Sept. 29, 1953 E. H. LAND 2,653,527

PROCESS FOR TREATING PHOTOSENSITIVE MATERIALS BY SPREADING THEREON A LAYER OF PROCESSING LIQUID AND APPARATUS FOR PERFORMING SAID PROCESS

Filed Feb. 19, 1947 2 Sheets-Sheet 1

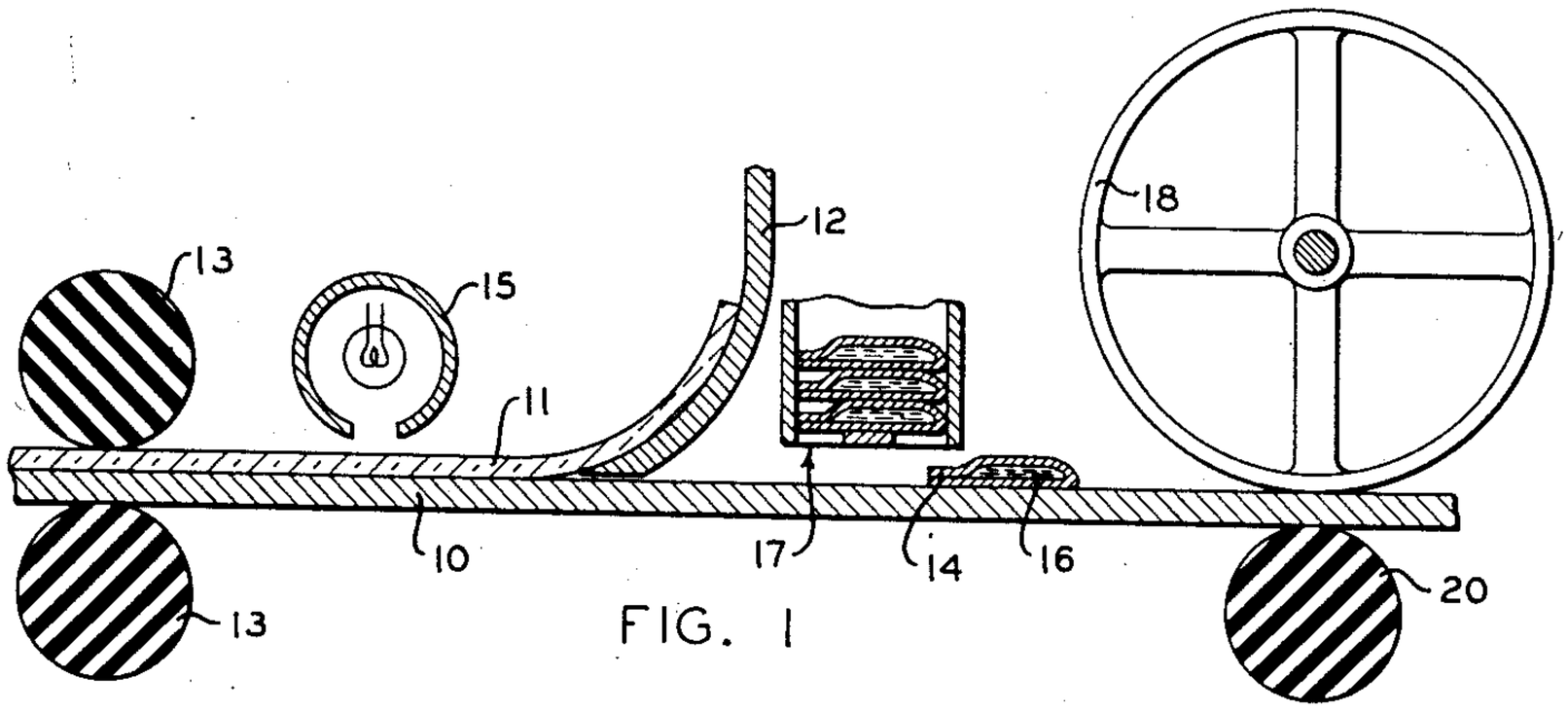

FIG. 1

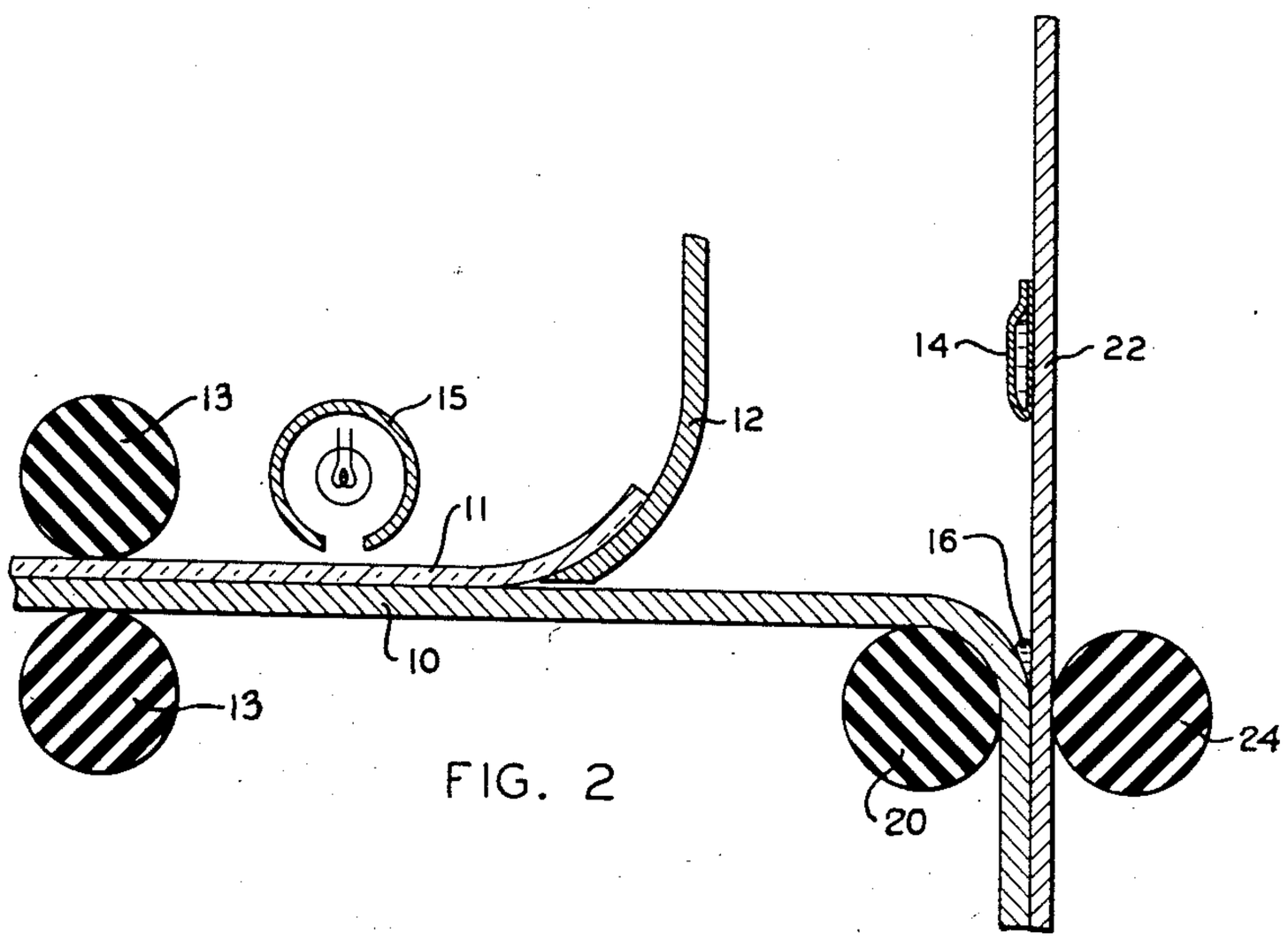

FIG. 2

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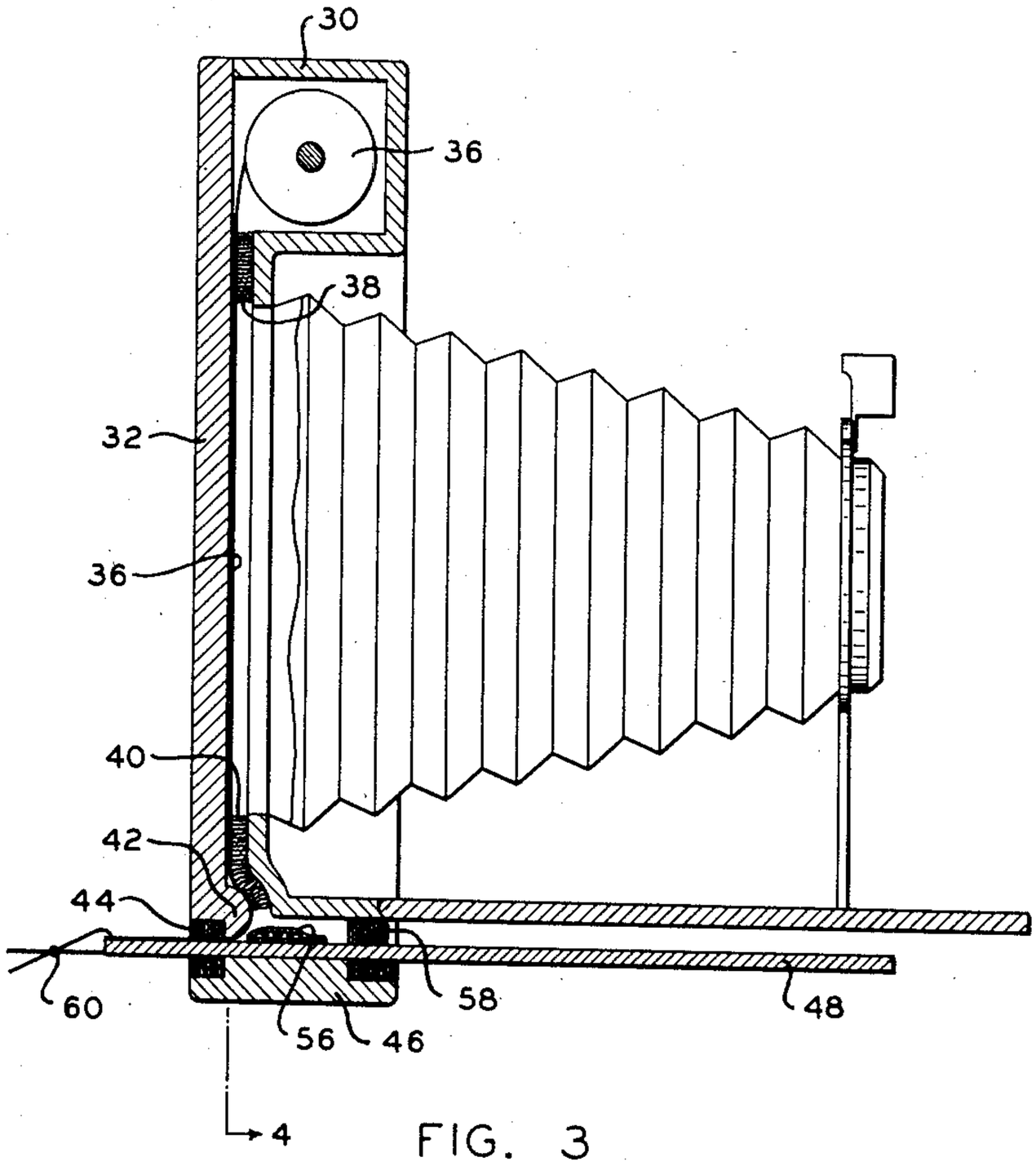

FIG. 3

