Sept. 29, 1953 E. H. LAND 2,653,872

PHOTOGRAPHIC PRODUCT COMPRISING A RUPTURABLE CONTAINER CARRYING A LIQUID FOR PROCESSING SAID PRODUCT

Filed Jan. 28, 1947

FIG. 1

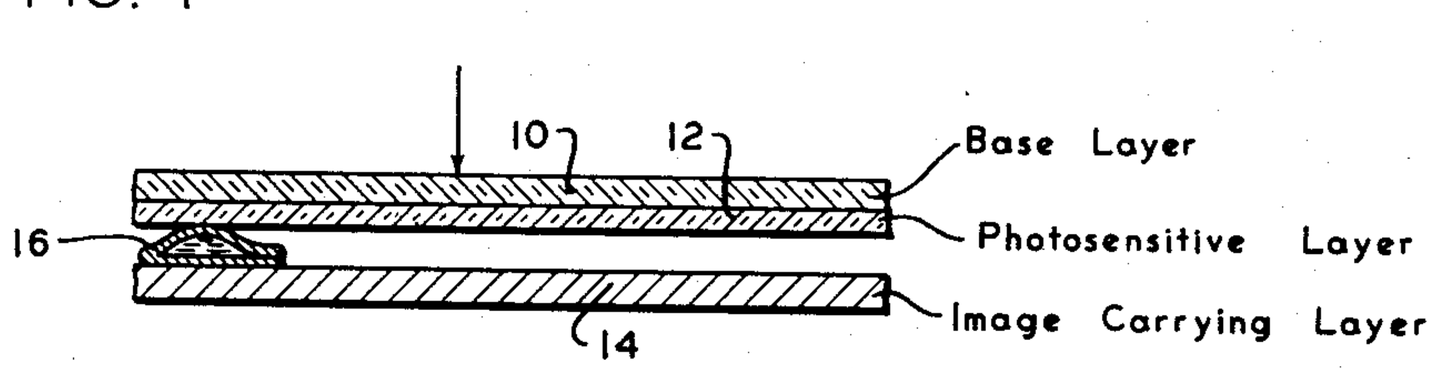


FIG. 2

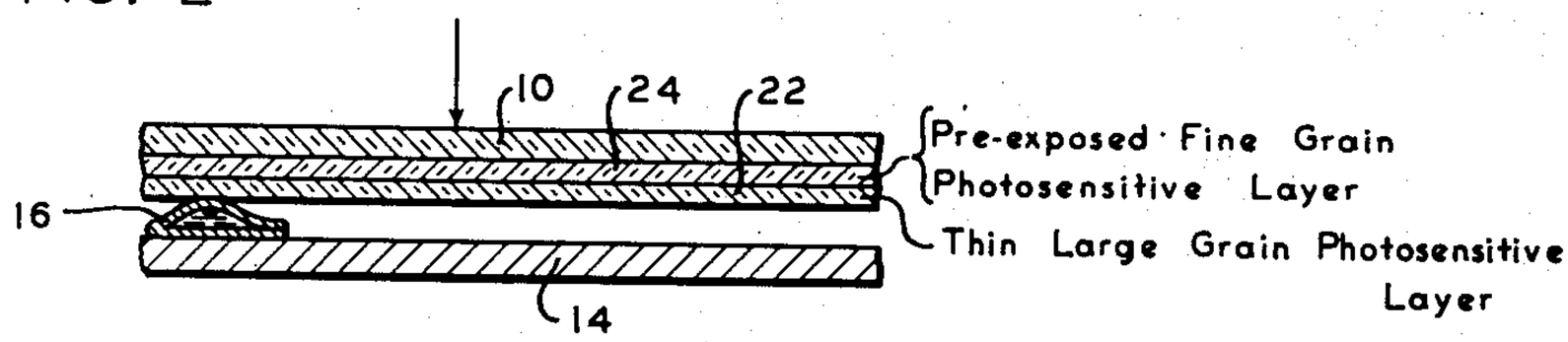
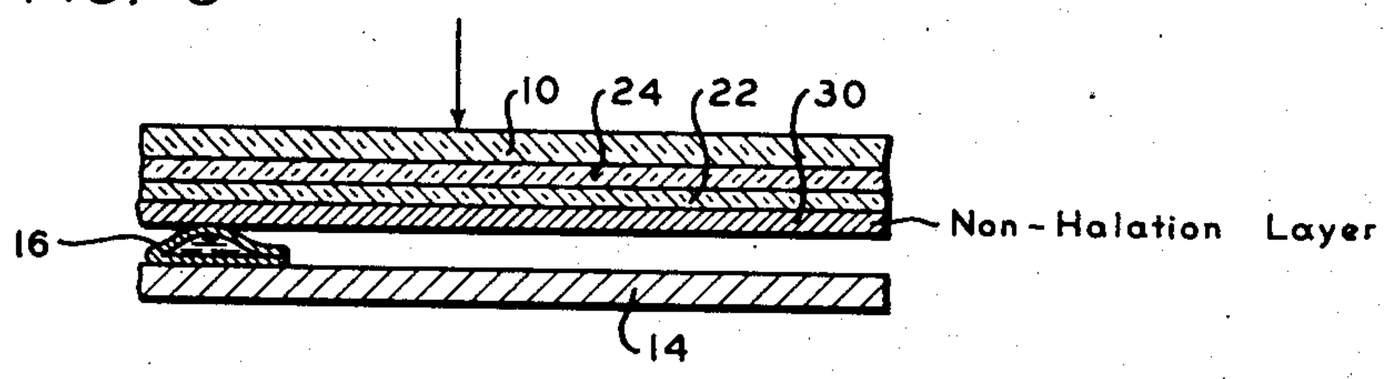


