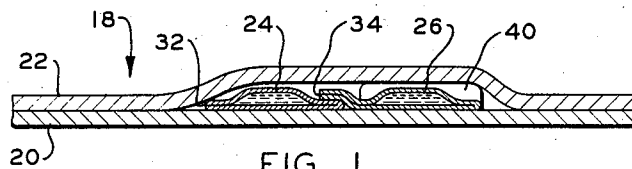


FIG. 1

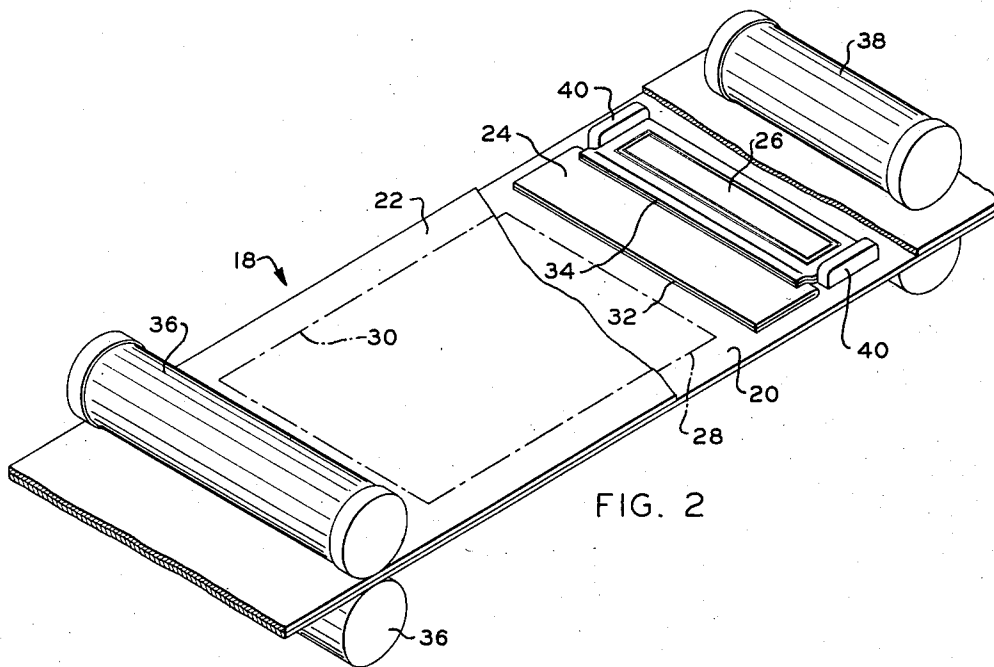


FIG. 2

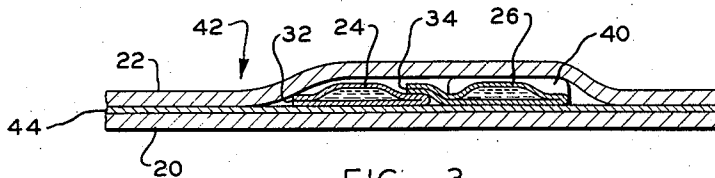


FIG. 3

INVENTOR

Edwin H. Land

Brown and Mikulka
and

BY *Sherald Altman*

ATTORNEYS

1

2,846,309

PHOTOGRAPHIC PRODUCTS

Edwin H. Land, Cambridge, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

Application July 17, 1952, Serial No. 299,358

15 Claims. (Cl. 96-76)

This invention relates to photography and more particularly to photographic products and photographic processes.

It is recognized in the art that many a photographic composition, once coated on or otherwise applied to the surface of a sheet intended to be photoexposed, has a short useful life. For example, certain photosensitive compositions, once coated on the surface of a support sheet, are relatively unstable. Similarly, once applied, many compositions intended to hypersensitize or to optically sensitize photosensitive coatings are able to effectively perform their respective functions only for a short period. Furthermore, many photosensitive coatings are mixtures of distinct components intended to react with each other only when photoexposed but nevertheless tending to react with each other though not photoexposed. It is frequently desired, therefore, that a photographic composition be applied to the surface of a sheet only shortly before the sheet is photoexposed.

An object of the present invention is to enclose within a rupturable protective container a photographic composition of the aforementioned type, or at least one of its components, so that it is capable of being readily applied to the surface of a sheet when desired.

Another object of the present invention is to associate with such a container at least an additional rupturable protective container carrying at least another photographic composition also capable of being readily applied when desired, the containers being so constructed and arranged as to be capable of sequentially discharging their contents for spreading on the surface of a sheet where they are adapted to perform related functions.

Still other objects of the invention are: to provide a photographic assemblage comprising a sheet and at least a container associated with a surface thereof, the container carrying a photographic composition and, upon application of opposed compressional forces thereto, being capable of releasing the photographic composition therefrom for spreading on the surface, the photographic composition being associated with the photosensitivity of the sheet; to provide a photographic assemblage comprising a sheet and at least a pair of containers associated with a surface of the sheet, one container carrying a photographic composition related to the photosensitivity of the sheet, the other container carrying another photographic composition, the containers being so constructed and arranged as to be capable of sequentially discharging their contents on the surface where they are adapted to perform related functions; and to provide an assemblage of this type having associated therewith means for permitting the application of opposed compressional forces to one container of the pair while preventing the application of opposed compressional forces to the other container of the pair.

