Dec. 1, 1953 E. H. LAND 2,661,293

PROCESS OF PRODUCING A COLORED PHOTOGRAPHIC IMAGE BY MEANS OF EXHAUSTION OF DEVELOPER

Filed Oct. 8, 1946

FIG. 1

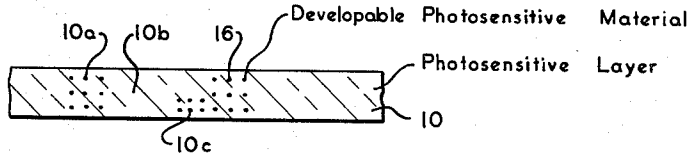


FIG. 2

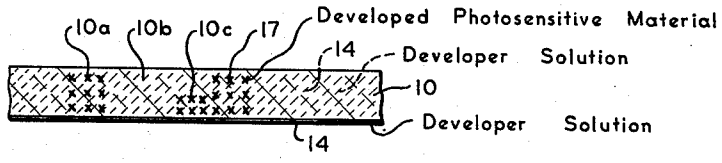


FIG. 3

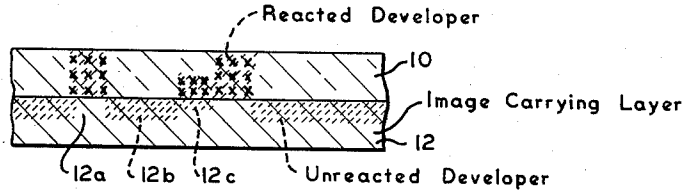


FIG. 4

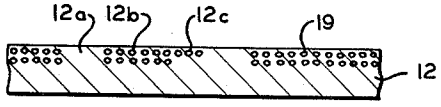


FIG. 5

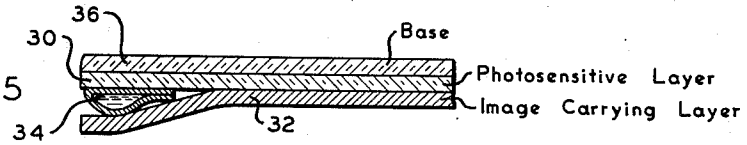


FIG. 6

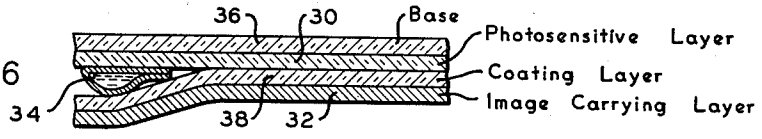
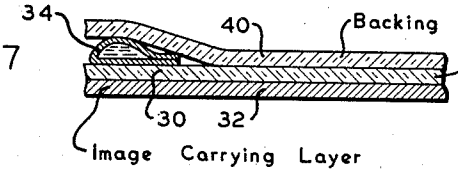


FIG. 7



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PROCESS OF PRODUCING A COLORED PHOTOGRAPHIC IMAGE BY MEANS OF EXHAUSTION OF DEVELOPER

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Application October 8, 1946, Serial No. 702,039

8 Claims. (Cl. 95—88)

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This invention relates to photography and more particularly to novel photographic processes and novel composite photographic film units for use with such processes.

This application is a continuation in part of my copending application Serial No. 539,550, filed June 9, 1944, for Photographic Product, Process and Apparatus (now abandoned and replaced by application Serial No. 64,870, filed December 11, 1948, and which issued as Patent No. 2,543,181 on February 27, 1951).

It is a principal object of this invention to provide an improved photographic process wherein a visible positive image is obtained from a photosensitive layer containing a latent or developed negative image, by utilizing the differential effect created by said photosensitive layer on a substance, usable in forming said visible positive image, to control the amount of said substance which is available for creating said positive image.

Another object of the present invention is to provide a photographic process wherein a photosensitive layer containing a latent or developed negative image is permeated with a substance having the capability of entering into a reaction which produces a visible effect on another layer, said substance is reacted with a material in said photosensitive layer to selectively make portions of said substance incapable of creating said visible effect, and the remainder of said substance is used to create said visible effect on said other layer, said visible effect, due to its selective creation, forming a positive image.