FIG. 3



INVENTOR
Edwin H. Land
BY
Donald L. Brown
Attorney

Patented Sept. 29, 1953

2,653,872

UNITED STATES PATENT OFFICE

2,653,872

PHOTOGRAPHIC PRODUCT COMPRISING A RUPTURABLE CONTAINER CARRYING A LIQUID FOR PROCESSING SAID PRODUCT

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

Application January 28, 1947, Serial No. 724,784

1 Claim. (Cl. 95—8)

1

This invention relates to photography and more particularly to novel, composite, photographic film units.

This application relates more specifically to improvements in the photographic products described in my copending application Serial No. 539,550, filed June 9, 1944, for Photographic Product, Process and Apparatus, and my copending application Serial No. 578,379, filed February 17, 1945, for Photographic Process, Apparatus and Product (both of which are now abandoned and replaced by my copending application Serial No. 64,870, filed December 11, 1948, and which issued as Patent No. 2,543,181 on February 27, 1951).

A principal object of the present invention is to provide photographic film units of the type described in my above-mentioned copending applications wherein a photographic film unit comprising a base layer, a photosensitive layer and another layer is exposed to actinic light through said base layer, and said film unit is developed to produce therein a final positive image by creating in said film unit a layer of liquid composition nearest the surface of said photosensitive layer which is farthest from said base layer, and improving on the products described in my said copending applications so as to permit the formation of a positive image having characteristics equal to those products where exposure of the photosensitive layer is made directly through the side of said photosensitive layer which is first contacted by said liquid composition.

Another object of this invention is to provide a photographic film unit comprising a layer of photosensitive material, a base for said layer, and another layer, said unit being arranged for exposure of said photosensitive material through said base layer and production of a positive image of a subject image on or in said other layer, said photosensitive layer having such optical characteristics as to substantially prevent scattering of light passing therethrough.

Another object of the present invention is to provide a composite photographic film unit containing a material capable of reacting with a liquid composition used for developing said photosensitive material to prevent the existence of any developer in stain-forming condition in the highlights of a positive image when an amount of developer is used which is in excess of the amount required to fully develop a fully developable portion of said photosensitive material.

Another object of the present invention is to provide in a product of the above type an amount of developer in excess of that required to fully

2

develop a fully developable portion of said latent image and to react said liquid composition with a material capable of preventing the existence of any developer in a stain-forming condition in the highlights of the positive image.

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

The invention accordingly comprises the product possessing the features, properties, and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claim.