Further objects of the present invention are: to provide an assemblage of photographic sheets having associated therewith containers carrying different photographic compositions that are capable of sequentially

2

performing different functions within the assemblage; to provide for use in an assemblage of the foregoing type a plurality of containers, each container being adapted to discharge the photographic composition therewithin when opposed compressional forces are applied thereto; to provide a photographic assemblage comprising a first sheet and a second sheet, the sheets being adapted to be superposed with a surface of the first sheet and a surface of the second sheet in contiguous relation, at least a pair of photographic composition containers secured to at least one of the surfaces, one container of the pair being adjacent to the other container of the pair at least when the sheets are superposed, the containers, upon application of mechanical stress thereto, being adapted to discharge their contents, and means associated with the containers for permitting the application of opposed compressional forces to one container of the pair while preventing the application of opposed compressional forces to the other container of the pair, whereby sequential discharge of the container contents may be accomplished; and to provide a means for permitting the application of opposed compressional forces to one container of the pair while preventing the application of opposed compressional forces to the other container of the pair, that portion of one of the containers of the pair being substantially a predetermined distance from a first of a pair of sheets of the foregoing type, this means including at least a crush-resistant element which provides a portion that is adapted to abut against a second of the pair of sheets and that is spaced from the first of the pair of sheets by a distance at least substantially as great as the predetermined distance.

Still further objects of the present invention are: to provide a photographic process comprising the steps of superposing a first sheet on a second sheet with a surface of the first sheet and a surface of the second sheet in contiguous relation and spreading a photographic composition between the surfaces, the photographic composition being related to the photosensitivity of at least one of the sheets; to provide a photographic process comprising the steps of superposing a first sheet on a second sheet with a surface of the first sheet and a surface of the second sheet in contiguous relation, spreading a first photographic composition between the surfaces, photoexposing at least one of the surfaces and thereafter spreading a second photographic composition between the surfaces; and to provide a photographic process comprising the steps of superposing a first sheet on a second sheet with a surface of the first sheet and a surface of the second sheet in contiguous relation, spreading a first photographic composition in a substantially predetermined direction between the surfaces and thereafter spreading a second photographic composition in the substantially predetermined direction between the surfaces.

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

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

Figure 1 is an exaggerated sectional view of an assemblage embodying the present invention;

Fig. 2 is an exaggerated perspective view of the assemblage of Fig. 1, shown in conjunction with cooperating pressure-applying means; and

3

Fig. 3 is an exaggerated sectional view of another assemblage embodying the present invention.

With reference now to the drawing, wherein like numerals denote like parts, Figs. 1 and 2 illustrate generally the physical structure of one example of a photographic assemblage, herein designated at 18, embodying the present invention. Generally, this assemblage comprises a pair of sheets 20 and 22 which are adapted to be superposed with their adjacent surfaces in contiguous relation, that is, with their surfaces either close to or in contact with each other. A pair of adjacent containers 24 and 26 are secured to sheet 20, container 24 carrying a predetermined quantity of a photosensitive composition and container 26 carrying a predetermined quantity of a processing composition. These compositions are adapted to perform related functions when spread sequentially between (Fig. 2) a frame 28 of sheet 20 and an area 30 of sheet 22.

Container 24, when deformed by opposed compressional forces, is capable of releasing its contents through a rupturable mouth 32 for spreading between frame 28 and area 30. Similarly, container 26, when deformed by opposed compressional forces, is capable of releasing its contents through a rupturable mouth 34 for spreading between frame 28 and area 30. It is to be noted that container 26 is shorter in length than container 24 and that mouth 34 of container 26 overlaps an edge of container 24. By virtue of this construction, container 26 is capable of discharging its contents from mouth 34 evenly and without obstruction.

Means are provided for enabling the sequential application of opposed compressional forces to containers 24 and 26 and the sequential spreading of their contents between frame 28 and area 30. In the form shown, this means includes a pair of crush-resistant, relatively incompressible elements 40, 40 secured to sheet 20 adjacent to the opposite ends of container 26. The portions of these elements farthest from sheet 20 are spaced from it by a distance at least substantially as great as the height, with respect to sheet 20, as is the processing composition-carrying portion of container 26.

The sequential application of opposed compressional forces to containers 24 and 26, together with the sequential spreading of their contents, may be accomplished by unidirectional movement of the assemblage with respect to such pressure-applying means as two pairs of rollers 36, 36 and 38, 38, the rollers of each pair being positioned on opposite sides of the assemblage. Rollers 36, 36 are provided with comparatively long, cylindrical, pressure-applying surfaces, rollers 38, 38 with comparatively short ones. Elements 40, 40 are spaced from each other by a distance less than the length of the pressure-applying surfaces of rollers 36, 36 and greater than the length of the pressure-applying surfaces of rollers 38, 38. Thus, as the assemblage advances unidirectionally between rollers 36, 36 and 38, 38, elements 40, 40 prevent rollers 36, 36 from compressing container 26, permit rollers 36, 36 to compress container 24 and permit rollers 38, 38 to compress container 26.