Another object of the present invention is to assure, in processes of the above type, a substantially complete reaction of said substance with said material prior to the creation of said visible effect.

Another object of the invention is to provide a novel photographic process wherein a developer is reacted with a layer of photosensitive material containing a latent negative image to cause a development of said latent negative image and the portions of said developer which are not reacted by said photosensitive material during said development reaction are utilized in forming a positive image of said latent negative image in or on another layer.

Another object of the invention is to provide a positive image-forming reaction in a process of the above type wherein said unreacted portions of said developer are utilized to form a dye constituting a positive image.

Another object of the invention is to provide

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a positive image-forming reaction in a process of the above type wherein said unreacted portions of said developer are utilized to form a pigment constituting a positive image.

Another object of the invention is to improve the contrast of a positive image produced in a process of the type described above by preventing migration of reacted portions of said developer from said photosensitive layer to said other layer.

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

The invention accordingly comprises the process comprising the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, 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 accompanying drawing wherein:

Figures 1 through 4 are diagrammatic representations of various steps of a preferred modification of the invention; Figure 1 showing a photosensitive layer containing a latent negative image; Fig. 2 showing the photosensitive layer after development; Fig. 3 showing an image-carrying layer formed into a permeable assembly with the developed photosensitive layer; and Fig. 4 showing the final positive image on the image-carrying layer;

Fig. 5 is a diagrammatic cross-sectional view of a composite photographic film unit showing one physical embodiment of the invention;

Fig. 6 is a diagrammatic cross-sectional view of a composite photographic film unit showing another physical embodiment of the invention; and

Fig. 7 is a diagrammatic cross-sectional view of a composite photographic film unit showing still another physical embodiment of the invention.

In general this invention relates to novel photographic processes and products for the production of a fixed stable positive image of a latent or developed negative image contained in a photosensitive layer, the positive image being formed in or on another layer hereinafter referred to as an image-carrying layer.

A real image of any object is a visible likeness or reproduction of that object. Photographically, an image may be recorded in a photosensitive layer by transforming said layer, which is originally substantially homogeneous throughout its

volume, to a layer such that a chemical characteristic thereof has an imagewise variation throughout the image area, the variation being a function of the brightness aspects of the original subject image. The resulting record image may be a real image, i. e., a visible image, or a latent image, i. e., an image which, while not visible per se, has the capacity upon suitable chemical treatment to produce a visible image. The term "record image," when used here in its photographic sense, may be characterized as a record of the brightness aspects of any predetermined subject matter such as a person, object, or real image, the record being in the form of a layer of material of predetermined small thickness having throughout its image area an imagewise variation of a chemical characteristic of the layer, this chemical characteristic being capable of producing a visible contrast either by virtue of imparting different optical characteristics per se to said layer or by making possible the differential chemical treatment of said layer whereby differential optical characteristics are imparted to said layer.

This invention relates to the use of such a record image in a photosensitive layer for forming another image on an image-carrying layer, said other image being reversed in the positive-negative sense with respect to said record image.

In its preferred aspect the process involves the production on an image-carrying layer of a positive image of a record negative image by permeating the layer containing said negative image with a uniform quantity of a substance in solution, selectively utilizing the differential chemical characteristic of said layer to produce an effect on said uniformly permeated substance, said effect being a function of the imagewise variation of said chemical characteristic, transferring unaffected portions of said substance to said image-carrying layer and utilizing said unaffected portions to creat a varying visible effect which gives a positive image of said negative image.

The creation of the visible effect on the image-carrying layer may be the result of the creation of a color.

The first step of the preferred process is to permeate a uniform quantity of a liquid composition into the photosensitive layer containing a record image comprising a latent or developed negative image. The liquid composition preferably comprises a solution of a reactive substance. The latent or developed negative image in the photosensitive layer preferably comprises a photosensitive material having an imagewise distribution which varies as a direct function of the exposure creating said latent or developed negative image.

The amount of reactive substance permeating a unit area of the photosensitive layer is substantially uniform throughout an area thereof at least coextensive with said negative image and is preferably such that it will be substantially completely reacted by the portion of said photosensitive layer containing a highest concentration of said imagewise distributed material.