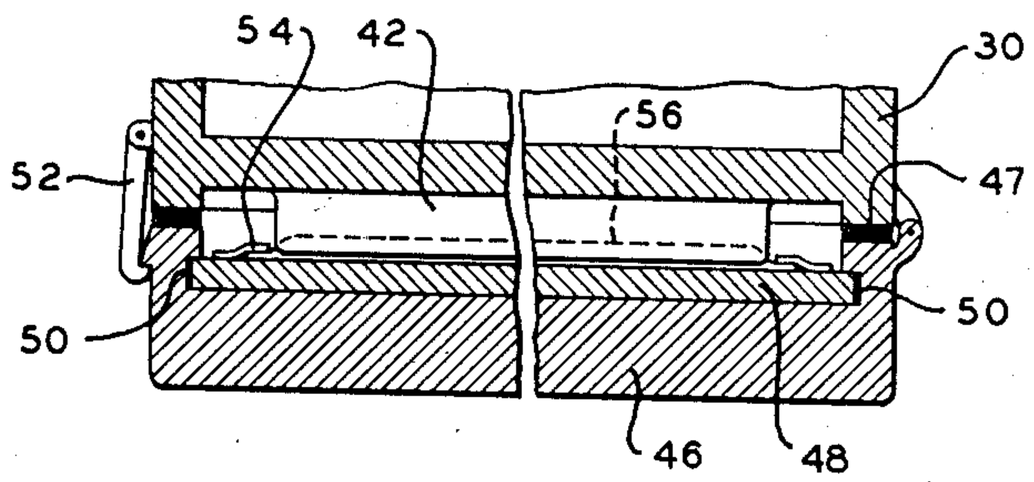

FIG. 4

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PROCESS FOR TREATING PHOTOSENSITIVE MATERIALS BY SPREADING THEREON A LAYER OF PROCESSING LIQUID AND APPARATUS FOR PERFORMING SAID PROCESS

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14 Claims. (Cl. 95—13)

1

This invention relates to photography and more particularly to novel photographic processes and apparatus for use therewith.

