

Aug. 21, 1951

E. H. LAND
PHOTOGRAPHIC PRODUCT
Filed Sept. 19, 1950

2,565,378

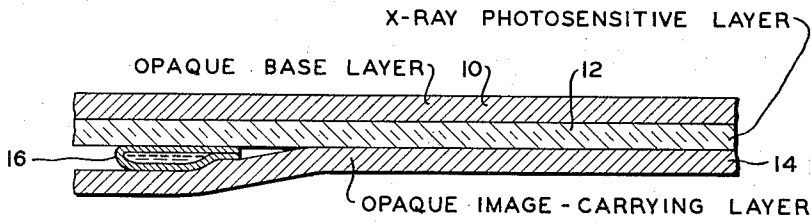


FIG. 1

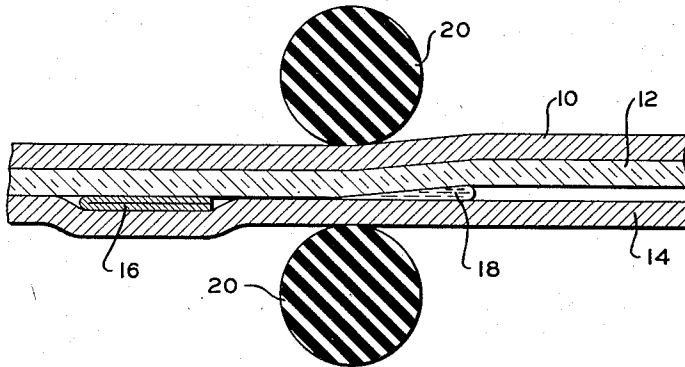


FIG. 2

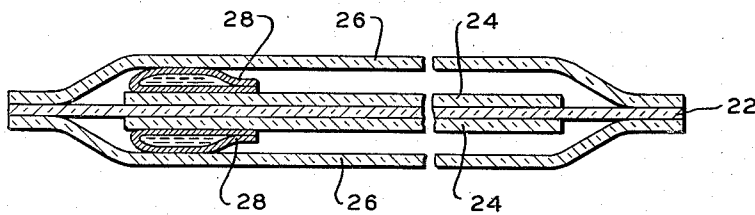


FIG. 3

INVENTOR
Edwin H. Land
BY *Donald R. Brown*
Attorney

UNITED STATES PATENT OFFICE

2,565,378

PHOTOGRAPHIC PRODUCT

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

Application September 19, 1950, Serial No. 185,642

4 Claims. (Cl. 250—68)

1

This application relates to novel photographic products particularly useful for employment with X-rays and other radioactive rays.

The present application is a continuation-in-part of and a substitute for my copending application, Serial No. 727,384, filed February 8, 1947, for Photographic Product, now abandoned.

A principal object of the present invention is to provide an improved photographic product which can be used to obtain negative or positive fixed stable images when exposed to X-ray or other radioactive rays and processed by the application thereto of a mechanical stress.

Another object of the present invention is to provide such products which are cheaper and give positive images of increased density and definition over that ordinarily obtained with the products of the prior art.

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

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

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

Figure 1 is an exaggerated cross-sectional diagrammatical view of a preferred type of film unit embodying the present invention;

Fig. 2 is an exaggerated diagrammatical sectional view of the film unit of Fig. 1 during processing thereof; and

Fig. 3 is an exaggerated diagrammatical sectional view of another form of the invention.