This reactive substance in the liquid composition is one having the capability of entering into a reaction with said material in said photosensitive layer and also of entering into a reaction which produces a visible effect on said image-carrying layer.

In the next step of the process, the reactive substance is reacted with the material in the photosensitive layer and portions of said substance are rendered incapable of producing a visible effect as the result of this reaction. The extent of reaction between the substance and the material in the photosensitive layer preferably varies, from point to point thereof, as a function of the point-to-point degree of exposure creating the negative image. There thus remains a distribution of unreacted substance whose capability of creating a visible effect varies in amount from point to point.

As another step of the process, the remainder of the reactive substance, i. e., that portion thereof which did not react with the material in the photosensitive layer, is thereafter transferred to said image-carrying layer from said photosensitive layer by superimposing one of said layers on the other of said layers, the superimposing being sufficiently intimate to permit the migration of said unreacted portions of said substance without any substantial degree of dispersion. The transferred unreacted portions of said substance are then utilized for creating a visible effect on said image-carrying layer. This visible effect preferably comprises the creation of a color and varies from point to point in accordance with the distribution of the unreacted substance. Due to the selective visible effect, i. e., color created, there is formed a positive image of said negative image on said image-carrying layer.

Referring now to Figs. 1 through 4 there is shown a diagrammatic representation of the various steps of a preferred embodiment of the process of the present invention.

Referring specifically to Fig. 1 there is provided a layer of photosensitive material **10**, which is shown as having been exposed to a subject image to create developable portions indicated by the dots **16**, these dots representing developable grains of photosensitive material. Various portions of the photosensitive layer **10** have different amounts of developable grains **16** therein, portion **10***a* having a maximum amount of developable grains, portion **10***b* having substantially no developable grains, and the portion **10***c* having about half of its grains developable.

In Fig. 2, the photosensitive layer **10** is shown as having been uniformly permeated with a solution of the reactive substance. This permeation is such that there exists a predetermined quantity per unit area of the substance distributed through the photosensitive layer **10**. The uniform permeation is accomplished such as by dipping the photosensitive layer in a concentrated bath of the reactive substance, the photosensitive layer being in contact with the bath only long enough to absorb a predetermined quantity of the concentrated substance **14**, either on its surface or within the layer **10**. The photosensitive layer **10** should not be left in the bath long enough to permit the transfer of reacted portions of the substance from the layer **10** to the bath. The concentration of the bath should be so high that the photosensitive layer **10** may take up and support a uniform quantity of the substance, the concentration of the substance per unit area supported by the layer **10** being preferably just enough to be completely reacted by a most reactive portion of the pohotosensitive layer **10**. Other methods of applying the solution of the substance to the photosensitive layer are equally feasible such as spreading a predetermined layer **14** of a viscous solution of the substance in contact with the surface of the photosensitive layer **10**. The substance may also be applied by other means such as by spraying, etc.

After the solution has permeated the photosensitive layer 10, the reactive substance reacts with the developable portions 16. The distribution of one of the products of this reaction is indicated by the crosses 17, which may represent developed grains of photosensitive material. As can be seen, portion 10a of the photosensitive layer has a maximum amount of reaction product 17, portion 10b has substantially no reaction product 17, and portion 10c has about half the amount of reaction product 17 as does the portion 10a. Since the amount of reactive substance with which the photosensitive layer 10 is permeated is preferably so adjusted as to be no more than enough to be completely reacted by the most reactive portion of the photosensitive layer, there remains in the portion 10a no unreacted substance. In the portion 10b, there remains a maximum quantity of unreacted substance, and in the portion 10c, there remains a quantity of unreacted substance which is about half that remaining in the portion 10b. Thus, in this case, the amount of reacted substance is a direct function of the exposure and the amount of unreacted substance is an inverse function of the exposure creating the negative image.