A principal object of the present invention is to provide improved processes for the treatment of photographically exposed photosensitive materials.

Another object of the invention is to provide such processes which are adaptable for wide photographic uses enabling the accomplishment of new photographic results with a minimum of expense and time.

Still another object of the invention is to provide new photographic apparatus particularly suitable for use with the above-mentioned processes.

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

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others, and the apparatus possessing the construction, combination of elements and arrangement of parts 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 a sectional diagrammatic view of a novel apparatus of the present invention as used in the process of the present invention;

Fig. 2 is a sectional diagrammatic view of another apparatus of the present invention;

Fig. 3 is a sectional diagrammatic view of still another form of the invention; and

Fig. 4 is a sectional diagrammatic fragmentary view of Fig. 3 taken along the line 4—4.

This application relates generally to the processing of a layer of photographically exposed photosensitive material by creating, in permeable relation with said layer, a film of a reagent which preferably contains at least a solvent for a substance capable of differentially reacting with portions of said photosensitive material to create a visible effect in said photosensitive layer which is a function of the degree of exposure thereof. In a preferred form of the invention the reagent is provided in a protective environment and positioned, during processing, adjacent one edge of an image area of said photosensitive layer to be processed. This reagent is preferably distributed within the protective environment along

2

the length of this edge. The protective environment preferably is such that the contained reagent may be released by the application of a mechanical stress thereto, this protective environment being preferably an elongated container adapted to have its contained reagent released along one of the edges thereof upon the application of a predetermined compression to a predetermined area of said container.

In the practice of the invention the container for the reagent is provided along one edge of the exposed area of the photosensitive layer and a relative motion is created between said container and a pressure-applying means in the processing apparatus, while the container is held fixed with relation to the exposed area. A compression is applied to the container which is parallel to the long axis of the container and which has a translatory relative motion perpendicular to the long axis of the container and parallel to the plane of the exposed area of the photosensitive layer. This compression is caused to apply such a stress to the container and/or the liquid contents thereof that the bulk of the liquid is forced out of the container and translated across the exposed area of the photosensitive layer, leaving a film of the liquid reagent on the surface of the photosensitive layer. In one modification of the invention the bulk of the liquid, in the form of a meniscus, is confined on one side by the photosensitive layer and on the other side by a portion of the apparatus which may be a part of the pressure-applying means. In another form of the invention the liquid is confined between the photosensitive layer and another layer. In both forms of the invention the liquid reagent preferably has such a high viscosity as to aid in controlling the film of spread liquid.

The film of spread liquid permeates the exposed area of the photosensitive layer and accomplishes a desired image-forming reaction which is a function of the degree of exposure of the various portions of the exposed area.

Referring now to Figure 1 there is shown a diagrammatic cross-sectional view of one preferred form of apparatus which is particularly adapted for photocopying and is suitable for practicing the present invention. There is provided a photosensitive layer 10 which may be fed from a suitable supply roll therefor (not shown). For propelling the photosensitive layer 10 in contact with a sheet 11 to be copied there is provided a pair of propelling rolls 13. These rolls carry the sheet 11 and layer 10 in contact past a strong light source 15 which is adapted to direct light through sheet 11 onto the photosensitive surface of layer 10. Other propelling or guide rollers

may be provided where desirable. A suitable means, such as a plow 12, is provided for removing sheet 11 from layer 10. A suitable housing, not shown, is provided for excluding actinic light from the photosensitive layer during storage and processing.

For the purpose of holding a plurality of containers 14 there is provided a magazine schematically shown at 17. This magazine may be automatically synchronized with the movement of the layer 10, or may be manually operated. If automatic synchronization is desired, layer 10 is preferably notched or otherwise marked to assist in this synchronization. It is also feasible to control the release of the containers from the magazine in accordance with the movement of sheet 11, such as by interrupting or closing an electrical circuit, or by operating upon a light circuit. One container 14 is shown in position on layer 10 adjacent the leading edge of the exposed area thereof.

For the purpose of applying a translatory compression to the liquid 16 in container 14 there is provided a pair of pressure means such as rolls 18 and 20. Roll 18 preferably has a smooth surface which is inert to the liquid 16 and to which the liquid 16 cannot adhere. A polished chromium, glass, enamel or plastic drum may be used for roll 18. Roll 20 is preferably a rubber roller, although it may be made of steel.

The photosensitive layer in one form of the process may comprise a diazonium compound such as that sold by the Boston Blue Print Co. under the trade name "Blackline #202." In this case the liquid reagent in the container preferably comprises the materials set forth in the following nonlimiting example:

Example 1

4 grams of medium viscosity sodium carboxymethyl cellulose
100 cc. of water
8 grams of "Blackline" developer #203½ (sold by the Boston Blue Print Co. and manufactured by Frederick Post Co., Chicago)

The container 14 for the liquid is preferably one which can, by the application of a mechanical stress thereto, be caused to release its contained liquid. A preferred type of container is one formed so that a mechanical stress applied thereto will cause one edge of the container to be open to release the liquid from this edge. The container is preferably positioned so that it extends transversely of the photosensitive layer and has a relatively short longitudinal dimension with respect to the longitudinal dimension of an image area on the photosensitive layer. A preferred container is formed of a single sheet of material which is impervious to the liquid. The sheet preferably comprises a paper-backed metal foil coated on its inner surface with polyvinyl butyral. The sheet is folded upon itself and as it is filled, it is sealed on the ends and along the edge opposite the fold, the end seals being preferably stronger than the edge seal.

During the use of the modification of the invention shown in Fig. 1, the photosensitive layer 10 is exposed to actinic light passing through the object 11 to be copied to differentially expose one or more images in the diazonium photosensitive layer. After exposure, container 14 is positioned along the leading edge of the exposed area extending at right angles to the direction of motion of the photosensitive layer. This layer, with the container thereon, passes between the rollers 18 and 20, which apply a sufficient compression to the container to cause the release of the liquid reagent 16 therefrom. The bulk of the liquid 16 is thus forced from the container 14 and, due to the relative motion between layer 10 and rolls 18—20, liquid 16 is translated across the surface of layer 10, covering one or more exposed image areas.