Crush-resistant elements 40, 40 are composed of any suitable material having a high Young's modulus, such as stiff cardboard or synthetic resin, the elements being at least substantially as great in height with respect to sheet 20 as is the photosensitive composition-carrying portion of container 26. Elements 40, 40 may be either integral with sheet 20 or distinct from it in accordance with the teachings of copending application Serial No. 141,905, filed by Edwin H. Land on February 2, 1950, for Image-Receiving Photographic Element Combined with a Processing Container.

It is to be understood that other arrangements of container 24, container 26 and elements 40, 40 are feasible within the scope of the present invention. For example, in a modification of assemblage 18, container 24 is affixed to one of sheets 20 and 22, container 26 is affixed to the

4

other of the sheets, and elements 40, 40 are affixed to either one or the other of the sheets. Alternatively, container 24, container 26 and elements 40, 40 all are affixed to sheet 22. Or container 24 and container 26 are affixed to one of sheets 20 and 22 and elements 40, 40 are affixed to the other of the sheets. In other alternative embodiments of assemblage 18, each of elements 40, 40 includes two sections, one section of which is affixed to sheet 20 and the other section of which is secured to sheet 22, these sections being adapted to abut against each other in order to prevent deformation of the container with which they are associated when sheets 20 and 22 are superposed.

In the operation of assemblage 18, sheets 20 and 22 are superimposed and the assemblage advanced between rollers 36, 36 in order to rupture container 24 and to spread its photosensitive composition between frame 28 and area 30 to form a photosensitive coating. Sheets 20 and 22 now are maintained in superposed relation for a predetermined period during which the photosensitive coating becomes securely bonded to the surface of sheet 20. The photosensitive coating now is exposed to actinic radiation in order to produce a latent image in frame 28. Thereafter, superposed sheets 20 and 22 are advanced between rollers 38, 38 in order to rupture container 26 and to spread its processing composition between the photosensitive coating and sheet 22. Sheets 20 and 22 now are maintained in superposed relation for a predetermined period in order to process the latent image in frame 28 and to form a visible print. The length of the period during which the sheets are superposed following spreading of the photosensitive composition between them and the length of the period during which the sheets are superposed following spreading of the processing composition between them depend upon the specific characteristics of the photosensitive and processing compositions, as will be apparent to persons skilled in the art.

In a preferred form of assemblage 18, the photosensitive composition within container 24 includes a ripened photosensitive silver halide emulsion in the form of a gel which is fluid enough under ambient conditions to be readily spread. In such an emulsion, one or more of the silver halides, of which silver chloride, silver bromide and silver iodide are examples, are dispersed in a suitable protective colloid material such as gelatin, agar, albumen, casein, collodion or a cellulose ester. Examples of specific formulations of conventional emulsions suitable for such use are described in T. T. Baker, *Photographic Emulsion Technique*, American Photographic Publishing Co., Boston, 1948, chapter IV.

The emulsion within container 24, when spread between sheets 20 and 22, forms a thin emulsion coating capable of receiving a latent image. Sheet 20, sheet 22 and this emulsion are so constituted that the adhesive forces between the emulsion coating and sheet 20 are greater than those between the emulsion coating and sheet 22, this arrangement being such as to facilitate stripping of the emulsion coating from sheet 22 when the processing composition within container 26 is spread between them. Sheet 20, for example, is composed of a paper at least one surface of which has been sized with a suitable material such as hardened gelatin or baryta in gelatin. Alternatively, sheet 20 is composed of a plastic material, for example cellulose nitrate or one of the organic acid cellulose esters such as cellulose acetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate or cellulose acetate butyrate. The surface of sheet 20 in the latter case, in order to insure good adhesion between it and the emulsion coating, is treated as, for example, with a mixture of gelatin and cellulose nitrate. Sheet 22, for example, is composed of a plastic material of the type mentioned above in reference to sheet 20.

In the preferred form of assemblage 18, either of sheets 20 and 22 is transparent so as to permit actinic

radiation to pass through it in order to form a latent image in the emulsion coating while the sheets are maintained in superposed relation. Alternatively, both sheets are opaque and must be stripped apart before the emulsion coating can be photoexposed. In the latter case, if either sheet 20 or 22 is composed of one of the plastic materials mentioned above in reference to sheet 20, it is rendered opaque by a suitable pigment or dye.

