

July 11, 1961

E. H. LAND

2,992,102

PHOTOGRAPHIC PROCESSES AND PRODUCTS

Filed March 29, 1955

2 Sheets-Sheet 1

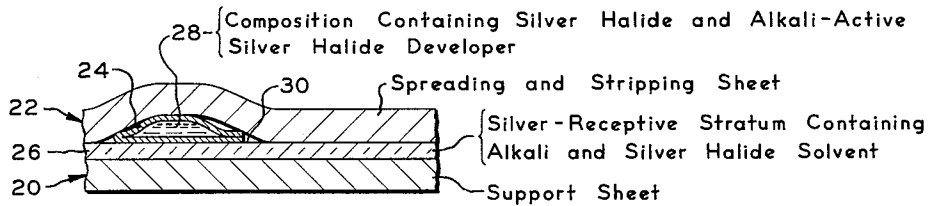


FIG. 1

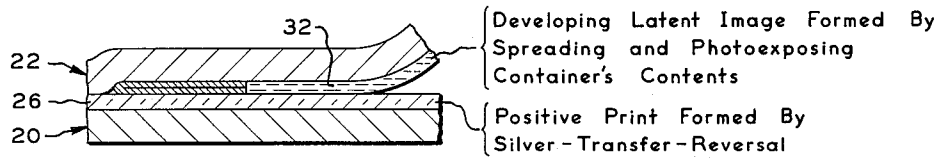


FIG. 2

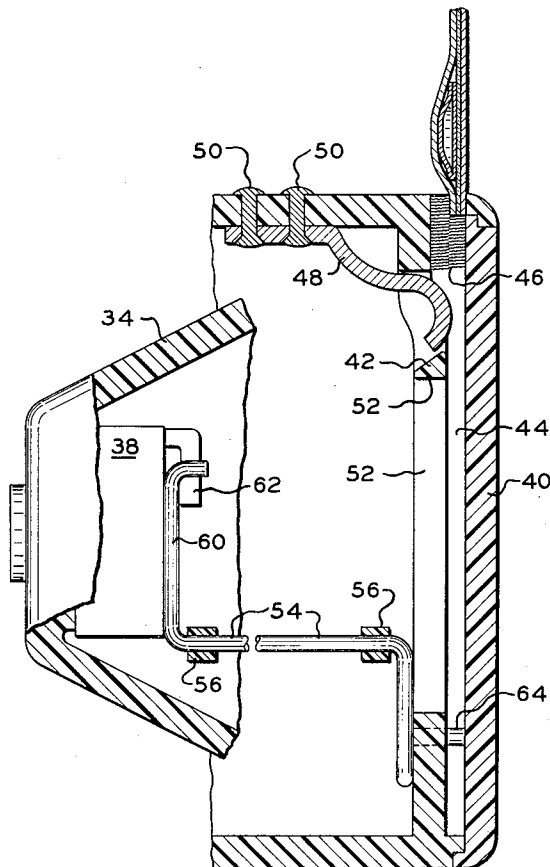


FIG. 3

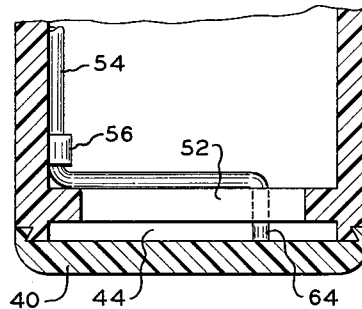


FIG. 4

INVENTOR

Edwin H. Land

Brown and Mellicka
and
BY *Gerald Altman*
ATTORNEYS

July 11, 1961

E. H. LAND

2,992,102

PHOTOGRAPHIC PROCESSES AND PRODUCTS

Filed March 29, 1955

2 Sheets-Sheet 2

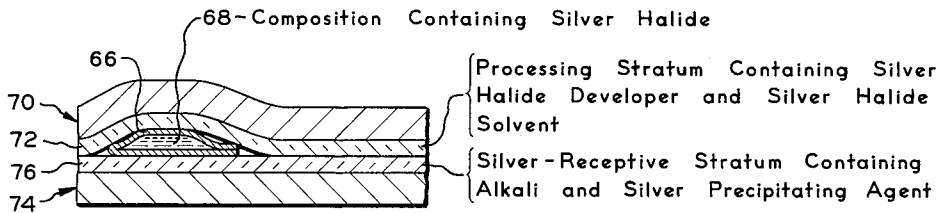


FIG. 5

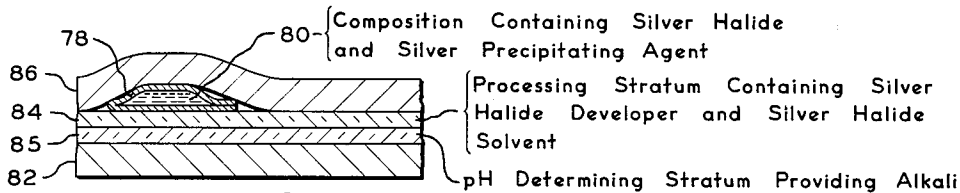


FIG. 6

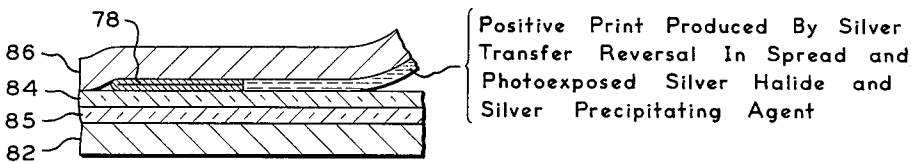


FIG. 7

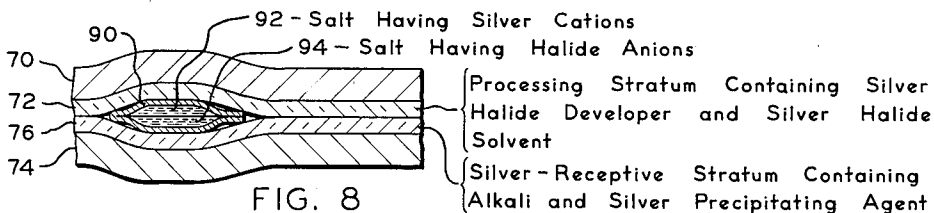


FIG. 8

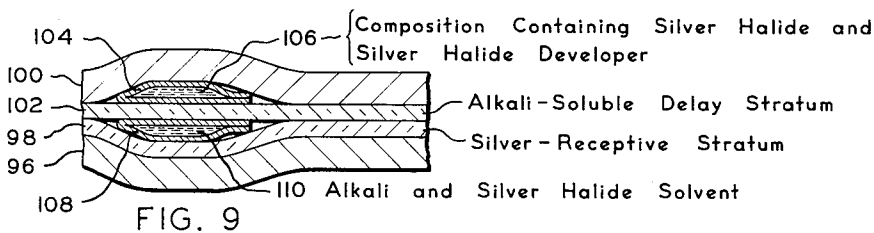


FIG. 9

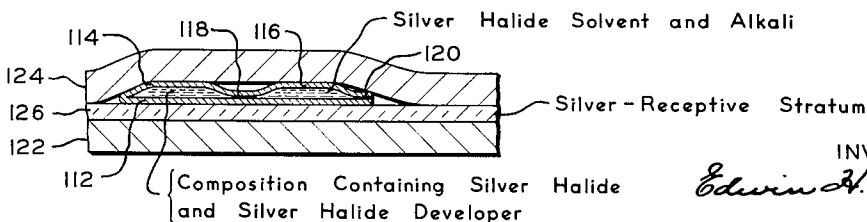


FIG. 10

INVENTOR

Edwin H. Land

BY *Brown and McKelvey*
and
Gerald Altman
ATTORNEYS

1

2,992,102

PHOTOGRAPHIC PROCESSES AND PRODUCTS
Edwin H. Land, Cambridge, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

Filed Mar. 29, 1955, Ser. No. 497,634
19 Claims. (Cl. 96—29)

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

This invention contemplates the spreading of a photosensitive composition in the presence of a developer to provide a stratum which, when photoexposed, shortly following its formation, receives a latent image that develops spontaneously. In one of its great variety of novel applications, this invention may be embodied in a product, requiring little or no shielding from environmental light, which comprises two sheets and a container of photosensitive composition to be spread between them in the presence of a developer. In this product, the developer may be carried in a variety of ways, for example, dispersed in dry condition on one of the sheets. Within the exposure chamber of a camera, the composition may be spread between the sheets to form a photosensitive stratum which, when photoexposed either through one of the sheets or after their separation, receives a latent image from which a useful print is formed without further manipulation or treatment.

This invention is applicable to a variety of processes involving the formation of latent images in dispersions of heavy metal salts such as the noble metal salts, particularly the silver halides. It is particularly applicable to processes of the silver transfer-reversal type. In one such process, a silver halide composition is spread from a container, in the presence of processing reagents including a silver halide developer and a silver halide solvent, between the adjacent surfaces of a pair of superposed sheets and is photoexposed immediately thereafter. The reagents develop exposed silver halide to silver and react with unreduced silver halide to form a soluble silver complex which, when reduced to silver on one of the sheets, form a positive print. In practice, the reagents are made available at any of a variety of locations on the sheets or in the container.

Accordingly, the primary objects of this invention are: to provide processes and products which involve forming a photosensitive stratum from a heavy metal salt in a reducing environment, and photo-exposing the stratum to produce a latent image from which a visible image spontaneously forms in terms of reduced heavy metal; and, more particularly, to provide processes and products of the foregoing type in which the heavy metal salt is silver halide.

Other objects of the present invention are: to provide processes and products involving the spreading of a silver halide composition in the presence of a silver halide developer and a silver halide solvent between two sheets; and to provide processes and products of the foregoing type involving the photo exposing of the silver halide composition immediately or shortly after its spreading to provide a latent image from which a positive print forms.