During this translatory motion of the liquid, the container is maintained fixed with respect to layer 10 and passes between the rolls. A thin film of liquid 16 is left on the layer 10 as the result of the liquid passage across this layer, the thickness of this layer being predetermined by the viscosity of the liquid, the spacing and pressure of the rolls, and speed of travel.

When the photosensitive layer comprises a sheet of "Blackline #202" and the liquid is of the type set forth above, a positive image of the object 11 is produced in the layer 10. Layer 10 is preferably kept in the dark or subdued light until such time as the photographic process is complete.

Another nonlimiting example of a diazonium photosensitive layer and a liquid reagent for the processing thereof is set forth below:

Example 2

The sensitizing bath contains:

Chlorostannate of para diazo di-n-butyl aniline	grams	20
Pontacyl Brilliant Blue 2R	gram	.4
Water	liter	1

This solution is applied to one side of a suitable stock and the coating dried. The liquid reagent contains 4 grams of medium viscosity sodium carboxymethyl cellulose, 100 cc. of water, 5.8 grams of sodium carbonate (monohydrate) and 2.3 grams of phloroglucinol.

Still another method of forming a positive image is set forth below:

Example 3

In this case the photosensitive layer is a sheet of paper which is dipped in a saturated water solution of DuPont Naphthanil Diazo Black B. The liquid 16 comprises a small amount of a solution containing 1500 cc. of a 5% water solution of sodium carboxymethyl cellulose to which 10 grams of resorcinol and 1 gram of sodium hydroxide are added.

While the container 14 has been shown as being fed from magazine 17, this container may be secured to the photosensitive layer 10 and fed with the layer 10 from a supply thereof. When this modification of the invention is employed, the means 12 must be so designed, such as being movable, as not to destroy the container as it passes under means 12.

When the container 14 is fed, as shown, from a magazine, it is desirable in some cases to provide a portion of the container which is adapted to make a strong frictional bond with the layer 10. This portion may comprise an adhesive coating on the bottom of the container or a staple extending through the ends of the container which penetrate the surface of layer 10. It is equally possible to provide clamping flanges on the edges of rolls 18 and 20 which clamp the ends of the container 14 tightly to layer 10 during the passage of the container 14 through the rolls. These flanges may also have the desirable effect of preventing end leakage from the container and also of helping to prevent spreading of the liquid reagent 16 past the edge of layer

10, where the liquid is sufficiently fluid as to tend to flow over this edge.

When the photosensitive layer 10 is a silver halide photosensitive material it may be processed to develop and fix a negative image therein or it may be processed to produce a positive image, as more fully discussed in connection with the description of Figs. 3 and 4 hereinafter.

Referring now to Fig. 2 there is shown a schematic cross-sectional view of a modification of the apparatus and process of Fig. 1. In Fig. 2 like numbers correspond to like numbers of Fig. 1, and 10 represents the photosensitive layer, 14 represents the container, 16 the reagent and 20 a pressure-applying means such as a roller. There is also provided another layer 22 to which the containers 14 may be secured at predetermined intervals. A second pressure roll 24 is adapted to cooperate with roll 20.

In the use of the modification of the invention shown in Fig. 2, the photosensitive layer 10 is exposed to actinic light and then brought into contact with layer 22, the container 14 being positioned along the leading edge of the exposed area and between layers 10 and 22. As the two layers and container pass between the pressure rollers 20—24, the liquid 16 is forced from container 14 and translated across the surface of layer 10 while being confined to the space between these two layers. The film of liquid thus created permeates the photosensitive layer 10 and creates a visible image therein.

At least the outer surfaces of layers 10 and 22 may be opaque, thus constituting an opaque lamination when they are discharged from the rolls 20—24. This permits the opaque lamination to be discharged directly from the apparatus into bright light without interfering with the photographic process. This feature of the invention is particularly desirable when the photosensitive layer 10 comprises a sensitive material such as a silver halide. In this latter case the liquid composition may comprise a developer and a silver halide solvent which can at least develop and fix a negative image in the photosensitive layer.

When it is desired to obtain a positive image from a latent negative image contained in a silver halide photosensitive layer, it is preferred that the reagent spread in contact with the photosensitive layer be such that it cannot, in its unmodified form, create a visible effect in the stratum which is to contain the positive image. This visible effect may be the creation of a white visible effect corresponding to the highlights of the positive or a dark visible effect corresponding to the shadows of the positive. When the dark visible effect is to be created, it can be by the formation of a pigment or a dye. This pigment can be most readily created by forming silver complexes with unexposed silver halide grains in the negative, transferring these complexes to the stratum of the positive image and there converting them into dark particles of silver. When a dark dye is to be formed to constitute the positive image, it is preferred that a portion of the dye-forming component be included in the negative layer so that this component does not transfer to the positive until it has been reacted with the negative and thus exhausted in proportion to the density of the negative. The total amount of this component per unit area of the negative is preferably no more than enough to be completely reacted and exhausted in a unit area of the negative having maximum exposure. When the dye is formed solely by self-coupling of a developer, the developer is included in the emulsion in an inert state, such as in a solid form. When the dye is formed by a reaction between a developer and a color-former, either or both of these components is included in the negative emulsion. The portion of the developer that is oxidized, by the development of exposed silver halide, couples in the negative and is there trapped, thus accomplishing either or both an exhaustion of the developer or the color-former in the area of the highlights of the positive.

In the above cases, the portion of the developer that is to couple to form the dye in the positive may be oxidized in the stratum of the positive image by the use of an oxidizing agent such as, for example, a reducible metal salt, sodium perborate, or air.

When a positive silver image is desired on the surface of layer 22, the negative and positive images are preferably formed by concurrently developing exposed and unexposed silver halide in different strata of the formed lamination. This is most conveniently accomplished by providing a reagent 16 which contains a developer and a silver halide solvent. A suitable liquid composition for this purpose is set forth in the following nonlimiting example:

Example 4

1860 cc. of water
93 grams of sodium carboxymethyl cellulose
78 grams of sodium sulfite
74.6 grams of sodium hydroxide
14.5 grams of sodium thiosulfate
38.5 grams of citric acid
52 grams of hydroquinone

A preferred layer 22 adapted to receive and carry on its surface a positive image of a latent negative image in photosensitive layer 10 may be prepared as set forth in the following nonlimiting example:

Example 5

A sheet of bond paper 22 is run through a bath containing by weight 10% cadmium acetate, 1% lead acetate and 30% zinc nitrate, the sheet being in contact with this bath for about 30 seconds.