In the preferred form of assemblage 18, the processing composition within container 26, when spread in a uniformly thin layer between the emulsion coating and sheet 22, is adapted to effectuate a silver halide transfer process whereby a latent image in the emulsion coating is processed and a positive print is formed on sheet 22. Preferably, this processing composition is a liquid which includes a developer such as hydroquinone, a silver halide solvent such as sodium thiosulfate and an alkali. This processing composition is adapted to develop the latent image in the emulsion coating to silver and to form from unexposed silver halide a soluble silver complex which, at least in part, may be transferred by imbibition to sheet 22 where it is developed to silver to produce a positive print. The photographic process and various species of processing compositions of the above type are further described in United States Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, for Photographic Product Comprising a Rupturable Container Carrying a Photographic Processing Liquid.

It is possible to provide sheet 22 with a silver precipitating layer containing certain materials whose presence during the transfer process has a desirable effect on the amount and character of the silver precipitated during positive print formation. For this purpose, such materials as metallic sulfides and selenides, thiooxalates and thioacetamides have been disclosed in copending applications Serial No. 727,385, filed by Edwin H. Land on February 8, 1947, for Photographic Product and Process; Serial No. 7,795, filed by Edwin H. Land on February 12, 1948, for Photographic Process; and Serial No. 164,908, filed by Edwin H. Land on May 29, 1950, for Photographic Silver Halide Transfer Product and Process. Other precipitating agents have been proposed, such as the colloidal metals and specifically colloidal silver. It is also desirable, as disclosed in these copending applications, to provide, as the vehicle for the silver precipitating agents, a macroscopically continuous film that consists of submacroscopic agglomerates of minute particles of a suitable water-insoluble, inorganic, preferably siliceous, material such as silica aerogel. The use of such a vehicle for the precipitating agents tends to aggregate the silver that is precipitated into its most effective condition for print formation.

It is to be expressly understood that the processing composition within container 26 need not effectuate a transfer but may act merely to develop the latent image in the emulsion coating.

In the preferred form of assemblage 18, containers 24 and 26 are similar in structure, each container being constructed from a blank of three-ply sheet material having a single fold. The outer ply serves as a backing or support and is composed of a thin, relatively inexpensive, tough material, preferably a paper such as kraft paper. The intermediate ply is composed of a substantially vapor-, liquid-impervious material, for example a metal foil such as silver, lead or nickel foil. The inner ply is composed of a suitable thermoplastic or thermosetting plastic material, for example a polyvinyl acetal such as polyvinyl butyral or polyvinyl formal, which protects the container contents from contamination. A composition comprising by weight approximately 60% to 70% polyvinyl butyral, approximately 10% to 23% nitrocellulose and approximately 5% dibutyl sebacate is particularly satisfactory. At opposite end portions of each container, the two folds of the inner

ply are sealed to each other as by the application of heat and pressure. Those sections of the two folds defining the mouth are bonded together by a strip of adhesive which is so constituted that the adhesive forces between the strip and the inner ply are less than the cohesive forces between end portions of the inner ply which are sealed together. A satisfactory strip may be composed, for example, of ethyl cellulose or of a mixture of ethyl cellulose and paraffin, the mixture including at least 50% by weight of ethyl cellulose. Since the bonding forces between those sections defining the mouth are less than the bonding forces between other sections of the container, the application of opposed compressional forces to the container causes discharge of the container's contents through its mouth.

In a modification of the preferred form of assemblage 18, sheet 20, sheet 22 and the silver halide emulsion within container 24 are so constituted that the adhesive forces both between the emulsion and sheet 20 and between the emulsion and sheet 22 are small. Both sheets 20 and 22, for example, are composed of a plastic material of the type mentioned above in reference to sheet 22. Sheet 20 is provided with a silver precipitating layer of the aforementioned type. The emulsion within container 24, when spread between sheets 20 and 22, forms a thin emulsion coating capable of being stripped both from sheet 20 and from sheet 22. Assemblage 18 is arranged so that the processing composition within container 26 can be spread in a uniformly thin layer between the emulsion coating and sheet 22. This composition includes a developer, a silver halide solvent and an alkali which are adapted to permeate the emulsion coating and to produce on sheet 20 a positive print of a latent image formed in the emulsion coating. This composition, additionally, is so constituted as, by the inclusion of a mixture of gelatin and a water-soluble cellulosic material, to cause the emulsion coating to adhere to sheet 22 when sheets 20 and 22 are stripped apart.

In another form of assemblage 18, the processing composition within container 24 includes a photosensitive ferric salt which, when photoexposed, is capable of being reduced to a ferrous salt. Sheet 20 here may be composed of a suitable paper the surface of which is adapted to absorb a solution of the photosensitive ferric salt. Or, sheet 20 may have laminated to it a suitable colloid material which is adapted to imbibe such a solution. Suitable photosensitive ferric salts, for example, are ferric chloride and ferric salts of organic acids such as ferric oxalate, ferric tartrate and ferric citrate. The processing composition within container 24 preferably includes a coupler which differentiates between ferric and ferrous salts to form a visibly distinguishable reduction product with one or the other. Examples of such a coupler are potassium ferricyanide, potassium ferrocyanide, the tannins, β -naphthoquinone sulfonic acid, silver salts, platinum and palladium salts and various colloid materials such as gelatin and gum arabic.