Referring now to Fig. 3, the photosensitive layer 10 is shown as having been formed into a permeable unit with an image-carrying layer 12 by being superimposed on said image-carrying layer in intimate relationship therewith such as in face-to-face contact. In this figure, the unreacted portions of the substance have migrated to the image-carrying layer 12, and exist within or on the surface of the image-carrying layer 12 in a quantity substantially inversely proportional to the amount of reaction of the substance in the corresponding portions of the photosensitive layer. In the portion 12a of the image-carrying layer, which corresponds to the portion 10a of the photosensitive layer, there is substantially no unreacted substance on or within the surface of the image-carrying layer 12. In the portion 12b of the image-carrying layer there is a maximum amount of unreacted substance. In the portion 12c, there is present about half the quantity of unreacted substance existing in the portion 12b. Thus, where a maximum amount of reaction between the substance and the photosensitive layer 10 has taken place, there is available in the image-carrying layer a minimum amount of unreacted substance. On the other hand, where there is a minimum amount of reaction with the photosensitive layer 10, there is a maximum amount of unreacted substance available on the image-carrying layer. The portions of the substance which have reacted with the photosensitive layer 10 are preferably trapped within the photosensitive layer 10 so that no reacted substance migrates to the image-carrying layer in those portions where maximum reaction of the photosensitive layer has taken place. This trapping may be accomplished by a tanning action of the substance upon the gelatin, or other colloid of the photosensitive layer, or it may be due to the decreased molecular or ionic mobility of the reaction product of the reaction, or it may, where the substance is a developer, be the result of coupling between the oxidized developer and a relatively immobile dye-forming component contained in the photosensitive layer, or in the viscous developer solution used in the processing. In this latter case the developer layer preferably adheres to the photosensitive layer. In some cases it is not essential that the reacted portions of the substance be trapped in the photosensitive layer or the viscous layer, but it is preferred that these reacted portions of the substance be kept away from the image-carrying layer, particularly where the reacted portions are capable of creating a color and thus spoiling the highlights and contrast of the positive image.

This selective distribution of the unreacted portions of the substance on the image-carrying layer 12 is assisted, in a preferred embodiment, by the use of a highly concentrated solution of the reactive substance and by superimposing the adjacent surfaces of the photosensitive layer 10 and the image-carrying layer 12 in intimate relationship during this transfer. Such an arrangement prevents any substantial dispersion of the reactive substance in its migration from the photosensitive layer to the image-carrying layer.

The image in unreacted substance which exists on or within the surface of the image-carrying layer 12 is next utilized to form a visible image, preferably by the creation of a color on or within the surface of the image-carrying layer 12. This color may be created by the formation of a pigment or by the formation of a dye, the intensity of color created being dependent upon the amount of substance available for the color-creating reaction.

In Fig. 4 the final positive image is shown as being composed of a number of colored points, schematically represented at 19, which may be color-created by a pigment, such as a colloidal metal, or which may be color-created by molecules of dye. For simplicity of description, the colored points 19 are represented as having an intensity depending on depth, while actually the intensity of color may be primarily at and near the surface of the image-carrying layer, the effect depending upon the intensity of dye created, the size of a pigment created, or the quantity per unit area of color created. In the portion 12a of the image-carrying layer where no unreacted substance existed, there is no formation of a color. In portion 12b there is produced a maximum intensity of color, and in portion 12c there is produced a color having about half the intensity of the color produced in the portion 12b. It can be seen, then, that there is thus produced a color which selectively varies from point to point, throughout the area of the image-carrying layer 12, substantially in inverse proportion to the amount of reacted photosensitve material in the corresponding portions of the photosensitive layer 10.

Where the image on the image-carrying layer 12 is formed in terms of a pigment 19 and the reactive substance comprises a developer, the unreacted portions of the developer may be used to form this pigment 19 by the reducing action of the developer on a reducible metallic salt. This reducible metallic salt can be a salt which is negligibly photosensitive such as mercurous chloride or a photosensitive salt such as a silver halide. In either case, the pigment formation is selective, due to the selective reduction of the salt, varying from point to point, and being a minimum where there was a maximum development of the latent negative image and being a maximum where there was a minimum development of the latent negative image. There is thus created on the image-carrying layer a positive pigment image of the latent negative image in the photosensitive layer.

When the reactive substance is a developer and

a dye image is formed on the image-carrying layer 12, there are a number of ways of accomplishing the dye formation, depending upon the type of developer utilized. In one method, there may be provided, for reaction with the unreacted portions of the developer, a color-former capable of coupling with these unreacted, i. e., unoxidized, portions of the developer to create a color 19. This color, due to its selective creation, varies in amount from point to point, being a minimum where there was a maximum development of the latent negative image, and being a maximum where there was a minimum development of the latent negative image. There is thus created, on the image-carrying layer 12, a positive dye image of the latent negative image in the photosensitive layer.