With the liquid composition of the type described in Example 4 and a sheet of paper 22 prepared as in Example 5, the photosensitive layer 10 preferably comprises a contrasty silver bromide photosensitive film such as that cold by Eastman Kodak Company under the trade name of "Kodabromide F4." This particular combination of elements is particularly suited for obtaining, in about 5 seconds, extremely contrasty positives with a gamma of about 11 or 12, thereby being particularly adapted for photocopy work. The developer develops the latent negative image; the silver halide solvent forms soluble complexes with the unexposed silver bromide and transfers these complexes to the layer of liquid and the surface of layer 22 where they are converted to particles of visible silver constituting the positive image.

The high contrast in the positive image formed by the above process is due to the fact that formation of the positive seems to depend upon the attainment of a predetermined degree of saturation of silver (in complex or ionic form) in the stratum of the positive image before precipitation of a silver speck and condensation of silver on this speck will occur. Once precipitation starts, the thiosulfate ion is free to dissolve

more silver and thus builds up the density in the shadows by further precipitation. The rapid development of the negative, coupled with the contrasty characteristics of the negative and the requirement for the predetermined degree of saturation tends to give an "all or none" effect in the formation of the positive. Where silver is deposited, it is a dense black, while where the saturation does not quite reach the predetermined amount, clear whites result.

After the positive image on layer 22 has been separated from the negative layer 10, a second positive image may be obtained with the above materials by laminating the negative layer 10 to a second positive layer 22 by means of another layer of liquid which may be identical to the liquid of Example 4. This should be accomplished in the dark and may be practiced conveniently by providing an automatic stripper in the apparatus of Fig. 2 to separate the first positive layer from the negative layer. In this case there is also preferably provided another supply of positive paper, with containers, and another pair of pressure rolls.

When it is desired to reproduce a photograph or other image having middle tones by use of the extremely high contrast process of Examples 4 and 5, this may be readily accomplished either by exposing the negative layer 10 through a half-tone screen at the time the latent negative image is created therein or by pre-exposing the negative to a half-tone screen.

The apparatus and process of Fig. 2 is widely adaptable to other photographic processes such as the printing of a pattern on wood, metal, etc. In this case the layer 22 may comprise a sheet of wood, the other elements being the same as previously described. With such a modification, a positive image is created on the surface of the wood which is an exact copy of the pattern on the object 11 originally photographed. This modification of the invention is thus of excellent utility in the woodworking arts.

Where a sheet of metal is used as the layer 22 for the purpose of producing a pattern on metal to guide, for example, subsequent cutting operations on the metal, the sheet of metal is first preferably coated with a film of plastic, or otherwise treated so as to improve the adhesion of the film-forming material in the liquid composition to the surface of the metal. In this case the positive image is formed in the layer of film-forming material contained in the spread liquid or in the precoated film on the metal. This precoated film and the film-forming material of the liquid are preferably water soluble so that they may be washed off the metal after it has been cut along the lines indicated by the positive image on its surface. This form of the invention is of particular advantage in the aircraft and other industries where the rapid production of patterns on sheet metal is desired.

In still another form of the invention the layer 22 may comprise a layer of a substance that can be photochemically hardened, such as a bichromated colloid, for example gelatin or polyvinyl alcohol, carried on a suitable base such as a cellulosic material or a metal sheet. In this case the positive image can be formed in the layer of liquid which forms a dimensionally stable film that adheres to the surface of the colloid layer 22. This layer 22, with the formed film on its surface, is separated from the negative layer 10 and exposed to strong actinic light, the positive image in the formed film masking the colloid (i. e. gelatin) layer and thus causing differential exposure of the bichromated gelatin, with consequent differential hardening thereof. The unhardened gelatin, along with the positive image, is then washed off, leaving a gelatin relief. The above process may be modified by forming a positive image on one side of a transparent layer which carries, on its other side, the bichromated gelatin. The exposure of the bichromated gelatin, in this latter case, is through the formed film and the base layer. These modifications of the invention thus give a very fast method of forming gelatin reliefs for printing, etc.

Instead of producing a positive image for masking the bichromated gelatin, the liquid composition may only develop the latent negative in the photosensitive layer and this developed negative may be used to modify light passing therethrough to harden differentially the gelatin. In such a case the liquid may conveniently contain a substance capable of desensitizing the unexposed silver halide of the negative when those grains would tend to become developable by exposure to the light used for hardening the gelatin. Development of these grains may also be inhibited, during the second exposure, by acidifying the liquid composition in contact therewith or drying out this liquid prior to this second exposure. The opacity of this negative can be intensified, if desired, by using a color-forming developer for developing the negative.

This negative image may also be formed by incorporating, on the surface of layer 22, an immobile dye-former capable of coupling with those portions of the developer oxidized by the development of the exposed silver halide grains in the photosensitive layer 10. Subsequent coupling in the undyed parts of the negative dye image may be prevented by acidifying the developer remaining in these parts to prevent coupling, this acidifying reaction being conveniently accomplished by dissolving a substance of acid reaction from the layer 22.

When the bichromated gelatin is coated on a metal base, the gelatin relief obtained may be used as a mask to cause the differential etching of the metal by an acid, for example. Thus this form of the invention is also particularly adapted to preparing metal printing plates.

In still another modification of the invention, the layer 22 comprises a sheet of unhardened gelatin supported on a suitable base. In this case the gelatin of layer 22 preferably includes a sulfide or selenide which assists in forming the positive silver image in the gelatin rather than in the layer of liquid spread between layers 10 and 22. The gelatin may be selectively hardened during formation of the positive by the use of a tanning developer, or the gelatin may be hardened afterwards by the use of a tanning agent whose action is catalized by colloidal silver. The unhardened gelatin may then be washed away and the layer 22 may be used as discussed previously.

In still another modification of the invention the support for the bichromated gelatin comprises a layer containing a solution of a dye or pigment-forming material or a solid dye or pigment, such as printing ink. In this case the hardened gelatin serves as a mask to permit the selective release and transfer of the dye or pigment to a piece of paper in a "mimeograph" or "hectograph" type of machine. This modification of the invention is therefore particularly adapted to the cheap, fast production of multiple copies of correspondence, etc.