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 schematic view of the invention as applied to a film unit of the type shown in my above-mentioned copending application Serial No. 578,379;

Fig. 2 is an exaggerated schematic, diagrammatic view of a modification of the invention; and

Fig. 3 is an exaggerated schematic, diagrammatic view of another modification of the invention.

In utilizing the products and processes described in my above-mentioned copending applications, it is in some instances highly desirable to provide a photographic film unit and process of treatment thereof which will permit the exposure of a photographic film unit through the back thereof, i. e., through the base layer which carries the photosensitive emulsion. This method of exposure has certain advantages over the exposure of the type where the photosensitive layer is exposed by light which does not pass through the base layer. One of these advantages is that it permits the use of an opaque image-carrying layer which is preferably a relatively cheap, densely white paper of the type known in the trade as baryta paper, without requiring the separation of the layer of photosensitive material from the image-carrying layer for exposure of the former. This obviously has certain advantages, such as simplification of camera structure and ease of manufacture of the film unit. It also aids in the manufacture of a sealed unit which is effective to prevent the escape of any of the liquid composition which is preferably used with the above-mentioned processes.

The present invention, therefore, relates to the provision of photographic products wherein a photographic film unit may be exposed through

the base layer with the resulting simplification of camera structure and manufacture of the film unit.

As shown in Fig. 1 there is provided a base layer 10 adapted to carry on one surface thereof a photosensitive layer 12. There is also provided another layer 14, hereinafter referred to as an image-carrying layer, which may be joined to the base layer or the photosensitive layer on the edge portions thereof. Between the photosensitive layer 12 and the image-carrying layer 14 there is preferably positioned a container 16 adapted to have therein a liquid composition. This container can be attached to either the photosensitive layer 12 or the image-carrying layer 14. Films of this general character are described in my above-mentioned copending application Serial No. 578,379.

The base layer 10 is preferably made of a suitable film base material such as a cellulosic ester or mixed esters such as cellulose nitrate, cellulose acetate, cellulose acetate propionate or other transparent materials capable of supporting a photosensitive emulsion. The photosensitive layer is preferably of the type rendered developable by exposure to light, such as a noble metal halide, and is preferably an emulsion of a silver halide or of a mixture of silver halides or of a mixed silver halide. The image-carrying layer 14 in a preferred embodiment of the invention is formed of a photographic material known in the art as baryta paper, although it can be made of other substances. This layer is preferably permeable to a substance contained in the liquid composition and may also be manufactured from other materials such as gelatin and paper. It may also be made of regenerated cellulose, polyhydroxy alkanes, such as polyvinyl alcohol, sodium alginate, certain of the cellulose ethers such as methyl cellulose, and their derivatives, such as sodium carboxymethyl cellulose, or hydroxyethyl cellulose. It may even be made of relatively impermeable materials such as glass and other materials commonly used in the photographic art.

The liquid composition in its preferred embodiment is composed of a developer such as hydroquinone, a film-forming substance such as sodium carboxymethyl cellulose, and a substance adapted to form from a latent photographic image a positive image-forming component. This latter substance in a preferred form of the invention is sodium thiosulfate. There are also preferably included other substances to aid the photographic reaction, such as a preservative, i. e., sodium sulfite (anhydrous) and an alkali, i. e., sodium hydroxide, plus water to carry the above-mentioned elements in solution. Suitable liquid compositions may be produced as shown in the following nonlimiting example:

Example

The following substances are put in a beaker and stirred with a plastic rod until dissolved:

Water	cc	476
Sodium thiosulfate	grams	18
Sodium hydroxide	do	17.5

The following substance is then stirred into the above mixture:

Sodium carboxymethyl cellulose, medium viscosity (Lot No. 1155 Hercules)	grams	42.62

The above mixture is stirred in a closed mixer having a nitrogen atmosphere over the liquid therein, and the temperature is raised to 178° F. The mixture is maintained at this temperature for approximately 3½ hours. During the first two hours 10 grams of sodium thiosulfate are added to the above mixture. During the last hour of heat treatment 18 grams of hydroquinone are added to the mixture. 249 cc. of water are then added to the mixture some time before the completion of the 3½ hour heating period.