In a modification of this form of assemblage 18, the photosensitive composition within container 24 includes a coupler as well as a photosensitive ferric salt. In such a case the processing composition within container 26 includes as a developer merely an alkali or an acid capable of providing the chemical environment necessary for combination of the coupler and either the ferrous or ferric salt.

Examples of specific formulations of conventional ferric-ferrous, photosensitive and processing compositions suitable for use in an assemblage of the foregoing type are described in Baker, supra, pages 268-275.

In a further form of assemblage 18, container 24 carries a photosensitive diazonium compound which decomposes upon photoexposure and container 26 carries a processing composition which includes as a developer a coupler capable of combining with an exposed or unexposed diazonium compound to form a dye. The proc-

essing composition further includes either an alkali or an acid capable of providing the chemical environment necessary for combination of the exposed or unexposed diazonium compound and the coupler. Sheet 20 here may be composed of a suitable paper the surface of which is adapted to absorb a solution of the photosensitive diazonium compound. Or, sheet 20 may have laminated to it a suitable colloid material which is adapted to imbibe such a solution. Suitable photosensitive diazonium compounds, for example, are prepared by treating aromatic amines with nitrous acid at low temperature. As suitable couplers, mention may be made of phenols, naphthols and amino compounds which are adapted to combine with an exposed or unexposed diazo compound to form a visibly distinguishable azo dye.

This form of the invention may be modified so that the photographic composition within container 24 includes a coupler as well as a photosensitive diazonium compound. In such a case the developing composition within container 26 includes merely an alkali or an acid capable of providing the chemical environment necessary for combination of the coupler and either the exposed or unexposed diazonium compound.

Examples of specific formulations of conventional diazonium photosensitive and processing compositions suitable for use in an assemblage of the foregoing type are given in Baker, *supra*, pages 277-278, in L. P. Clerc, *Photography, Theory and Practice*, Pitman, New York, 1937, page 444, and in J. S. Friedman, *History of Color Photography*, American Photographic Publishing Co., Boston, 1944, pages 487-493.

Fig. 3 illustrates in detail the structure and operation of another assemblage, generally indicated by 42, embodying the present invention, like components of assemblage 42 being designated by the same numerals which designate like components in assemblage 18. Assemblage 42, in accordance with the present invention, makes practicable the intermingling of at least two photographic compositions immediately before they are used. By means of assemblage 42, a hypersensitizing or optical sensitizing composition may be applied to a photosensitive coating immediately before it is photoexposed. Alternatively, by means of assemblage 42, mixtures of distinct components of a photosensitive composition which are not intended to participate in a given chemical reaction until photoexposed may be maintained in separate locations until immediately before being photoexposed.

Generally, assemblage 42 includes a pair of sheets 20 and 22, a pair of containers 24 and 26 and a pair of crush-resistant elements 40, 40, components which are generally similar to their counterparts in assemblage 18. Here, however, sheet 20 has laminated to one of its surfaces a coating 44, which includes at least one component of a photosensitive composition. A photosensitizing composition, which includes either another component of the photographic composition or a photosensitizing agent capable of modifying the characteristics of the photographic composition, is carried in container 24 so as to be capable of being readily spread on the surface of coating 44. Another photographic composition, for example a processing composition, is carried within container 26.

In the operation of assemblage 42, sheets 20 and 22 are superposed and the assemblage advanced between rollers 36, 36 in order to rupture container 24 and to spread its sensitizing composition between frame 28 and area 30. Sheets 20 and 22 now are maintained in superposed relation for a predetermined sensitizing period. In certain forms of assemblage 42, at this point, sheet 20 is stripped from sheet 22 and dried. Coating 44 is now exposed to actinic radiation in order to produce a latent image in frame 28. Thereafter, superposed sheets 20 and 22 are advanced between rollers 38, 38 in order to rupture container 26 and to spread its processing composition between photosensitive coating 44 and sheet 22. Sheets

20 and 22 now are maintained in superposed relation for a predetermined processing period during which a visible print is formed. The lengths of the predetermined sensitizing and processing periods are dependent upon the specific characteristics of coating 44 and of the photosensitizing and processing compositions, as will be apparent to persons skilled in the art.

In one form of assemblage 42, coating 44 includes a conventional silver halide emulsion the spectral sensitivity characteristics of which it is desired to modify, container 24 carries an optical sensitizing composition and container 26 carries a silver halide processing composition such as one of the processing compositions previously described. The optical sensitizing composition, for example, includes an extremely weak solution of a suitable dye in alcohol and/or water. As examples of suitable dyes, mention may be made of derivatives of fluorescein, such as erythrosine and eosine, and of various cyanines such as thiazole, thiazoline, pyridine, benzoxazole, benzothiazole, benzoselenazole, 3,3 dimethylindolenine, naphtho (2,1) thiazole, and naphtho (1,2) thiazole. Further examples of specific formulations of conventional optical sensitizing compositions suitable for use in an assemblage of the foregoing type are described in Baker, *supra*, chapter VI.