In another method of forming a dye image there is utilized, to create a color, a color-former capable of coupling with oxidized, rather than unoxidized, portions of the developer. In this case, the developer is reacted with the photosensitive material containing a latent negative image to cause a development of the negative image resulting in a selective oxidation of the developer and a trapping of the oxidized developer within the developed portions of the photosensitive layer 10, it being necessary to prevent migration of the oxidized developer from the photosensitive layer 10. The remainder of the developer is then utilized to create a color 19 on the image-carrying layer 12. In order to form this color, it is necessary to oxidize these unreacted portions of the developer, after the selective reaction of the developer with the latent negative image. This oxidation may be accomplished by providing an oxidizing agent on the image-carrying layer, in which case the oxidizing agent may be either a photosensitive material such as a silver halide or a nonphotosensitive oxidizing agent such as sodium perborate. It is also contemplated to oxidize the unreacted portions of the developer on the image-carrying layer by aerial oxidation which may be carried out by separating the image-carrying layer from the photosensitive layer whereby to permit the ready access of oxygen from the atmosphere to the unreacted portions of the developer. After the developer has been oxidized on the image-carrying layer it is reacted with a suitable color-former to cause a coupling and the creation of a color, the concentration and distribution of which varies from point to point substantially in inverse proportion to the amount of development in corresponding portions of the latent negative image.

In both of the above methods of dye image formation, the color-former, which is reacted with the developer to cause a coupling therebetween, is preferably located on the image-carrying layer 12 in solid form. It may, however, be coated on, or included in, the photosensitive layer 10, or it may be, in some cases, included in solution in the liquid composition. This latter modification of the invention is particularly feasible where the developer is coated on one of the layers in solid form rather than being in solution in the liquid composition.

In still another method of forming a dye image, a self-coupling developer is used. This developer may be one of the type known in the art as a direct color-forming developer, i. e., one which couples with itself when oxidized. The developer is selectively reacted with the photosensitive material containing a latent negative image, and the reacted portions are preferably trapped in the photosensitive layer. Then the unreacted portions of the developer are utilized to selectively create a color 19 on the image-carrying layer 12, by oxidizing the unreacted portions of the developer.

A preferred method of permeating the photosensitive layer with a uniform quantity per unit area of a liquid composition containing the reactive substance is to release the liquid composition between the photosensitive layer and the image-carrying layer and to spread this liquid composition in a uniform thin layer between the photosensitive layer and the image-carrying layer. Such a method of uniform permeation has certain advantages and is particularly adaptable for use with film units of the type shown in Figs. 5, 6 and 7 which show preferred examples of the physical embodiments of the present invention.

Each of these film units may be processed by the application thereto of a single mechanical stress to cause the release and spreading of the liquid composition, thus making possible the processing of the film unit either within a hand camera, or as the result of ejection of the film unit from a hand camera.

The construction of the film unit also permits accurate spreading of the liquid composition in a uniform thin layer in a position to permeate the photosensitive layer with a uniform amount of a solution of the reactive substance.

Since the liquid composition is spread between two layers, which may be only slowly permeable to oxygen, it substantially prevents the access of oxygen to the liquid composition during the time it exists in a layer form within the confines of the film unit. This arrangement prevents the aerial oxidation of the reactive substance, where such a substance is oxidizable. Separation of the image-carrying layer from the film unit renders the surrounding atmosphere available for effecting the aerial oxidation of oxidizable material on the image-carrying layer. This feature permits the use of reactive substances which are quite easily oxidized and prevents such oxidation until the positive image has formed, or until it is desired, to oxidize the reactive substance for the purpose of creating a positive image.

When the outer surface of the layers of the film unit are opaque to actinic light, the construction of the film unit permits the liquid composition, particularly where the liquid is viscous, to form a lightproof laminate of the film unit so that the film unit may be ejected from a camera into daylight immediately after the mechanical treatment. Exposure of the photosensitive layer is effected prior to the formation of said lightproof laminate and with the photosensitive and the image-carrying layers in spread apart or separated relation with respect to each other. Since the composite laminate is opaque to actinic light, the photographic process may be carried to completion outside of the camera with no danger of destroying the latent image as the result of light reaching the photosensitive material.