Various equivalents may be used in the above-mentioned liquid composition and it is equally possible to substitute for the thickening and film-forming sodium carboxymethyl cellulose other film-forming agents, such for example as hydroxyethyl cellulose. Equally other developers, preservatives, and alkalies may be used, and other substances such as restrainers may be added.

The container 16 is preferably formed of a substance such as an oxygen and water-vapor impervious material, such, for example, as a sheet of wax impregnated, metal coated paper or wax coated metal foil, or a metal foil coated with a resin, such as polyvinyl butyral, which is inert to alkali.

In the use of the invention as described above, the photosensitive layer 12 is exposed to actinic light through the base layer 10 and, without further exposure to light, the whole assembly is subjected to a mechanical stress such as by passing through a wringer, not shown, starting with the container end. As the film is squeezed through the wringer, the container 16 is ruptured and the liquid composition is uniformly spread between the photosensitive layer 12 and the image-carrying layer 14.

When the liquid composition is spread between the photosensitive layer 12 and the image-carrying layer 14, the developer develops the latent photographic imade and the sodium thiosulfate forms silver complexes with the unexposed silver halide grains and carries these complexes into the image-receiving layer, being formed by the solidification of the film-forming substance contained in the liquid composition. These complexes are then developed and formed into a positive image. While this process is in operation, as stated above, the film-forming substance, i. e., the sodium carboxymethyl cellulose is being solidified into a dimensionally stable film.

The photosensitive layer in this modification of the invention is preferably made of a very fine-grained emulsion, so as to prevent scattering of light during its passage through the emulsion layer. Thus, the latent image which is formed on the lower surface of the photosensitive layer is substantially as sharp as the latent image formed on the upper surface of the photosensitive layer. It should also be noted that the developer composition shown in the example is quite a contrasty developed. It therefore accentuates the contrast and compensates somewhat for any scattering or diffusion of the image caused by the scattering or diffusion of light passing through the photosensitive layer. There is thus produced an image which has substantially the same detail as an image produced by exposing first the side of the photosensitive material which is first contacted by the liquid composition.

There is a disadvantage in the use of a very fine-grained silver halide emulsion, in that such a fine-grained emulsion is ordinarily not so sensitive to light as a large-grained emulsion, and

therefore requires a greater exposure to give the same density.

Although an acceptable image is produced in accordance with the process and products outlined above in the discussion of Fig. 1, it has been found that superior results are obtained by utilizing a very thin layer of photosensitive material. Such a layer is made so thin that, even though it may comprise relatively large grains of silver halide, it does not have sufficient depth to create any appreciable scattering of light within the photosensitive layer, and it maintains a high sensitivity due to the use of larger grains. When this very thin layer of photosensitive material is used, it is desirable to use a very thin layer of liquid composition, since, with most developers, it is preferred to exhaust the developer in the area of the highlights of the positive image, so that no developer remains to cause a stain therein. The use of an extremely thin liquid layer, however, involves certain mechanical difficulties, such as the necessity for extremely careful spreading of the liquid layer, so that there may not be any inequalities of layer thickness. Also, it has the added disadvantage that a small error in thickness with a thin layer of liquid gives a much larger percentage error in total thickness of the layer.

Another modification of the invention, therefore, includes the additional provision in the film unit of a layer of a material which is capable of reacting with the liquid composition to prevent the existence of any developer in stain-forming condition in the highlights of the positive image. Such a material may take the form of an oxidizing agent associated with the photosensitive layer, which oxidizes the developer and renders the developer relatively immobile, thereby trapping the developer in the place where it is oxidized. Such an oxidizing agent may be a layer of very fine-grained, pre-exposed photosensitive emulsion, or it may be an oxidizing agent such as sodium perborate. It is also possible for such a material to be a substance such as lead acetate or an acid which has the ability of lowering the pH of the liquid composition, at least in the highlights of the positive image, to a point where staining by the developer cannot take place. It is also possible to utilize a developer which, when oxidized, is capable of coupling with a dye-coupler to form an immobile dye. If this be the case, a dye-coupler should be incorporated in the layer with the oxidizing agent and thus, as the excess developer becomes oxidized, it couples to form an immobile dye and is thereby kept from the highlights of the positive image.