This invention relates generally to new and improved products useful in obtaining photographic records of latent images created by X-ray or other radioactive rays. In a preferred process of the present invention, a silver halide photosensitive layer is exposed to X-rays or other radioactive rays, and the latent negative image thus created is developed by spreading a viscous liquid solution of a developer in a layer adjacent said photosensitive layer. This layer of liquid preferably also includes a silver halide solvent and the spreading thereof is preferably accomplished by releasing said liquid from a container therefor and translating the bulk of the released liquid across said photosensitive layer. In a preferred form of the invention, the liquid is held in a protective environment, such as an oxygen

2

and water vapor impervious elongated container, the container being positioned along the edge of a predetermined area to be covered by said liquid, the container being sufficiently elongated so that the liquid is distributed along one dimension of said area. In a preferred product this container is positioned between the photosensitive layer and another layer which assists in spreading this liquid in a uniform thin layer adjacent said photosensitive layer. This second layer preferably also serves to carry, on or in its surface, a positive image of a latent negative image created by exposure of said photosensitive layer to actinic rays, this layer being hereafter referred to as an image-carrying layer. At least the outer surfaces of both of these layers are preferably opaque to actinic light and at least one of these layers is transparent to X-rays or other radioactive rays. This positive image is preferably formed as the result of the development of the negative image and the transfer of undeveloped silver complexes from the photosensitive layer to the image-carrying layer, these complexes being formed by means of the silver halide solvent.

Referring now to Fig. 1, there is shown a cross-sectional exaggerated view of one preferred modification of a film unit embodying the present invention. This film unit comprises a base layer 10 which is opaque to actinic light but transparent to X-rays and other radioactive rays. On the inner surface of the base 10 there is provided a layer 12 of a silver halide photosensitive material adapted to have created therein a latent negative image upon exposure to X-rays and other radioactive rays. There is also provided an image-carrying layer 14 which is preferably opaque to actinic light and transparent to X-rays. Between the photosensitive and image-carrying layers there is positioned an elongated container 16 having therein a predetermined quantity of a liquid composition.

In a preferred form of the invention the base layer 10 is a black paper, or black dyed cellulosic film base, or a transparent film base provided with a light-opaque backing such as paper. The photosensitive layer 12 is an ordinary silver halide photosensitive material suitable for use in X-ray work. The image-carrying layer 14 preferably comprises a sheet of baryta paper having a light-opaque backing. The inner surface of the image-carrying layer is preferably coated as set forth in the following nonlimiting example:

Example 1

A sheet of baryta paper is run through a bath containing a ¼% water solution of neutral lead

3

acetate, the sheet being in contact with this bath for about 30 seconds. The sheet is dried and next run through a bath containing a $1/40\%$ water solution of sodium sulfide, the sheet being in contact with the bath for about $1\frac{1}{2}$ seconds. The sheet is dried and then run through a bath containing a water solution of 1.5% neutral lead acetate, 15% cadmium acetate and 45% zinc nitrate, the sheet being in contact with this bath for about 20 seconds.

The container 16 is preferably formed of a relatively flexible material, folded upon itself to provide a longitudinally sealed edge. A preferred container comprises a paper-backed metal foil coated on its inner surface with an alkali-inert resin, such as polyvinyl butyral, the sealed edge of the container having incorporated therebetween a layer of a material such as ethyl cellulose which imparts less strength to the sealed edge than the end of the container which is sealed by means of the polyvinyl butyral lining.

A preferred liquid composition for inclusion in the container comprises an alkaline viscous solution of a film-forming material, a developer and a silver halide solvent. A preferred liquid composition is made in accordance with the following nonlimiting example:

Example 2

The following ingredients are placed in a mechanical mixer and mixed at room temperature for three hours:

	Grams
Sodium carboxymethyl cellulose (Hercules #1658 medium viscosity)-----	247.2
Sodium carboxymethyl cellulose (Hercules #1672 high viscosity)-----	31.8
Water-----	5580

To the above mix, the following ingredients are added in the order named and mixed under an inert atmosphere for two hours at $50^{\circ}\text{C}.$:

	Grams
Sodium sulfite-----	235
Sodium hydroxide-----	223.8
Sodium thiosulfate-----	43.5
Citric acid-----	115.5
Hydroquinone-----	156