Such film units should have certain features in order that they may fulfill the requirements of the process. In the first place, it is preferable that the film units have within their confines all the materials necessary for the complete processing thereof to produce the final positive image. In the second place, the film units should be so designed that they may inherently assure the proper sequence of reactions, or can be so used as to assure this proper sequence of reactions.

The physical embodiment of the broad in-

vention, shown in Figs. 5, 6 and 7, generally involves a composite film unit comprising a photosensitive layer, an image-carrying layer and a container for a liquid composition, the container being positioned in the film unit for release of its liquid composition so as to permit the permeation of the liquid into at least the surface portions of the photosensitive and image-carrying layers. The liquid composition is preferably viscous and preferably includes the reactive substance, and at least includes a solvent therefor.

The film unit of Fig. 5 preferably comprises a photosensitive layer **30**, an image-carrying layer **32**, and a container **34** having therein a liquid composition and positioned to release its liquid between the two layers **30** and **32**. For supporting the photosensitive layer **30** there is provided a usual film base **36**.

In another physical embodiment of the invention, shown in Fig. 6, there is provided a film unit of the general type described in connection with the discussion of Fig. 5, the embodiment of Fig. 6 being particularly useful in those processes described previously when the reactive substance reacts with a material on the image-carrying layer to create a color.

Referring now to Fig. 6, where like numbers correspond to like elements of Fig. 5, there is provided the usual layer **30** of photosensitive material, carried by a base layer **36**. An image-carrying layer **32** is also provided. On that surface of the image-carrying layer **32** which is closest to the photosensitive layer **30** there is provided a coating or layer **38** of a material which is only slowly permeable to a liquid composition within a container **34**.

In general the embodiment of the invention of Fig. 6 is usable with all processes of the type discussed previously and is particularly useful for those processes wherein a developer is the reactive substance and the image-carrying layer **32** contains a material which is quite reactive with the developer, the reaction of the developer with the material being that which creates a color constituting the positive image.

In still another physical embodiment of the invention there is provided a composite film unit comprising a photosensitive layer and an image-carrying layer similar to the embodiment of Figs. 5 and 6 but having its various layers so arranged with respect to the introduction of the liquid composition that the liquid composition must permeate through the layer of photosensitive material before reaching the image-carrying layer. Such an embodiment of the invention is shown in Fig. 7, where like numbers correspond to like elements of Figs. 5 and 6.

Referring specifically to Fig. 7 there is provided a usual photosensitive layer **30** coated on the upper surface of an image-carrying layer **32**. A container **34** is provided in the film unit in a position to discharge its liquid composition adjacent that surface of the photosensitive layer **30** which is farthest from the image-carrying layer **32**. For assisting in spreading the liquid composition in a uniform thin layer adjacent the surface of the photosensitive layer **30** there is provided a relatively impermeable backing layer **40**.

The embodiment of Fig. 7 may be utilized with any of the processes previously described and it has particular advantage in those processes wherein the reaction of the reactive substance with the negative must be completed before the

liquid composition permeates the image-carrying layer.

In the above-described processes portions of a reactive substance, such as a developer, are selectively rendered incapable of creating a color by reaction with a layer of photosensitive material containing a latent negative image to cause the development thereof, and the unreacted portions of the reactive substance are utilized in a color-creating reaction to form a positive image on an image-carrying layer. In such processes it is essential to carry the first reaction to substantial completion before the second reaction commences. The proper sequence of the two reactions is obtainable in numerous ways.

One way of obtaining the proper sequence is described above in connection with the discussion of Figs. 1 through 4, where the development of the latent negative image is accomplished while it is separate from the locale of the second reaction, i. e., before it is formed into a permeable assembly with the image-carrying layer **12**. This way of assuring the proper sequence between the two reactions is not as preferred as those ways to be discussed hereinafter, since it is not particularly adaptable for use with a compact apparatus such as a hand camera.