Turning now to Fig. 2, there is shown a modification of the invention wherein a very thin, relatively large-grained photosensitive layer is provided. As shown in Fig. 2, there is provided a base layer **10**, which corresponds to the base layer 10 of Fig. 1. Coated on the lower surface of this layer **10**, there is provided a layer **24** of a very fine-grained photosensitive emulsion which has been uniformly exposed to actinic light to make it developable. There is next provided on this uniformly pre-exposed photosensitive layer a very thin layer **22** of a relatively large-grained photosensitive emulsion adapted to be exposed in a camera to a subject image. As in Fig. 1, there is also provided an image-carrying layer **14** and a liquid container **16**, positioned between the thin photosensitive layer **22** and the image-carrying layer **14**.

In this modification of the invention, the base layer **10** is preferably formed of a suitable cellulosic film base, such as cellulose acetate, cellulose nitrate, etc. The pre-exposed photosensitive layer **24** preferably comprises a very fine-grained silver halide emulsion, and the photosensitive layer **22** comprises a relatively large-grained silver halide emulsion. The layer **24** may however comprise a nonphotosensitive silver salt or a slightly photosensitive silver salt of an organic linear high polymer. The liquid composition carried by the container **16** may be of the type described in the example above, although it preferably contains about half the amount of hydroquinone and sodium thiosulfate listed in that example. Other suitable developers, of course, may be used in the practice of the present invention. The image-carrying layer **14** is preferably formed of a sheet of bartya-coated paper, and, in a preferred example, the baryta paper has coated thereon a material, or materials, which will insolubilize the film-forming material, increase the contrast, and reduce the alkalinity in the highlights of the positive image. A preferred example of such a material is lead acetate.

In the use of the embodiment of the invention described in connection with Fig. 2, the photosensitive layer **22** is exposed to actinic light from the subject image, through the base layer **10** and the fine-grained pre-exposed photosensitive layer **24**. Due to the extremely fine grains in the layer **24**, there is substantially no scattering or diffusion of the light passing therethrough, and the latent image formed in the photosensitive layer **22** has a sharpness comparable with that obtained by exposing this layer from the side thereof which is first contacted with the liquid composition.

The film unit is processed, in a preferred example, by passing it through a pair of pressure rollers, the container end going first. This releases the liquid composition from the container and spreads it in a uniform layer between the image-carrying layer **14** and the photosensitive layer **22**. As in the previous discussion of the photographic process involved, the developer develops the latent image in the photosensitive layer **22**. The sodium thiosulfate forms soluble silver complexes with the unexposed silver halide, and these silver complexes are developed by the developer into a positive image on and within the film formed by the film-forming material of the liquid composition. If a relatively thin layer of liquid composition is utilized, the amount of developer available for reacting with any portion of the photosensitive layer **22** may be such that it will be completely exhausted by developing a fully developable portion thereof. However, since the formation of such a thin, very uniform layer requires accuracy of controls not desired in a camera apparatus, it is preferred to use a thicker layer of developer. The developer in excess of that required to fully develop a fully developable portion of the photosensitive layer **22** is exhausted by developing the developable photosensitive material in the pre-exposed photosensitive layer **24**. Thus, there are combined, in a film unit of the type described above, the advantages of extremely small-grained photosensitive material with a consequent reduction of scattering and diffusion of light passing therethrough, the high sensitivity of the large photosensitive grains, and the freedom from the requirements of extreme accuracy in spreading the liquid developer layer.