Instead of forming a relief of a substance such as gelatin, the differentially hardened substance may be used for printing due to differential absorption of, or substantivity to, different dyes or inks. The portion hardened (i. e., negative or positive) will depend upon the material used in printing. For example, with a "pina type" dye the hardened portion constitutes the highlights of a positive image, the dye being substantive to unhardened gelatin and being transferable therefrom to a sheet such as paper. When a greasy ink is employed, the unhardened portion absorbs water and repels the greasy ink, which adheres only to the hardened portion. Therefore, in this case, the hardened portion is that portion corresponding to the shadows of the positive image.

Referring now to Figs. 3 and 4, there is shown another modification in the invention particularly suited for use as a hand camera. Fig. 3 is a schematic cross-sectional view of an apparatus in the form of a hand camera, and Fig. 4 is a fragmentary sectional view of Fig. 3 taken along the line 4—4. In these figures, there is schematically shown a folding camera having a usual bellows, lens and shutter. The camera has a housing 30 to which is hinged a back plate 32. In the housing there is provided a roll 36 of a photosensitive film which is preferably a silver halide emulsion. This film is fed from the supply roll through a light-tight opening 40. The film is then passed over a pressure member 42, which may be a part of the back plate 32, and the film is passed out of the camera through another light-tight opening 44. This second opening 44 is preferably defined by a portion of the pressure member 42 and a pivoted end plate 46. A light seal 47 is provided at the junction between end plate 46 and housing 30. Carried by the pivoted end plate 46 is a slidably mounted pressure plate 48 which is preferably mounted in grooves 50 in the end plate 46. Means, such as a catch 52, are provided for holding the end plate 46 in a predetermined relation to the pressure member 42. Thus the pressure plate 48 is predeterminedly spaced from the pressure member 42, providing a gap which is a few thousandths of an inch greater than the thickness of layer 36. Provided on the inner surface of pressure plate 48 is a pair of clamps 54 adapted to hold a fluid container 56 in a predetermined position on the pressure plate. The portion of the pressure plate 48 adapted to hold the container 56 may be slightly recessed to aid in the movement of the container past the pressure member 42, in those cases where the material from which the container is made has a considerable thickness with respect to the gap. The pressure plate 48 may be a rigid member or can be relatively flexible, it being rigidly backed, in this latter case, by the end plate 46. This pressure plate is also preferably inert to the liquid composition in container 56 and preferably has a surface to which the liquid does not adhere as well as it adheres to the film 36.

Adjacent the top of the end plate 46 and mounted on the housing 30 is a light-seal 58 which, in conjunction with the other light-seals 40, 44 and 47, defines a light-tight chamber into which the exposed photosensitive layer may be brought for processing without danger of fogging.

On the bottom of the pressure plate 48 there may be provided a clamp 60 adapted to hold the end of the film 36 in fixed relation to the end of the pressure plate 48.

In the use of the invention described in connection with Figs. 3 and 4, the roll of photosensitive film 36 is inserted in the camera by removing the back plate 32 and threading the film through the light-tight openings 30, 38 and 44. The end plate 46 is then swung to the side and a container is positioned on the pressure plate 48, preferably being held by the clamps 54, although it may be secured thereto by means of a weak adhesive bond. The end plate is then moved to its closed position, thus placing the container in a light-tight chamber within the camera apparatus. The user of the camera may then pull the end of the film 36, if he has not already done so, until a photosensitive frame of the film is brought into the focal plane of the camera. The camera shutter is operated to expose this frame and the end of the film extending from the camera is engaged by the clamp 60 carried by the pressure plate 48. The user of the camera then draws the pressure plate downwardly, as shown in Fig. 3, thus applying a progressive mechanical stress to the liquid in the container 56 which causes the liquid to be released from the container and which translates the bulk of the liquid across the surface of the exposed photosensitive film and laminates this exposed film to the pressure plate 48. This layer of liquid can then be used for accomplishing a desired processing of the exposed film such as the development and fixing of a latent negative image in the film 36. When the above processing is completed, the processed film may be separated from the pressure plate.

In a preferred modification of the invention the film 36 has an opaque back so that when it is laminated to the pressure plate, which is also preferably opaque, the photographic processing may take place within this opaque lamination unhampered by actinic light.

If a positive image is desired, when using the process and apparatus in the above type, the photosensitive emulsion may be a "tintype" emulsion, a "solarized" emulsion, or it may be a standard silver halide emulsion. In this latter case the liquid composition in the container may comprise a liquid of the type shown in Example 4, to which a white pigment such as titanium dioxide or zinc sulfide has been added. The zinc sulfide is preferred since it has the ability of replacing its surface zinc ions with silver ions transferred in the form of silver complexes from the negative image by means of the silver halide solvent included in the liquid. An acceptacle image is obtained by the use of titanium dioxide, however, this image being formed by reduction in the layer of liquid of silver complexes transferred from the negative to the layer of liquid.

Where sufficient light is available for exposure of the photosensitive layer, a diazonium photosensitive material may be used in the apparatus and process described above.

The apparatus of Figs. 3 and 4 is also usable with those processes where a positive image is formed on or adjacent the surface of a separate layer of paper which is laminated to the negative photosensitive paper during the processing thereof. In this case, such a piece of paper may have the container 56 secured to its surfaces and this piece of paper may be suitably mounted on the pressure plate 48 by means such as clamps 54 adapted to engage the edges of the piece of paper. In this case the operation of the device is the same as that described above with the exception that the liquid in the container 56 is

discharged and spread between the surface of the photosensitive layer 36 and the sheet of paper. The spacing between the pressure plate and the fixed pressure member should be increased to compensate for the added thickness of the positive sheet.

When the positive image is formed on a sheet of paper, this paper may be prepared as set forth in the following nonlimiting example:

Example 6

A sheet of baryta paper is treated in a bath of the type described in Example 5, dried and then coated with a thin film of a mixture made by thoroughly mixing 3 grams of silica aerogel ("Santocel") in 28 cc. of a 1% water solution of sodium sulfide.

For use with the above sheet, the liquid composition is preferably similar to that set forth in Example 4, and the photosensitive layer 36 may comprise a "fast" film such as Eastman "Verichrome."

When a sheet of paper is used for receiving and carrying a positive image of a latent negative image in film 36 it may conveniently be provided with a trap on its trailing end so as to trap any excess liquid which might otherwise be spread beyond the end thereof. This trap may take the form of an embossed depression near this trailing end. The pressure plate preferably has, in this case, a corresponding depression therein. Thus, as this depression in the sheet passes between the gap defined by the pressure member 42 and the depression in the pressure plate 48, the increased effective size of the gap becomes large enough so that the liquid is no longer spread and remains within this depression on the paper.