In a modification of this form of assemblage 42, container 24 carries a hypersensitizing composition rather than an optical sensitizing composition. Such a hypersensitizing composition, for example, includes any one of ammonia, a thiourea such as palmityl thiourea or styrene fumaryl allyl thiourea, allyl isothiocyanate, thiazole, quinoline and pyridine. The hypersensitizing composition alternatively consists merely of distilled water. Further examples of specific formulations of conventional hypersensitizing compositions suitable for such use are more fully described in Baker, *supra*, chapter XV.

In an alternative form of assemblage 42, coating 44 includes a material capable, after being treated with a suitable dichromate solution, of becoming differentially insolubilized or tanned when photoexposed. The various regions of such a differentially insoluble coating are capable of forming a visible print by differentially absorbing a suitable coloring material. Coating 44, for example, includes a hydrophilic colloid material such as gelatin, glue or gum arabic. Here the sensitizing composition within container 24 includes, for example, a dichromate solution such as an aqueous solution of chrome alum, potassium dichromate or ammonium dichromate. The processing composition within container 26 includes a coloring material such as a water-soluble dye. Examples of specific formulations of conventional dichromate materials suitable for such use are described in Clerc, *supra*, pages 434-437 and page 419, section 645.

Many chromate colloid materials are photoexposed most effectively when dry. If such materials are employed in the foregoing form of assemblage 42, following the spreading of the chromate solution between sheets 20 and 22, sheet 20, before being exposed, is stripped from sheet 22 and dried.

Preferably though not necessarily, the photographic compositions carried by containers 24 and 26 are relatively viscous so as to be easily controlled when spread. If desired, the viscosity of any of these compositions can be increased by including within it a suitable thickener, for example, a polymeric material such as a water-soluble cellulosic material, and insoluble emulsifiable oil, a starch or a gum.

It is to be expressly understood that assemblages of the herein disclosed type may be provided with more than two rupturable containers and that more than one of these containers may be provided with crush-resistant elements of the herein disclosed type. For use in color photography, for example, such an assemblage in one form comprises three rupturable protective containers, the first container carrying a conventional composition which

includes a red-sensitive emulsion and a cyan coupler, the second container carrying a conventional composition which includes a green-sensitive emulsion and a magenta coupler, and the third container carrying a conventional composition which includes a blue-sensitive emulsion and a yellow coupler. These containers are arranged with respect to a support sheet in association with crush-resistant elements of the herein disclosed type in a manner which will now be apparent to one skilled in the art. In practice, the red-sensitive emulsion is spread on a support sheet to form a first separation layer which then is photoexposed through a suitable red filter, the green-sensitive emulsion is spread on the first separation layer to form a second separation layer which then is photoexposed through a suitable green filter, and the blue-sensitive emulsion is spread on the second separation layer to form a third separation layer which then is photoexposed through a suitable blue filter. The first, second and third separation layers thus formed constitute a photoexposed integral tripack capable of being processed in conventional fashion to form a subtractive trichromatic print.

In alternative forms of the present invention, the means for enabling the sequential application of opposed compressional forces to the rupturable protective containers of the herein disclosed type are embodied in the pressure-applying means in conjunction with which the assemblage is employed rather than in crush-resistant elements directly associated with the assemblage. For example, obvious mechanical expedients can be utilized to relieve, at appropriate intervals, the opposed compressional forces exerted by the pressure-applying means.

The present invention contemplates a novel process comprising the steps of spreading a photographic composition in a uniformly thin layer between adjacent surfaces of a first sheet and a second sheet, the adjacent surfaces of the first sheet and the second sheet being in contiguous relation, this photographic composition being related in a predetermined manner to the photosensitivity of at least the surface of the first sheet, and maintaining the sheets with their adjacent surfaces in contiguous relation until the photographic composition has performed at least one of its functions.

By such means as assemblage 18 or assemblage 42, it is feasible to carry out this process when desired with little or no special equipment in order to form a photosensitive layer which is adapted to receive a latent image when photoexposed or in order to intermingle at least two photographic compositions shortly before they are used.

When appropriate, the foregoing steps are combined with the additional steps of photoexposing the first sheet, spreading a processing composition in a uniformly thin layer between adjacent surfaces of the first sheet and another sheet, the adjacent surfaces of the first sheet and the other sheet being in contiguous relation, and maintaining the first sheet and the other sheet with their adjacent surfaces in contiguous relation for a predetermined processing period. The other sheet is either the aforementioned second sheet, for example sheet 20 in assemblages 18 and 42, or a third sheet (not shown) the construction of which will now be apparent to those skilled in the art.

The step of photoexposing the first sheet can occur while the first and second sheets remain superposed if one of them is transparent. If both first and second sheets are opaque, they are stripped apart before the step of photoexposing the first sheet occurs.

Further particulars of the process contemplated by the present invention will be apparent from a consideration of the enumerated details of the above-described assemblages.

The term "photosensitive" and other terms of similar import are herein employed in the generic sense to describe materials possessing physical and chemical proper-

ties which enable them to form usable images when photoexposed by actinic radiation.