During the use of the above described film unit, it is exposed to X-ray or other radioactive rays which preferably pass through the light-opaque image-carrying layer and impinge upon that surface of the photosensitive layer 12 which is closest to the image-carrying layer 14, thus giving the sharpest image at this surface of the photosensitive layer. The film unit is then processed by the application of a mechanical stress thereto, such as by passing the film unit through a pair of pressure rollers 20 as shown in Fig. 2, the container end of the film unit going first. The pressure rollers release the liquid 18 from the container 16 and translate the bulk of the liquid across the surface of the photosensitive layer 12, leaving a very thin layer of the liquid between layers 12 and 14. When this layer of liquid composition is composed of ingredients of the type set forth in the preferred Example 2, the developer develops the latent negative image and the silver halide solvent forms soluble silver complexes with the undeveloped silver halide. These silver complexes are transferred to the image-carrying layer where they are converted into a visible positive image. It is believed that the lead sulfide on the image-carrying layer assists in the formation of the posi-

4

tive image by (1) forming insoluble specks of silver sulfide with silver in the transferred complex, these specks acting as precipitation nuclei for the positive image, and (2) forming an insoluble lead thiosulfate to aid in the reduction of the complex to silver. The other salts on the image-carrying layer increase the stability of the positive image by slowly lowering the pH of the image to a point where staining does not occur. This neutralizing or acidifying reaction is preferably so adjusted that the pH is not appreciably lowered until the positive and negative images have been formed.

The film unit of Fig. 1 and the process of forming an image by the use of such a film unit have certain definite advantages which make them particularly suitable for clinical use. In the first place the film unit is completely opaque to actinic light and, therefore, may be handled in daylight without danger of fogging. This characteristic enables the film unit to be exposed to radioactive rays without the requirement of any special exposure housing for the photosensitive film. The photographic process allows the production of a finished positive image, in a time of from a few seconds to about 1 minute, depending upon the processing materials employed. This latter feature of the invention is of extreme importance when rapid clinical diagnosis is essential, now abandoned. This processing requires no baths or tanks and can be readily accomplished by the simple application of a progressive mechanical stress to the film unit.

The photographic process enables the use of cheaper photosensitive emulsions since the silver grains precipitated in the positive image have a smaller average grain size than the silver halide grains from which they are derived and therefore have an increased covering power. This characteristic of the process obviates the necessity for the use of the double layer photosensitive emulsions ordinarily employed in X-ray photography for obtaining the desired density. The thinness of the photosensitive layer, which is feasible in this process, gives a higher definition since there is less scattering of the X-rays by the silver halide grains during exposure.

The speed, cheapness and freedom from complicated processing apparatus make this product particularly suitable for use during surgical operations and enable the surgeon to determine immediately the results of his surgery. For example, by the use of the present invention it is possible to tell, within a few seconds after the setting of a broken limb, whether or not the limb was properly set. The other advantages of such a process or product are so numerous in the fields of surgery, dentistry and clinical diagnosis as to be obvious to those skilled in the art.

While the invention has been discussed in connection with preferred modifications thereof wherein a positive image is directly obtained from a latent negative image, there are some cases where the negative image is desired rather than the positive image. In such a circumstance the developed negative image may be used in place of the positive image and such a modification of the invention is to be considered as being within the scope of this application.

In those cases where a negative is desired and a double photosensitive layer is employed, a modification of the invention of the type shown in Fig. 3 is particularly useful. In this figure there is shown a base layer 22 on each side of which

is a photosensitive layer 24. Positioned adjacent each of the two photosensitive layers 24 is a container 28, and surrounding the assemblage is a light-opaque and X-ray permeable envelope 26. With such a modification of the invention, the materials of the film unit are preferably those discussed in connection with previous forms of the invention. During processing, the liquid from the two containers is spread in parallel layers across the two photosensitive layers and, at least, develops and fixes these two layers.