Further objects of the present invention are: to provide a film unit comprising photographic elements including a container means and two sheets, and carrying photographic materials including a silver halide composition, an alkali-active, silver halide developer, a silver halide solvent and an alkali, the silver halide composition being carried in the container means for spreading between the sheets, the silver halide developer and the alkali being carried apart from each other and the silver halide solvent

2

being carried apart from the silver halide composition, the silver halide developer, the alkali and the silver halide solvent being present when the silver halide composition is spread; to provide a film unit of the foregoing type wherein the silver halide developer is mixed with the silver halide composition and the alkali is carried by one of the sheets; to provide a film unit of the foregoing type wherein the silver halide developer, the silver halide solvent and the alkali are carried by one of the sheets and a silver-receptive stratum is carried by the other of the sheets; to provide a film unit of the foregoing type wherein a silver precipitating agent is mixed with the silver halide composition and the silver halide developer and the silver halide solvent are carried by one of the sheets; to provide a film unit of the foregoing type wherein the silver halide composition is divided into components including a salt having silver cations and a salt having halide anions, the container means providing two compartments for keeping the components apart until used; and to provide a film unit of the foregoing type wherein an alkali-soluble stratum is interposed between the sheets to keep the silver halide composition and the alkali apart for a predetermined delay period after spreading.

Still other objects are: to provide a photographic product comprising a deformable container which defines a cavity having a mouth through which the contents of the container are ejected when the container is compressed, and a silver halide composition and an alkali-active silver halide developer mixed within the container; to provide a photographic product comprising a deformable container which includes a plurality of wall portions, at least one of which is flexible, defining a cavity having a mouth through which the contents of the container are ejected when the container is compressed, and a silver halide composition and a silver precipitating agent mixed within the cavity; to provide container means providing two cavities, one of which carries a silver halide composition and the other of which carries at least one of the components necessary to provide the silver halide composition with a reducing environment; and to provide container means providing two cavities, one of which carries a salt having silver cations and the other of which carries a salt having halide anions.

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 and order 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 drawings wherein:

FIGURE 1 is an exaggerated sectional view of a film unit designed to effectuate a process of the silver transfer-reversal type in accordance with the present invention;

FIG. 2 is an exaggerated sectional view of the film unit of FIG. 1 in operation;

FIG. 3 is an enlarged sectional elevation, partially broken away, of a camera designed to process the film units of FIG. 1 and of the other figures referred to below;

FIG. 4 is a sectional view taken substantially along the line 4—4 of FIG. 3; and

FIGS. 5, 6, 7, 8, 9 and 10 are exaggerated sectional views of other film units designed to effectuate other processes of the silver transfer-reversal type in accordance with the present invention.

Generally, each of the film units herein specifically de-

scribed comprises two sheets and a quantity of at least one of the components of a silver halide composition to be spread between them in the presence of reagents, including a silver halide developer and a silver halide solvent, for effecting silver-transfer-reversal. In practice, the reagents are made available at any of a variety of locations in the film unit in such manner that the developer and the solvent do not act on the silver halide composition until it has been spread. In other words, the developer and/or solvent either are kept apart from the silver halide composition or are kept together with the silver halide composition in inactive condition. For example, either or both the developer and the solvent may be dispersed in dry condition on one or both of the sheets so as not to contact the silver halide composition until spread. Or an alkali-active developer may be mixed with the silver halide composition and kept in a nonalkaline environment until spread in the presence of an alkali dispersed in dry condition on one or both of the sheets. Some or all of the silver halide composition and the various reagents may be carried in one or more compartments provided by one or more containers. For example, two compartments may be provided to carry separately the silver halide composition and one or more of the components necessary to provide it with a reducing environment. Or two compartments may be provided to carry separately silver halide components, such as a salt having silver cations, and a salt having halide anions, which do not form a photosensitive compound until mixed. A silver precipitating agent may be dispersed on whichever sheet the transfer image is to form or may be mixed with the silver halide composition when the transfer image is to form in the photosensitive stratum itself. It is apparent then that the chemical organization within a film unit of the present invention may be varied as desired in response to a wide variety of requirements.

Ordinarily, it is desired that photoexposure occur immediately after, say within one second after, spreading in order to avoid desensitization of the photosensitive material by the developer. However, when a short delay between spreading and photoexposing the silver halide composition is desired, development may be postponed, for example, by interposing, between the photosensitive stratum and one of the components necessary to the provision of a reducing environment, a temporary barrier such as an alkali-soluble stratum that dissolves in the presence of the reagents after a predetermined delay.

Generally, the film unit of FIG. 1 comprises a pair of sheets 20 and 22 adapted to be superposed with their inner surfaces in contiguous relation, that is, with their inner surfaces either close to or in contact with each other. Secured to sheet 20 is a container 24 carrying, in predetermined quantity, a nonalkaline aqueous composition 28 containing a silver halide salt and a silver halide developer that is active only in alkaline solution. The inner surface of sheet 20 is coated with a silver-receptive stratum 26 in which are dispersed an alkali, a silver halide solvent and a silver precipitating agent. Container 24, when deformed by opposed compressional forces, releases composition 28 through a rupturable mouth 30 for spreading between the sheets to form a photosensitive stratum 32 (FIG. 2). This stratum, when photoexposed immediately after its formation, receives a latent image from which a positive print is formed in stratum 26 as follows. The developer from container 24 activated by the alkali from stratum 26 reduces silver halide in stratum 32 to silver, and the silver halide solvent from stratum 26 reacts with unreduced silver halide to form complex silver salts which diffuse to stratum 26 where, in the presence of unexhausted silver halide developer and the silver precipitating agent, they are reduced to silver. At the end of a predetermined period following the spreading of composition 28, sheet 22 together with stratum 32 is stripped from sheet 20 to make available

the print formed in stratum 26. Or under the proper conditions, the print, at the end of this period, may be used without stripping. The duration of this period depends upon the specific properties of the material used, as will be apparent to persons skilled in the art.