As stated previously, it is possible to use, as the material which is capable of reacting with the liquid composition to prevent the existence of any

developer in stain-forming condition in the highlights of the positive image, a material other than a fine-grained pre-exposed photosensitive material, and such materials may be a nonphotosensitive oxidizing agent such as sodium perborate. In this latter case, the layer 24 might be formed of an emulsion of very small crystals of sodium perborate coated onto base 10 prior to the casting thereon of the photosensitive layer 22. It is equally apparent, of course, that the oxidizing agent may be placed on the surface of the base layer by any other suitable means such as by evaporating or precipitating from a concentrated solution thereof. It is also desirable in some instances to utilize, with the above process, a color-forming developer, such as diethylparaphenylenediamine hydrochloride. If such a developer is used, a color former adapted to couple with the oxidized developer may be incorporated in layer 24 along with the oxidizing agent. Such a color former may be p-nitrophenylacetonitrile or 2,4 dichloro-1-naphthol. It is obvious, from the above discussion, that the immobile dye-forming materials may be used either with a pre-exposed photosensitive layer or with an oxidizing agent layer.

It is also possible to utilize, instead of an oxidizing agent for preventing stain-forming in the highlights, a substance which will act to lower the pH of the liquid composition in the area of the highlights of the positive image to such an extent that, even though there may be some unoxidized developer in the highlights of the positve image, it is incapable of forming a stain due to the fact that the pH is sufficiently low to prevent formation of such a stain.

For this purpose it has been found possible to use various metallic salts such as those of lead, zinc, and cadmium, either alone or in combination. It is believed that these salts have the effect of forming insoluble metal hydroxides with the sodium hydroxide of the liquid composition and thus lowering the alkalinity of the liquid. When a comparatively thick layer of liquid composition is utilized with the result that there is a considerable excess of unused developer in the highlights, it is desirable to use a proportionately larger amount of the material for preventing stain in the highlights.

While the above discussion of the invention has been limited primarily to the preferred form thereof, it is equally apparent that the layer 24 of material capable of preventing stain due to excess developer may be placed in a position other than between the base layer and the photosensitive layer. This layer is preferably positioned so that its reaction with the liquid composition is somewhat delayed so that it does not interfere with either the development of the latent image or the production of the positive image. This layer can, therefore, be placed beneath the image-carrying layer. If such be the case, the position of this layer will depend upon the color of the reaction product of the liquid therewith. When this reaction product is a colored substance this layer is preferably covered by a coating, such as baryta, which will hide the colored product. When the reaction product is white or colorless this layer may be coincident with the surface of the image-carrying layer.

In many cases it is desirable to provide, in film units of the above type, a nonhalation layer on the side of the photosensitive layer opposite from that which is first reached by the actinic light used in exposing said photosensitive layer. In the

present invention it is desirable to use a nonhalation layer which has such permeability as not to interfere with the ionic transfer of image-forming components and also one which is not dissolved by the liquid composition utilized in developing the photosensitive layer and creating the final positive image. Such a layer should also be so formed that the materials thereof are non-migratory and do not enter into the photosensitive layer to any considerable extent, since otherwise they might reduce the sensitivity of the photosensitive layer. This particular feature is of considerable importance in those cases where an extremely thin photosensitive layer is utilized.

In Fig. 3, there is shown one modification of the present invention having incorporated therein a nonhalation layer. In Fig. 3, where like numbers correspond to like elements of Fig. 2, there is provided the usual base layer 10, a layer 24 of material capable of reacting with a liquid composition used for developing the photosensitive material to prevent the existence of any developer in stain-forming condition in the highlights of the positive image. Next, there is provided a very thin layer 22 of a large grain photosensitive material. Coated on this photosensitive layer 22 there is a nonhalation layer 30. The usual container 16 for a liquid composition is provided and there is also included an image-carrying layer 14.

The materials best suited for the above elements of the combination have been discussed in considerable detail above. In one preferred modification of the invention, the layer 30 is formed by coating on the photosensitive layer 22 an emulsion of gelatin and very finely comminuted carbon, such as carbon black or a lamp black. Such a layer is permeable to the liquid composition and does not appear to interfere with the ionic transfer of the image-forming components. This nonhalation layer may, however, be made of other permeable materials having incorporated therein immobile, insoluble dyes. This layer 30 should be formed of a film-forming material in which silver will not form as readily as in the film-forming material from container 16.