When a negative image is the end product most desired, the gelatino silver halide emulsion preferably comprises an emulsion similar to Motion Picture Release Positive made by Eastman Kodak Co. In this case, one preferred processing liquid includes the ingredients listed in the following nonlimiting example:

Example 3

100 grams 5% water solution of sodium carboxymethyl cellulose
15 grams sodium sulfite
20 grams sodium hydroxide
12 grams hydroquinone
30 grams sodium thiosulfate

With such an emulsion and liquid composition, the backing layers 26 preferably comprise outer layers of a suitable opaque material such as leader stock laminated to inner layers of baryta paper, for example.

When the liquid of Example 3 is spread between the two exposed photosensitive layers 24 and their superposed backing layers 26, the developer develops the exposed silver halide grains and the silver halide solvent forms soluble silver complexes with the unexposed silver halide grains, transporting the silver complexes from the silver halide layers to the liquid layers and the inner surfaces of layers 26 to fix the developing negative images.

For convenience, the expression "X-ray" has been used in the specification and the claims and is intended to cover all photographically useful radioactive rays such as those emanating from an X-ray tube, radium, or radioactive isotopes.

A preferred form of the invention has been described wherein the liquid composition includes in solution all the materials, such as the developer and the silver halide solvent, for carrying out the chemical processing of the film unit. It is equally possible, however, to include any or all of these materials in solid form in the film unit in position to be dissolved by the liquid as it is spread. Such modifications of the invention are intended to be included within the scope of the present application.

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

What is claimed is:

1. A photographic product containing all of the material, including a photographic developer and in the amount required to develop at least two X-ray images in said product, said product comprising a first liquid-confining layer, a second liquid-confining layer, a base layer positioned between said liquid-confining layers, a first silver

halide photosensitive layer carried by one side of said base layer, a second silver halide photosensitive layer carried by the other side of said base layer, each said photosensitive layer including a predetermined area adapted to have a latent image formed therein upon exposure to X-rays, a first liquid-carrying container positioned between said base and said first liquid-confining layer, and a second liquid-carrying container positioned between said base and said second liquid-confining layer, each said container holding a viscous processing liquid and including a sealed mouth rupturable by increased hydraulic pressure within the confined liquid, each of said liquid-confining layers including a stratum which is opaque to actinic light, said two liquid-confining layers being sealed together so as to provide a liquid-confining envelope including therewithin said two containers, said two photosensitive layers and said base layer, said containers being secured within said envelope adjacent edges of their associated image areas, at least one of said liquid-confining layers and said base layer being substantially transparent to X-rays to permit exposure of said two photosensitive layers to X-rays, at least one of said two liquid-confining layers and at least one wall of each of said containers being flexible to permit pressure applied to the outer surfaces of said envelope to increase the hydraulic pressure within the viscous liquid carried by said two containers so as to rupture the sealed container mouths, said envelope being sufficiently impervious to said liquid to confine said liquid therewithin when said liquid is released from said two rupturable containers and spread under pressure across said photosensitive layers on both sides of said base layer, said liquid being in the amount required for developing latent images in said two photosensitive layers, said product including a developer for silver halide.

2. The product of claim 1 wherein the liquid in each container comprises a viscous aqueous alkaline solution of a silver halide developer and a silver halide solvent.

3. The product of claim 1 wherein said two containers are positioned adjacent one edge of the product so that the liquid can be released and spread from both said containers by passing said product once between a pair of pressure rolls.

4. The product of claim 1 wherein said two liquid-confining layers serve as image-receiving sheets upon which positive prints of the subject matter of the latent images in said photosensitive layers are obtained.

EDWIN H. LAND.

REFERENCES CITED

The following references are of record in the file of this patent.

UNITED STATES PATENTS

Number	Name	Date
916,325	Kelley	Mar. 23, 1909
2,126,769	Goldschmidt	Aug. 16, 1938
2,144,392	Saffir	Jan. 17, 1939
2,286,748	Martin	June 16, 1942
2,435,718	Land	Feb. 10, 1948

FOREIGN PATENTS

Number	Country	Date
370,821	Germany	Mar. 8, 1923
879,995	France	Mar. 10, 1943