In one form, composition 28, a gel which is fluid enough under ambient conditions to be readily spread, is prepared by stirring an aqueous solution of a silver halide developer into a ripened photosensitive silver halide emulsion.

In one such 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, for example, gelatin, agar, albumen, casein, collodion, a cellulosic such as a carboxymethyl cellulose, a vinyl polymer such as a polyvinyl alcohol, or a linear polyamide such as polyhexamethylene adipamide (6, 6 nylon). Examples of specific formulations of conventional emulsions suitable for such use are described in T. T. Baker, *Photographic Emulsion Technique*, American Photographic Publishing Company, Boston, 1948, chapter IV.

The developer is alkali active, i.e., active only in alkaline solution, so that, in the absence of an alkali, it has no developing effect on the silver halide emulsion in the nonalkaline environment provided by container 24. Examples of developers of this type are pyrogallol, hydroquinone, metol, amidol, p-aminophenol and glycine. An antioxidant for the developer may be provided. For example, sodium sulfite may be carried by stratum 26 or ascorbic acid by container 24.

Silver-receptive stratum 26, in one form, is prepared from an organic plastic vehicle such as sodium carboxymethyl cellulose into which has been stirred an aqueous solution of: a silver halide solvent, for example, a silver complexing agent such as sodium thiosulfate; a silver precipitating agent, for example, one or more of the zinc, cadmium and lead sulfides and selenides; and an alkali, for example, a carbonate such as sodium carbonate, a borate such as borax, or a phosphate such as dibasic sodium phosphate.

It will be noted that the alkalies here used are relatively weak. Such weak alkalies should be used when the alkali is made available in dry condition on one of the sheets, particularly when in the presence of the silver halide solvent. If a strong alkali, for example, a hydroxide such as sodium hydroxide, is here used, unless spreading is effected immediately after the alkali is disposed in stratum 26, the alkali should be dispersed on the inner surface of sheet 22 or should be carried in a container apart from the developer in a manner to be described below.

The materials of which the elements of the product of FIG. 1 are composed can be so constituted that the adhesive forces between composition 28 and stratum 26 are less than those between the composition and sheet 22, this arrangement being such as to facilitate stripping of stratum 32 from stratum 26 at the end of a predetermined processing period. One of the sheets, for example sheet 20, may be 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. One or both of the sheets may be composed of glass or 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. When sheet 20 is composed of such a plastic material, in order to assure good adhesion between it and stratum 32, it is treated, for example, with a mixture of gelatin and cellulose nitrate. Either or both of the sheets is transparent for transmitting actinic radiation to form a latent image in stratum 32 while the sheets are maintained in superposed relation.

The product of FIG. 1 before being used may be han-

died in environmental light by virtue of the fact that the only photosensitive material carried by it is confined within container 24, which is light-tight and hermetically sealed. This container, in one form, is 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- and liquid-imperious material, for example, a metal foil such as silver, lead or nickel foil. The inner ply is composed of a 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% of nitrocellulose and approximately 5% dibutyl sebacate is particularly satisfactory. At opposite end portions of the container, the two folds of the inner ply are sealed to each other by the application of heat and pressure. Those two sections of the two folds defining mouth 30 are bonded together by a strip of adhesive so constituted that the bonding forces between it and the inner ply are less than the cohesive forces between end portions of the inner ply that are sealed together. A satisfactory strip may be composed, for example, of ethyl cellulose or 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.

Example

In one specific form of the film unit of FIGS. 1 and 2: composition 28 was prepared by heating 10 cc. of a moderately high speed gelatino iodobromide emulsion to the liquid state and stirring into it a solution of 0.19 g. of amidol in 1 cc. of water. Approximately 0.7 cc. of the resulting mixture was injected into container 24 from a syringe. Stratum 26 was prepared by treating a silver-receptive stratum containing a silver precipitating agent of the type above described. This stratum, supported on a sheet of baryta paper, was dipped for approximately 20 seconds into an aqueous solution containing, by total weight, 4.6% of sodium carbonate, 5.7% of sodium sulfite and 3.6% of sodium thiosulfate. The excess solution was doctored from the sheet by a stirring rod and the sheet was thoroughly dried under heat. The film unit was drawn between a pair of steel rollers and the resulting photosensitive stratum was exposed within one second after being formed. Then the sheets, after remaining superposed for a period of 120 seconds, were stripped apart to display in stratum 26 a positive print.