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 drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic assemblage comprising a sheet and at least a container on a surface thereof, said sheet providing at least a frame, said container including a plurality of wall portions predetermined adjacent sections of which are joined together to define a cavity, and a predetermined quantity of photosensitive silver halide emulsion within said cavity, a first section and a second section of said wall portions defining a mouth communicating with said cavity, said first and second sections being joined, the bonding forces between said predetermined sections being greater than the bonding forces between said first section and said second section, said silver halide emulsion, when opposed compressional forces are applied to said container, separating said first and second sections in order to be ejected from said cavity through said mouth and to be spread in a uniformly thin layer from one edge of said frame toward the opposite edge thereof.

2. A photographic product comprising a deformable container, said container including a plurality of wall portions predetermined adjacent sections of which are joined together to define a cavity and a predetermined quantity of silver halide emulsion within said cavity, a first section and a second section of said wall portions defining a mouth communicating with said cavity, said first and second sections being joined, the bonding forces between said predetermined sections being greater than the bonding forces between said first section and said second section, said silver halide emulsion being capable of separating said first and second sections and of being ejected from said cavity through said mouth when opposed compressional forces are applied to said container.

3. A photographic product comprising a deformable container, said container including a plurality of wall portions predetermined adjacent sections of which are joined together to define a cavity and a predetermined quantity of photographic composition within said cavity, said photographic composition containing a material selected from the class consisting of the silver halide optical sensitizers and the silver halide hypersensitizers, a first section and a second section of said wall portions defining a mouth communicating with said cavity, said first and second sections being joined, the bonding forces between said predetermined sections being greater than the bonding forces between said first section and said second section, said photographic composition separating said first and second sections and being ejected from said cavity through said mouth when opposed compressional forces are applied to said container.

4. The photographic product of claim 3 wherein said photographic composition is a weak solution of a silver halide sensitizing dye.

5. A photographic assemblage comprising a first sheet provided with at least a frame and a second sheet provided with at least an area, said sheets, when so superposed that a surface of said first sheet and a surface of said second sheet are in contiguity, having said frame and said area in aligned relation, at least two containers, one container of said two being secured to at least one of said surfaces, the other container of said two being secured to at least one of said surfaces, said one container being adjacent to said other container at least when said first sheet and said second sheet are so superposed, said one container carrying a first photographic composition therewithin and, upon being subjected to opposed compressional forces, releasing said first composition therefrom for spreading between said surfaces

from one edge of said frame toward at least another edge thereof, said first composition including a photosensitive material selected from the group consisting of the silver salts, the chromates, the ferric salts and the diazonium compounds, said first composition, when spread upon said frame, predetermining the photosensitivity of said frame so that it receives an image of predetermined character when photoexposed, said other container carrying a second photographic composition therewithin and, upon being subjected to opposed compressional forces, releasing said second photographic composition therefrom for spreading between said surfaces from said one edge of said frame toward at least another edge thereof, said second composition, when spread upon said frame, reacting therein to produce a visible print, and means for permitting said one container to be subjected to opposed compressional forces while preventing said other container from being subjected to said opposed compressional forces.

6. The photographic assemblage of claim 5 wherein the last-mentioned means comprises at least a crush-resistant element on one of said sheets, said element providing a portion that is adapted to abut against the other of said sheets, said portion being spaced from the last-mentioned one of said sheets by a distance at least substantially as great as the distance from said last-mentioned one of said sheets of that portion of said container farthest therefrom.

7. A photographic product comprising a deformable container, said container including a plurality of wall portions predetermined adjacent sections of which are joined together to define a cavity and a predetermined quantity of a photosensitive composition selected from the group consisting of the silver salts, the chromates, the ferric salts and the diazonium compounds within said cavity, a first section and a second section of said wall portions defining a mouth communicating with said cavity, said first and second sections being joined, the bonding forces between said predetermined sections being greater than the bonding forces between said first section and said second section, said photosensitive composition separating said first and second sections and being ejected from said cavity through said mouth when opposed compressional forces are applied to said container.

8. The photographic product of claim 7 wherein said photosensitive composition includes a silver halide.

9. A photographic assemblage comprising a sheet, a first elongated container having a rupturable mouth along one of its longitudinal edges, said first container being secured to said sheet, and a second elongated container having a rupturable mouth along one of its longitudinal edges, said second container being secured to said sheet adjacent to said first container, said first container carrying a first photographic composition therewithin and, upon application of opposed compressional forces thereto, releasing said first photographic composition therefrom for spreading on a surface of said sheet, said first composition containing a photosensitive material selected from the group consisting of the silver salts, the chromates, the ferric salts and the diazonium compounds, said second container carrying a second photographic composition therewithin and, upon application of opposed compressional forces thereto, releasing said second photographic composition therefrom for spreading on said first container and on said surface, said second composition performing an additional photographic function.

10. The photographic assemblage of claim 9 wherein the length of said second container is less than the length of said first container.

11. The photographic assemblage of claim 10 wherein a means is provided for permitting the application of opposed compressional forces to said first container while preventing the application of opposed compressional forces to said second container.