When another layer, hereinafter referred to as an image-carrying layer, is used in the apparatus of Fig. 3 for receiving and carrying a positive image of a latent negative image created in the photosensitive layer 36, it may be prepared as set forth in the following nonlimiting example:

Example 7

A sheet of baryta paper is run over a bath containing a ⅛% water solution of neutral lead acetate with preferably only one surface of the sheet touching the bath and being in contact with the bath for about 1 minute. The sheet is dried by passing over a drum and then is passed over a bath containing a 1/40% water solution of sodium sulfide, being in contact with this bath for about 4 seconds.

When the photosensitive layer 36 comprises a fast silver bromiodide film such as Eastman "Verichrome" or Ansco "Triple S Pan" and the liquid composition is like that described in Example 4, an image-carrying layer of the type described immediately above gives excellent sepia images having extremely high resolving power and very good stability to humidity, heat and radiation. This is particularly true if the liquid composition is spread in a very thin film between the two layers. This high stability is believed to be due to the fact that the amount of developer per unit area of the spread film is less than enough to develop fully a fully developable portion of the negative and is thus substantially completely exhausted and trapped in the fully exposed portions of the negative. This complete exhaustion of the developer in the highlights of the positive thus prevents any subsequent staining of the highlights. The excellent detail, high density and contrast of the positive is due to the thinness of the spread liquid and the high covering power of the transferred silver in the positive image. The silver halide emulsion can be coated on an opaque paper base, thus being considerably cheaper than ordinary film since the negative does not have to be used for modifying light to print the positive. This feature of the invention is thus particularly useful in all fields of photography where cheap, excellent pictures are desired and is particularly advantageous for X-ray and radium ray pictures, since a cheap, fast emulsion coated on paper and used with an image-carrying layer of the type described above gives excellent photographs which appear to be better than those obtained with the expensive double photosensitive layers of the usual X-ray film.

The silver complex transfer process described in connection with the use of Examples 4, 5, 6 and 7 is particularly useful in controlling the photographic quality of the positive. It has been found that the contrast and gamma of the positive image increases with time of development thereof. Thus when the contrast of the subject is low and it is desired that the positive have a higher contrast, development is allowed to continue for a relatively long time (e. g. a minute and a half). Where the subject is very contrasty or a soft scale is desired, development of the positive is stopped in a shorter time (e. g. 45 seconds), development of the positive being stopped by separating the image-carrying layer from the photosensitive layer.

From the above description of the invention, it can be seen that it is of extremely wide application. It can be used with all types of photosensitive materials such, for example, as diazonium, silver halide, lead halides and azides, ferric salts, bichromates and others. These photosensitive materials may range in sensitivity from the slowest, such as the bichromates, to the fastest, such as silver bromiodide. Their spectral response may range from radiations of less than 1 angstrom, such as alpha and gamma rays, to the infrared.

The invention may be used for obtaining negative images in the photosensitive layer or on another layer. Positive images may be obtained in the photosensitive layer, in the formed film from the liquid, or in the surface of another layer. The positive may be the final positive or may be a printing master for producing multiple positive or negative copies of the original object photographed. The invention is also of extreme utility in the woodworking, metal working, printing, duplicating, and other arts.

While the various reactive ingredients of the reagent are preferably included in the liquid composition, they may be included in an inert state in the photosensitive or other layers processed. In this case the liquid reagent may only comprise a solvent for the reactive ingredients and preferably a viscosity-increasing material to assist in controlling the spreading of the reagent. It is equally possible to include part of the active ingredients in the liquid and part on the layer or layers to be processed.

In some cases it may be desirable to process one or more of the exposed photosensitive areas by ordinary tank development. In these cases the process and apparatus of the invention are particularly useful since they permit the laminating of the exposed photosensitive layer to a sheet of opaque material such as paper. For such a laminating the liquid in the container may

comprise a solution of a suitable adhesive which is inert to the photosensitive material, such as a viscous solution of sodium carboxymethyl cellulose in water. This feature of the invention is particularly useful with the modification of Figs. 3 and 4, wherein the user of the camera may wish to save a few frames of roll 36 for subsequent development in a tank so as to give special toning, shading, or background effects during the processing. In order to accomplish this, it is only necessary to place, on plate 48, an opaque piece of paper having a container secured thereto, the container holding the inert viscous solution of the adhesive.

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

What is claimed is:

1. The method of transforming an image in a predetermined area of a photographic, photosensitive sheet material, said image having been formed in the photosensitive layer of said sheet material by photoexposure, which method comprises locating a liquid-tight, rupturable container adjacent one edge of said area with the long dimension of said container substantially parallel to said edge, said container having an elongated liquid-containing cavity of a length at least equal to the width of said area, said cavity holding a viscous processing liquid at least in sufficient quantity to provide all the liquid for said image transformation, said processing liquid containing a solid film-forming colloid for substantially increasing the viscosity thereof, and, while maintaining said container and said sheet material fixed with respect to one another, moving the same relative to a pair of pressure-applying members, said relative motion causing said members to squeeze the contents from said container along substantially the entire length of the liquid containing portion of the container, one of said members contacting the surface of said container and thereafter contacting the released liquid to spread the same in a thin layer during the continuance of said relative motion, the surface of said last-named pressure-applying member in contact with said liquid having substantially less affinity for said liquid than has said element whereby the liquid and the film-forming material therein adhere almost entirely to the photosensitive sheet material upon separation of said last-named pressure-applying member and said sheet material.

2. The process of claim 1 wherein the photosensitive sheet material has a silver halide emulsion as its photosensitive layer, and the processing liquid contains a silver halide developer in sufficient quantity to develop a latent image in said photosensitive layer.

3. The process of claim 1 wherein the pressure-applying members are a pair of rolls, the roll contacting the container and the liquid having a polished surface inert to the liquid.

4. The process of claim 1 wherein the pressure-applying member contacting the container and the liquid is a plate having a polished surface inert to the liquid.

5. The process of claim 1 wherein the photosensitive sheet material comprises a diazonium compound as its photosensitive material and the processing liquid contains a developer for the diazonium compound.