The film unit of FIG. 1 is shown as comprising a container of a composition containing silver halide salt, an alkali-active silver halide developer, and a stratum carrying an alkali, a silver halide solvent and a silver precipitating agent. It is to be understood that these materials may be distributed as desired on either sheet or in the container, provided that the silver halide salts in the container be kept from contact with the silver halide solvent and that the alkali-active silver halide developer be kept from contact with the alkali. It is to be understood also that no silver halide solvent need be present if it is desired merely to develop a latent image in stratum 32 rather than to effectuate silver-transfer-reveal. Alternative embodiments of the present invention will be described following a description of the camera of FIGS. 3 and 4 which is designed to process the film units of FIG. 1 and of FIGS. 5 through 9 to be discussed below.

The camera of FIGS. 3 and 4 is of the type disclosed in my copending patent applications Serial No. 463,848, filed October 22, 1954, now U.S. Patent 2,819,662 and

Serial No. 463,886, filed October 22, 1954, now U.S. Patent 2,740,343. In response to a single movement of the film unit of FIG. 1 into exposure position within the camera, composition 28 is spread between sheets 20 and 22 and stratum 32, thus formed, is photoexposed to receive a latent image from which a positive image forms in stratum 26 without further manipulation of the film unit or treatment of the stratum. The camera comprises a housing 34 at the front of which is a lens and shutter 38 and at the rear of which is a section 40 detachable from the remainder of the housing to provide access, when desired, to its interior. Within the camera, adjacent to section 40, is a cross web 42 which cooperates with section 40 to guide the film unit into the focal region 44 of the lens. The film unit is introduced to this focal region through a lighttight passage 46. A pressure-applying element in the form of a resilient sheet metal stamping 48, riveted to housing 34 at 50, projects through an opening in cross web 42 to present a curved surface that cooperates with section 40 to spread composition 28 from container 24 between sheets 20 and 22 as the film unit moves into focal region 44. Cross web 42 is provided with a rectangular aperture 52 through which actinic radiation is transmitted from lens 38 when the film unit comes to rest. The opening of shutter 38 is automatically effected by a shaped rod 54 rotatably mounted in housing 34 at 56 and 58. This rod is provided with an arm 60 bearing against an actuating lever 62 of shutter 38, and an arm 64 projecting into the exposure region so as to be contacted by the forward edge of the film unit at the end of its movement into the exposure region. It will be observed in FIG. 3 that before the forward edge of the film unit comes to rest at its lowermost position, it abuts against arm 64 to cause rod 54 to rotate and arm 60 to actuate shutter 38. Following photoexposure, the film unit is permitted to remain in the camera for a predetermined processing period. At the end of this period, it is removed from the camera to permit the photosensitive and image-receptive elements to be stripped apart.

Another embodiment of the present invention appears in FIG. 5 as a film unit comprising a container 66 carrying a predetermined quantity of silver halide composition 68, a sheet 70 coated with a processing stratum 72 and a sheet 74 coated with a silver-receptive stratum 76. Processing stratum 72 contains a silver halide developer and a silver halide solvent. Silver-receptive stratum 76 contains an alkali, such as sodium hydroxide, and silver precipitating nuclei, such as colloidal heavy metals, metal sulfides and selenides, thiooxalates and thioacetamides, dispersed in an inorganic vehicle composed for example, of a siliceous material such as silica aerogel.

The silver halide developer, the silver halide solvent and the alkali of stratum 72 are similar to their counterparts in the film unit of FIG. 1. The materials of which stratum 76 is composed are described in my U.S. Letters Patents Nos. 2,698,237 and 2,698,245, issued on December 28, 1954. The stratum formed from silver halide composition 68 between strata 72 and 76, when exposed immediately after being formed, receives a latent image from which a positive print develops spontaneously in stratum 76.

A further embodiment of the present invention appears in FIG. 6 as a film unit comprising: a container 78 carrying, in predetermined quantity, a composition 80 containing a silver halide salt and a silver precipitating agent; a sheet 82 coated with a processing stratum 84 containing a silver halide developer and a silver halide solvent and a pH determining stratum 85 providing an alkali, for example, a carbonate such as sodium carbonate, a borate such as borax, or a phosphate such as dibasic sodium phosphate; and a sheet 86 for spreading the composition on the surface of stratum 84. Composition 80, for example, may be prepared by stirring a silver precipitating agent, for example, one or more of the zinc, cadmium and lead sulfides and selenides, into a silver halide emul-

sion of the type described in connection with the embodiment of FIG. 1. Container 78, when deformed by opposed compressional forces, releases composition 80 for spreading between the sheets. In consequence, as shown in FIG. 7, a photosensitive stratum 88 is formed which, upon being photoexposed, receives a latent image from which, by silver-transfer-reversal, a positive print is produced in situ.

It is often desirable, for example, when storage of a product embodying the present invention for a prolonged period is expected, to separate the components of the silver halide composition until used. The film unit of FIG. 8 is designed for such prolonged storage. It comprises a container 90 divided into two compartments 92 and 94 carrying components which, when mixed, form a photosensitive silver halide composition. For example, compartment 92 contains a salt having a silver cations, such as silver nitrate, and compartment 94 contains a salt having halide anions, such as sodium chloride, bromide or iodide, or a mixture thereof. The sheets between which the content of compartments 92 and 94 are to be spread are similar in all respects to their counterparts in the film unit of FIG. 5 and are designated by the corresponding numerals. Container 90, when deformed by opposed compressional forces, releases the contents of compartments 92 and 94 for spreading between the sheets where they react to form a photosensitive silver halide stratum. This stratum, upon photoexposure, receives a latent image from which, in the presence of processing stratum 72, a positive print is formed in silver-receptive stratum 76.