12. A photographic assemblage comprising a first sheet provided with at least a frame and a second sheet pro-

vided with at least an area, said sheets, when so superposed that a surface of said first sheet and a surface of said second sheet are in contiguity, having said frame and said area in aligned relation, at least two containers, one container of said two being secured to at least one of said surfaces, the other container of said two being secured to at least one of said surfaces, said one container being adjacent to said other container at least when said first sheet and said second sheet are so superposed, said first container carrying a first photographic composition therewithin and, upon being subjected to opposed compressional forces, releasing said first composition therefrom for spreading between said surfaces from one edge of said frame toward at least another edge thereof, said first composition including as a photosensitive material a silver halide, said first composition, when spread upon said frame, predetermining the photosensitivity of said frame so that it receives an image of predetermined character when photoexposed, said other container carrying a second photographic composition therewithin and, upon being subjected to opposed compressional forces, releasing said second photographic composition therefrom for spreading between said surfaces from said one edge of said frame toward at least another edge thereof, said second composition, when spread upon said frame, reacting therein to produce a visible print, and means for permitting said one container to be subjected to opposed compressional forces while preventing said other container from being subjected to said opposed compressional forces.

13. A photographic assemblage comprising sheets and containers, a first sheet and a second sheet having contiguous surfaces upon being superposed, a first container being secured to at least one of said contiguous surfaces, a second container being secured to at least one of said contiguous surfaces, said first container being adjacent to said second container when said first sheet and said second sheet are so superposed, the contents of said first container including a photosensitive material selected from the group consisting of the silver salts, the chromates, the ferric salts and the diazonium compounds, said contents of said first container, upon being spread between said surfaces, predetermining the photosensitivity of at least one of said surfaces so that it receives an image of predetermined character upon being photoexposed, the contents of said second container, upon being spread between said surfaces, performing at least an additional photographic function, and means for permitting said first container to be subjected to opposed compressional forces while preventing said second container from being subjected to said opposed compressional forces, said means comprising crush-resistant elements positioned at opposite ends of one of said containers on one of said surfaces, each of said elements providing a portion that abuts against the other of said surfaces, the last-mentioned portion being spaced from the surface upon which said each of said elements is positioned by a distance at least substantially as great as the distance from the last-mentioned surface of that portion of said container farthest from said last-mentioned surface.

14. A photographic assemblage comprising sheets and containers, a first sheet and a second sheet having contiguous surfaces upon being superposed, a first container and a second container being secured to at least one of said contiguous surfaces, said first container being adjacent to said second container when said first sheet and said second sheet are so superposed, the contents of said first container including a sensitizing agent selected from the class consisting of the silver halide optical sensitizers and the silver halide hypersensitizers, said contents of said first container, upon being spread between said surfaces, predetermining the photosensitivity of at least one of said surfaces so that it receives an image of predeter-

13

mined character upon being photoexposed, the contents of the second container, upon being spread between said surfaces, performing at least an additional photographic function, and means for permitting said first container to be subjected to opposed compressional forces while preventing said second container from being subjected to said opposed compressional forces, said means comprising crush-resistant elements positioned at opposite ends of one of said containers on one of said surfaces, each of said elements providing a portion that abuts against the other of said surfaces, the last-mentioned portion being spaced from the surface upon which said each of said elements is positioned by a distance at least substantially as great as the distance from the last-mentioned surface of that portion of said container farthest from said last-mentioned surface.

15. A photographic assemblage comprising a sheet, a first elongated container having a rupturable mouth along one of its longitudinal edges, said first container being secured to said sheet, and a second elongated container having a rupturable mouth along one of its longitudinal edges, said second container being secured to said sheet adjacent to said first container, the rupturable mouth of said second container overlapping the other of the longitudinal edges of said first container, said first container, upon application of opposed compressional forces thereto, releasing its contents for spreading on a surface of said first sheet, said contents of said one container including a material selected from the class consisting of

14

the silver salts, the chromates, the ferric salts and the diazonium compounds, said second container, upon application of opposed compressional forces thereto, releasing its contents for spreading on said first container and on said surface, means for permitting the application by a pair of pressure-applying rollers of opposed compressional forces to said first container while preventing the application of opposed compressional forces to said second container, said means including at least one crush-resistant element secured to said surface, said crush-resistant element having a portion which is spaced from said surface by a distance at least substantially as great as the distance from said surface of that portion of said second container farthest from said surface.

References Cited in the file of this patent

UNITED STATES PATENTS

2,209,914	Gerber et al. -----	July 30, 1940
2,269,169	Van Der Hoef et al. ----	Jan. 6, 1942
2,500,421	Land -----	Mar. 14, 1950
2,520,641	Land -----	Aug. 29, 1950
2,543,181	Land -----	Feb. 27, 1951
2,603,565	Land -----	July 15, 1952
2,606,121	Peters -----	Aug. 5, 1952
2,644,755	Wolff et al. -----	July 7, 1953

OTHER REFERENCES

Wall: Photographic Emulsions; pub. American Photographic Pub. Co., Boston, 1929, pages 159 and 188.