6. The method of forming copies of documents which comprises positioning the document to be copied on the surface of a photographic, photosensitive element capable of having a developable image formed therein upon photoexposure, photoexposing said element through said document so as to form in the photosensitive layer thereof an image of the subject matter of said document, advancing the photosensitive element with the document superposed thereon past a document-removing station capable of separating the document from said element, locating a liquid-tight, rupturable container adjacent one edge of the exposed area of said photosensitive element with the long dimension of said container substantially parallel to said edge, said container having a liquid-containing cavity of a length at least equal to the width of said area and holding a viscous processing liquid which contains a solid film-forming colloid for increasing the viscosity thereof and a developer in sufficient quantity to develop the image formed in said area and, while maintaining said container and said element fixed with respect to one another, moving the same relative to a pair of pressure-applying members, said relative motion causing said members to squeeze the contents from said container along substantially the entire length of the liquid containing portion of the container, one of said members contacting the surface of said container and thereafter contacting the released liquid to spread the same in a thin layer during the continuance of said relative motion, the surface of said last-named pressure-applying member in contact with said liquid having substantially less affinity for said liquid than has said element whereby the liquid and the film-forming material therein adhere almost entirely to the photosensitive element upon separation of said last-named pressure-applying member and said element.

7. The process of claim 6 wherein the photosensitive element has a silver halide emulsion as its photosensitive layer and the processing liquid contains a silver halide developer in sufficient quantity to develop a latent image in said photosensitive layer.

8. The process of claim 6 wherein the pressure-applying members are a pair of rolls, the roll contacting the container and the liquid having a polished surface inert to the liquid.

9. The process of claim 6 wherein the pressure-applying member contacting the container and the liquid is a plate having a polished surface inert to the liquid.

10. The process of claim 6 wherein the photosensitive element comprises a diazonium compound as its photosensitive material and the processing liquid contains a developer for the diazonium compound.

11. In a photographic apparatus, mechanism for subjecting an exposed photosensitive film to a predetermined processing by spreading thereon the contents of a rupturable container, said mechanism comprising means defining a first lighttight chamber in said apparatus, means defining a second lighttight chamber in said apparatus adjacent said first chamber, a passageway connecting said first and second chambers so that an exposed photosensitive film may be fed directly from said first chamber to said second chamber, said second chamber comprising a pair of passages connecting with the exterior of the

apparatus, each said passage being at least as wide as the width of said film and each having a light seal associated therewith, said passages being located opposite one another, a platelike member slidably mounted in said passages so as to extend through said second chamber and being adapted to have the photosensitive film superposed thereon in said second chamber, and means adjacent one of said passages providing a withrawal area at said passage having a thickness less than the combined thickness of a filled container, said platelike member and said film whereupon the rupture and spreading of the contents of a container are obtained when the latter is passed through said withdrawal area between said member and the film superposed thereon.

12. A photographic apparatus for exposing a photosensitive film and for subjecting the same to a predetermined processing by spreading thereon the contents of a rupturable container, said apparatus comprising means for mounting a supply of said photosensitive film, means defining an exposure chamber wherein a predetermined area of said photosensitive film may be exposed to predetermined subject matter, means defining a withdrawal opening from said exposure chamber, said last-named means being located adjacent one edge of said chamber and comprising a light seal, means providing a processing chamber with which said withdrawal opening connects, said last-named chamber means comprising a pair of passages connecting with the exterior of the apparatus, each said passage being at least as wide as the width of said film and each having a light seal associated therewith, said passages being located opposite one another so that a platelike member, at least as wide as the width of the film, is capable of being inserted into said processing chamber through one of said passages and withdrawn from the processing chamber through the other of said passages, and means adjacent said second passage for so confining the withdrawal area as to effect the rupture and spreading of the contents of a container when the latter is passed therethrough between a platelike member and said film.

13. A photographic apparatus for exposing a photosensitive film and for subjecting the same to a predetermined processing by spreading thereon the contents of a rupturable container, said apparatus comprising means for mounting a supply of said photosensitive film, means defining an exposure chamber wherein a predetermined area of said photosensitive film may be exposed to predetermined subject matter, means defining a withdrawal opening from said exposure chamber, said last-named means being located adjacent one edge of said chamber and comprising a light seal, means providing a processing chamber with which said withdrawal opening connects, said last-named chamber means comprising a pair of passages connecting with the exterior of the apparatus, each said passage being at least as wide as the width of said film and each having a light seal associated therewith, said passages being located opposite one another and being spaced by a distance greater than the width of one of said rupturable containers and less than the length of the film adapted to be exposed in said exposure chamber, a rigid platelike member at least as wide as said film and longer than the length of the film frame capable of exposure in said exposure chamber, said platelike member being slidably mounted in said passages so as to have both ends thereof projecting from said apparatus and including means for affixing thereto one of said containers, and means in said chamber adjacent the withdrawal passage for said platelike member and said film for cooperating with said platelike member during the slidable movement thereof for rupturing the container and releasing the contents thereof so as to spread the same over the photosensitive film as the latter is withdrawn from the camera together with said platelike member.

14. A photographic apparatus for exposing a photosensitive film and for subjecting the same to a predetermined processing by spreading thereon the contents of a rupturable container, said apparatus comprising means for mounting a supply of said photosensitive film, means defining an exposure chamber wherein a predetermined area of said photosensitive film may be exposed to predetermined subject matter, means defining a withdrawal opening from said exposure chamber, said last-named means being located adjacent one edge of said chamber and comprising a light seal, means providing a processing chamber with which said withdrawal opening connects, said last-named chamber means comprising a pair of passages connecting with the exterior of the apparatus, each said passage being at least as wide as the width of said film and each having a light seal associated therewith, said passages being located opposite one another and being spaced by a distance greater than the width of one of said rupturable containers and less than the length of the film adapted to be exposed in said exposure chamber, a rigid platelike member at least as wide as said film and longer than the length of the film frame capable of exposure in said exposure chamber, said platelike member being slidably mounted in said passages so as to have both ends thereof projecting from said apparatus and including means for affixing thereto one of said containers, means located adjacent the leading edge thereof for clamping thereto the leading edge of the film, and means in said chamber adjacent the withdrawal passage for said platelike member and said film for cooperating with said platelike member during the slidable movement thereof for rupturing the container and releasing the contents thereof so as to spread the same over the photosensitive film as the latter is withdrawn from the camera together with said platelike member.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,285,015	Browning	Nov. 19, 1918
1,841,653	Van Der Grinten	Jan. 19, 1932
1,956,230	Schmidt	Apr. 24, 1934
2,196,226	Murray	Apr. 9, 1940
2,352,014	Rott	June 20, 1944
2,435,717	Land	Feb. 10, 1948
2,435,718	Land	Feb. 10, 1948
2,435,719	Land	Feb. 10, 1948
2,455,735	Condax	Dec. 7, 1948

FOREIGN PATENTS

Number	Country	Date
879,995	France	Dec. 10, 1942
896,127	France	Apr. 17, 1944
900,266	France	Sept. 25, 1944
59,365	Netherlands	Apr. 17, 1947