In modifications of the film unit of FIG. 8, one of the compartments of container 90 may carry a photosensitive composition or one of its components, and the other of the compartments of container 90 may carry a processing composition or one of its components, the remaining components of the photosensitive composition and the processing composition being distributed in strata 72 and 76 as will now be apparent to persons skilled in the art. Alternatively, container 90 may provide but one compartment containing one of the components of a photosensitive composition, for example, a salt having halide anions, and the other components of the photosensitive composition, for example, including a salt having silver cations, may be distributed in either stratum 72 or 76.

When a short delay between spreading and photoexposing the silver halide composition is desired, it is possible to postpone the application of the silver halide developer to the silver halide composition. The film unit of FIG. 9 is designed for such a time delay. It comprises a sheet 96 coated with a silver-receptive stratum 98 and a spreading and stripping sheet 100. Interposed between the sheets are an alkali-soluble stratum 102, a container 104 of a composition 106 containing a silver halide salt and a silver halide developer, and a container 108 of a composition 110 containing an alkali and a silver halide solvent. Composition 106 is to be spread between stratum 102 and sheet 100 and composition 110 is to be spread between stratum 102 and stratum 98. Stratum 102, for example, is composed of a material that dissolves or becomes permeable in solution. One such material that dissolves rapidly in alkaline solution is cellulose acetate hydrogen phthalate. Containers 104 and 108, when simultaneously deformed by opposed compressional forces, release their contents to form a photosensitive stratum designed to be photoexposed shortly after its formation, and to form a processing stratum designed to contact the photosensitive stratum after dissolving stratum 102.

The film unit of FIG. 10 illustrates an alternative two-compartment container that permits the silver halide composition to be mixed with some or all of the processing materials before being spread. Here, mixing within the container eliminates turbulence among the contained materials before spreading. This container, designated by

112, is divided into two compartments 114 and 116, which are joined by a mouth closed by a rupturable seal 118. Compartment 116 is provided with a discharge mouth closed by a rupturable seal 120. In the form shown, compartment 114 carries a silver halide composition and an alkali-active silver halide developer, and compartment 116 contains an alkali and a silver halide solvent. When opposed compressional forces are applied to compartment 114 but not to compartment 116, as when compartment 114 advances first between a pair of pressure-applying members, rupturable seal 118 is broken and the contents of the two compartments are mixed. Continued application of opposed compressional forces, as when compartment 116 advances next between the pair of pressure-applying members, causes the mixed contents to rupture seal 120 and to be discharged between a pair of sheets 122 and 124 one of which is provided with a silver-receptive stratum 126. Immediately after spreading is effected, the resulting photosensitive stratum is photoexposed to provide a latent image from which a positive print is spontaneously formed in silver-receptive stratum 126.

The present invention thus contemplates the spreading and photoexposing of a silver halide composition in the presence of a developer to produce a latent image from which a visible print is spontaneously produced without additional manipulation or treatment. The materials so used may be handled without precaution against light until the moment the silver halide composition is spread, for example, within the lighttight exposure chamber of a camera.

Since certain changes may be made in the above process and 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 photographic assemblage comprising a deformable container, a first sheet, and a second sheet, a fluid photosensitive silver halide composition in said container, said first sheet and said second sheet having contiguous surfaces upon being superposed, said container being secured to at least one of said contiguous surfaces and providing at least one cavity having a rupturable mount positioned between said contiguous surfaces through which said composition is ejected when said container is compressed, and processing materials in said container and on at least one of said first and second sheets, said processing materials including an alkali-active silver halide developer, an alkali and a silver halide solvent, at least one of said silver halide developer and said alkali being in said container, the remainder of said materials including said silver halide solvent being coated on at least one of said first and second sheets.

2. The photographic assemblage of claim 1 wherein said container provides two cavities, said composition being in one of said two cavities, at least one of said materials being in the other of said two cavities, said two cavities being adapted to be opened at substantially the same time.

3. A photographic assemblage comprising a deformable container, a first sheet, a delay stratum interposed between said first sheet and said container, a fluid photosensitive silver halide composition in said container, and processing materials in said container and on said first sheet, said processing materials including a silver halide developer in inactive condition and an activating agent for placing said silver halide developer in active condition, said container providing a rupturable mouth through which said composition is ejected for spreading in a thin layer on said delay stratum when said container is compressed, said delay stratum being normally impenetrable to said activating agent, said delay stratum being rendered penetrable to said activating agent when

permeated by said composition, at least one of said silver halide developer and said activating agent being positioned between said delay stratum and said first sheet whereby said activating agent and said developer are prevented from intermingling at once with said composition by said delay stratum for a predetermined period following spreading of said composition.