In the use of the modification of the invention shown in Fig. 3, the photosensitive layer is exposed to actinic light through layers 10 and 24, and is then processed, such as by passing through a pair of pressure rollers, the container end going first. The liquid composition is released from the container 16 and is spread in a uniform layer between the layer 30 and the image-carrying layer 14. The developer develops the latent image in the photosensitive layer 22, and the sodium thiosulfate creates positive image-forming components with the unexposed silver halide, and transfers these components through the nonhalation layer 30 to the film created by the film-forming material. These image-forming components are then formed into a final, stable, positive image by means of some of the unused developer. The excess developer remaining is made incapable of forming a stain in one of several ways. It is either used up by oxidizing the material in layer 24 or the alkalinity of the liquid composition is lowered, by the material in layer 24, to such an extent that oxidation of the excess developer cannot take place.

Although the nonhalation layer 30 has been described in connection with a film unit of the type shown in Fig. 2, it is apparent that this nonhalation layer may be equally incorporated in the embodiments of the invention shown in Fig.

1. When incorporated in this embodiment of the invention it will act in the same manner. That is, it prevents halation in the photosensitive layer and does not interfere with the photographic process.

It should also be understood that, although the invention has been described in terms of individual film units, it may be practiced with roll films wherein a plurality of images are produced and the roll film may be treated so as to produce each image separately or all images simultaneously.

Since certain changes may be made in the above product without departing from the scope of the invention, 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:

A composite film unit having a photosensitive element which comprises a transparent base layer on one side of which two silver halide layers are superposed and through the second side of which actinic light is transmitted for exposing said photosensitive element, a first of said silver halide layers comprising a pre-exposed fine grain silver halide emulsion supported upon the first-mentioned side of said transparent base, and a second of said silver halide layers constituting an unexposed thin, large grain silver halide emulsion in which a latent image is adapted to be formed upon exposure of said photosensitive element, said second silver halide layer being supported upon the outer surface of said first silver halide layer, an image-carrying layer for a transfer image secured to said photosensitive element in superposed relation thereto on the same side thereof as said second silver halide layer, and a rupturable container holding a liquid composition comprising a silver halide developer and a silver halide solvent rendered effective upon rupture of said container to develop a latent image in said second silver halide layer to silver and to form with unexposed silver halide in the second silver halide layer a soluble silver complex for transfer by imbibition to said image-carrying layer for formation therein of a reversed image in silver of said latent image, said rupturable container being mounted between said photosensitive element and said image-carrying layer at a position therebetween for releasing its liquid content upon rupture and, without removal of its ruptured portion, for permeation into said photosensitive element, including the second silver halide layer thereof, and into said image-carrying layer.

EDWIN H. LAND.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
742,405	Eichengrun	Oct. 27, 1903
1,173,429	Ives	Feb. 26, 1916
1,306,904	Ives	June 17, 1919
1,320,760	Ives	Nov. 4, 1919
1,447,759	Christensen	Mar. 6, 1923
1,597,727	Sperati	Aug. 31, 1926
1,841,653	van der Grinten	Jan. 19, 1932
1,956,230	Schmidt	Apr. 24, 1934
2,315,966	Knott	Apr. 6, 1943
2,327,828	Simmons	Aug. 24, 1943
2,352,014	Rott	June 20, 1944
2,415,666	Weissberger	Feb. 11, 1947
2,500,421	Land	Mar. 14, 1950
2,543,181	Land	Feb. 27, 1951

FOREIGN PATENTS

Number	Country	Date
324,394	Great Britain	Jan. 27, 1930
326,559	Great Britain	Mar. 20, 1930
328,336	Great Britain	May 1, 1930
511,180	Great Britain	Aug. 9, 1939
879,995	France	Dec. 10, 1942

OTHER REFERENCES

Mees: "The Theory of the Photographic Process," published by the MacMillan Co., New York, 1942, pages 34–58.

Mees: "The Theory of the Photographic Process," published by the MacMillan Co., New York, page 392.

Mees: "Photography," published by the MacMillan Co., New York (1937) pgs. 68 and 69.

James & Higgins: "Fundamentals of Photographic Theory," published by John Wiley and Sons, New York, pgs. 97 and 98.