4. A photographic assemblage comprising a deformable container, a first sheet, a second sheet and a delay stratum interposed between said first sheet and said second sheet, an aqueous photosensitive silver halide composition in said container, said container providing a rupturable mouth positioned between said first sheet and said delay stratum through which said composition is ejected from said container to be spread in a thin layer between said first sheet and said delay stratum, an alkali-active silver halide developer in said silver halide composition, and an alkali between said delay stratum and said second sheet, said delay stratum being soluble in aqueous alkali whereby, when said composition is spread between said first sheet and said delay stratum in a layer, said alkali is prevented from intermingling with said layer by said delay stratum for a predetermined delay period during which water from said composition permeates said delay stratum and dissolves said alkali and in turn said delay stratum.

5. A photographic assemblage comprising a deformable container, a first sheet, a second sheet and a delay stratum interposed between said first sheet and said second sheet, an aqueous photosensitive silver halide composition in said container, said container providing a rupturable mouth positioned between said first sheet and said delay stratum through which said composition is ejected from said container to be spread in a thin layer between said first sheet and said delay stratum, an alkali-active silver halide developer mixed with said silver halide composition, an alkali between said delay stratum and said second sheet, silver precipitating nuclei on said second sheet, and a silver halide solvent on one of said first sheet and said second sheet, said delay stratum being soluble in aqueous alkali whereby, when said composition is spread between said first sheet and said delay stratum in a layer, said alkali is prevented from intermingling with said layer by said delay stratum for a predetermined period during which water from said composition permeates said delay stratum and dissolves said alkali and in turn said delay stratum.

6. 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 first cavity and a second cavity, a predetermined quantity of a salt having silver cations within said first cavity, and a predetermined quantity of a salt having halide anions within said second cavity, at least a first section and a second section of said wall portions defining at least a mouth communicating with said first cavity and said second cavity, said first section and said second section being joined, the contents of said first cavity and of said second cavity being capable of separating said first section and said second section and of being ejected from said cavity through said mouth when opposed compressional forces are applied to said container.

7. A photographic process comprising the steps of creating a photosensitive stratum by spreading between two sheets, at least one of which is sufficiently transparent to permit photoexposure therethrough, a fluid composition containing first materials, said first materials being intermingled with second materials including processing reagents for photosensitive silver halide salt as said fluid composition is spread between said sheets, one of said first materials and said second materials including a salt having silver cations, the other of said first materials and said second materials including a salt having halide anions, said processing reagents including

a silver halide solvent and a silver halide developer for silver halide salt in condition to develop the photosensitive stratum formed by the reaction of said salt having silver cations and said salt having halide anions, said silver halide solvent being maintained apart from said salt having silver cations before said spreading, and immediately thereafter photoexposing through said one of said sheets said photosensitive stratum to form therein a latent image from which a positive image is formed spontaneously, said positive image being formed by reacting said silver halide developer with exposed silver halide salt to reduce said exposed silver halide to silver in said photosensitive stratum, reacting said silver halide solvent with silver halide salt unreduced by said silver halide developer to form a complex silver salt, and converting said complex silver salt to silver to form said positive image.

8. A photographic process comprising the steps of creating a photosensitive stratum by spreading between two sheets, at least one of which is sufficiently transparent to permit photoexposure therethrough, a fluid composition containing first materials including a photosensitive silver halide salt capable of having a latent image formed therein by photoexposure and an alkali-active silver halide developer, said first materials being intermingled with second materials as said fluid composition is spread between said sheets, to provide a plurality of reagents including an alkali capable of activating said silver halide developer for the purpose of developing said photosensitive stratum, and immediately thereafter photoexposing through said one of said sheets said photosensitive stratum to form therein a latent image from which a visible image is formed spontaneously.

9. A photographic process comprising the steps of forming a photosensitive stratum by spreading between two sheets, at least one of which is sufficiently transparent to permit photoexposure therethrough, a first group of materials including a dispersion of a photosensitive silver halide salt, said first group of materials being intermingled with a second group of materials as said first group of materials is spread, to provide a plurality of reagents including a silver halide developer and a silver halide solvent, said silver halide solvent being maintained apart from said photosensitive silver halide salt before said spreading, and immediately thereafter photoexposing through said one of said sheets said photosensitive stratum to form therein a latent image from which a positive image is formed spontaneously, said positive image being formed by reacting said silver halide developer with exposed silver halide salt to reduce said exposed silver halide to silver in said photosensitive stratum, reacting said silver halide solvent with silver halide salt unreduced by said silver halide developer to form a complex salt, and converting said complex silver salt to silver to form said positive image.

10. The process of claim 9 wherein said silver halide developer is one of said first group of materials.

11. The process of claim 9 wherein an alkali is present on one of said sheets before said spreading is effected.

12. The process of claim 9 wherein a silver precipitating agent is one of said first group of materials.

13. The process of claim 9 wherein a silver precipitating agent is present on one of said sheets before said spreading is effected.

14. A photographic process comprising the steps of forming a photosensitive stratum by spreading between two sheets, at least one of which is sufficiently transparent to permit photoexposure therethrough, a first group of materials including a dispersion of a photosensitive silver halide salt and an alkali-active silver halide developer, said first group of materials being intermingled with a second group of materials as said first group of materials is spread between said sheets, said second group of materials including an alkali and a

silver halide solvent, and immediately thereafter photoexposing through said one of said sheets said photosensitive stratum to form therein a latent image from which a positive image is formed spontaneously, said positive image being formed by reacting said silver halide developer with exposed silver halide salt to reduce said exposed silver halide to silver in said photosensitive stratum, reacting said silver halide solvent with silver halide salt unreduced by said silver halide developer to form a complex silver salt, and converting said complex silver salt to silver to form said positive image.

15. A photographic process comprising the steps of forming a photosensitive stratum on a support by discharging from a lighttight container a first group of materials, including a photosensitive silver halide salt, spreading said first group of materials in a layer upon said support in order to intermingle said first group of materials with a second group of materials, to provide a plurality of reagents including a silver halide developer in condition to develop said photosensitive stratum, and immediately thereafter photoexposing said photosensitive stratum to form therein a latent image from which a visible image is formed spontaneously.

16. The process of claim 15 wherein said silver halide developer is one of said first group of materials.

17. The process of claim 15 wherein an alkali is present on said support before said spreading is effected.

18. The process of spreading a first group of materials in a thin layer between the closely adjacent surfaces of a pair of superposed sheets, at least one of said sheets being sufficiently transparent to permit photoexposure therethrough, at least one of said surfaces having distributed thereupon a second group of materials, said first group of materials including a photosensitive silver halide salt, one of said first group of materials and said second group of materials containing an alkali-active silver halide developer, the other of said first group of materials and said second group of materials containing an alkali, one of said first group of materials and said second group of materials containing a silver halide solvent, said silver halide solvent being maintained apart from said photosensitive silver halide salt before said spreading, and immediately thereafter photoexposing through said one of said sheets said silver halide salt to form therein a latent image from which a positive image is formed spontaneously, said positive image being formed by reacting said silver halide developer with exposed silver halide salt to reduce said exposed silver halide to silver in said photosensitive stratum, reacting said silver halide solvent with silver halide salt unreduced by said silver halide developer to form a complex silver salt, and converting said complex silver salt to silver to form said positive image.

19. The process of spreading a first group of materials

in a thin layer between the closely adjacent surfaces of a pair of superposed sheets, at least one of said sheets being sufficiently transparent to permit photoexposure therethrough, at least one of said surfaces having distributed thereupon a second group of materials, said first group of materials including a photosensitive silver halide salt, one of said first group of materials and said second group of materials containing an alkali-active silver halide developer, the other of said first group of materials and said second group of materials containing an alkali, one of said first group of materials and said second group of materials containing a silver halide solvent, said silver halide solvent being maintained apart from said photosensitive silver halide salt before said spreading, immediately thereafter photoexposing through said one of said sheets said silver halide salt to provide therein a latent image, said spreading being accomplished in such a manner that said alkali and said silver halide developer are initially on opposite sides of an alkali-soluble stratum, and allowing said alkali to dissolve said alkali-soluble stratum, whereby said alkali-soluble stratum introduces a time delay between said spreading and the steps of reacting said silver halide developer with exposed silver halide salt to reduce said exposed silver halide to silver in said photosensitive stratum, reacting said silver halide solvent with silver halide salt unreduced by said silver halide developer to form a complex silver salt, and converting said complex silver salt to silver to form a positive image.

References Cited in the file of this patent

UNITED STATES PATENTS

	7,458	Whipple	June 25, 1850
	742,405	Eichengrün et al.	Oct. 27, 1903
35	786,536	Thornton et al.	Apr. 4, 1905
	1,503,595	Mees	Aug. 5, 1924
	2,214,446	Albers et al.	Sept. 10, 1940
	2,269,169	Van Der Hoef	Jan. 6, 1942
40	2,315,966	Knott	Apr. 6, 1943
	2,352,014	Rott	June 20, 1944
	2,543,181	Land	Feb. 27, 1951
	2,600,064	McCune	June 10, 1952
	2,627,459	Land	Feb. 3, 1953
45	2,740,717	Yutzy et al.	Apr. 3, 1956
	2,819,662	Land	Jan. 14, 1958

FOREIGN PATENTS

	59,365	Netherlands	Dec. 16, 1946
50	814,449	France	Mar. 15, 1937

OTHER REFERENCES

Levenson: Journal of Scientific Instruments, vol. 27, 1950, pp. 170 and 171. Copy in Sci. Lib.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,992,102

July 11, 1961

Edwin H. Land

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 44, for "form" read -- forms --; column 3, line 53, for "containtr" read -- container --; column 4, line 38, for "cadminum" read -- cadmium --; column 5, line 68, for "-reveral" read -- -reversal --; column 7, line 17, strike out "a", second occurrence; line 21, for "content" read -- contents --; column 8, line 46, for "mount" read -- mouth --; column 10, line 55, after "complex", first occurrence, insert -- silver --.

Signed and sealed this 31st day of March 1964.

SEAL)
ttest:

RNEST W. SWIDER

ttesting Officer

EDWARD J. BRENNER

Commissioner of Patents