When film units of the type of Figs. 5, 6 and 7 are utilized with the process of the present invention and the liquid composition is spread in a uniform layer within the film unit while the various layers thereof are in permeable relationship to each other, the proper sequence of reactions may be assured by providing the proper physical and/or chemical relationship between the various materials.

There are a number of forms that this relationship may take. The first form, which is particularly useful with the embodiment of Fig. 5, involves the provision of materials such that the development of the latent negative image is inherently faster than the color-creating reaction which forms the positive image. An example of this modification of the invention is one wherein the silver halide in the latent negative image is more readily reducible than the metallic salt on the image-carrying layer. Another modification of this form of the invention, useful with the embodiment of Fig. 5, involves the provision of an oxidizing agent on the image-carrying layer which oxidizes the developer more slowly than the developer develops the latent negative image.

Another form of a relationship of material for assuring the proper sequence of reactions is the provision of some means for temporarily preventing the color creating reaction. This means may comprise a coating, as shown in Fig. 6, on the surface of the image-carrying layer or a hardened surface on the image-carrying layer which is adapted to retard penetration of the developer into the image-carrying layer until such time as the developer has been selectively reacted by the latent negative image in the photosensitive layer. Materials suitable for such a coating, as will appear in the more detailed examples which illustrate the invention, comprise polyvinyl alcohol, cellulose nitrate and the like.

Another way of assuring the proper sequence of reactions is to provide a process, particularly useful with the embodiment of Fig. 5, wherein the image-carrying layer must be subjected to a definite treatment before the unreacted developer, on its surface, may enter into the color creation reaction. In one form of this modification of the invention there is provided, on the

image-carrying layer, a layer of unexposed photosensitive material. In this case, the unreacted developer cannot reduce this unexposed photosensitive material until it has been made developable by exposure to light. In another form, where there is used a developer which, when oxidized, couples with itself or another substance, this coupling can be prevented, if no oxidizing agent is included on or within the image-carrying layer, or if the oxidizing agent must be treated, such as by exposure to light, before it is capable of oxidizing the unreacted portions of the developer. In this case, the developer cannot couple until the image-carrying layer has been exposed to aerial oxidation or the oxidixing agent has been activated such as by being exposed to actinic light.

Still another way of assuring the proper sequence of reactions, as shown in Fig. 7, is to adjust the direction of permeation of the developer so that it permeates through, and is substantially completely reacted by, the photosensitive layer before reaching the image-carrying layer.

In the above discussion of the processes applicable to Figs. 1 through 4 and Figs. 5, 6 and 7, no mention is made of the preferred materials. These materials vary in accordance with the specific processes involved and are discussed in more detail hereinafter.

In the following discussion of preferred examples of the various processes of the present invention it may be assumed that all the processes may be practiced as shown in Figs. 1 through 4 and are usable with the modifications of the physical embodiments of the invention shown in Figs. 6 and 7, by suitably arranging the reactive material on the image-carrying layer and either supplying a protective slowly permeable coating thereover or causing the reactive substance to permeate through the photosensitive layer before it contacts the reactive material. Where the process is also particularly well suited for use with a film unit of the type shown in Fig. 5, it is so stated. In the following examples the numbers refer to Figs. 1 through 4 unless the process is particularly applicable to one of Figs. 5 through 7.

One method of creating a dye positive image from a latent negative image is to use on the image-carrying layer a material capable of coupling with unreacted portions of a reactive substance, such as a developer, to form a dye. This dye may be formed by the use of a color-former, or dye base such as a diazonium fast salt, on the image-carrying layer, which is capable of coupling with unreacted portions of an amine or phenol developer. Such a process is set forth in the following non-limiting example.

Example 1

The image-carrying layer **12**, which may be conventional baryta coated paper, is prepared by coating with a water solution of Naphthosol Fast Orange Salt G C and allowed to dry. Naphthosol Fast Orange Salt G C is stabilized and diazotized meta chlor aniline (American Dyestuff Reported, 1939, vol. 28, No. 4, pp. 82–83). The photosensitive layer **10** comprises a relatively slow, high contrast orthochromatic silver halide emulsion, such as is employed with copying film, commonly known to the trade as contrast process ortho film. The photosensitive layer is exposed to actinic light and permeated with a developer by dipping for a few seconds in a solution of 1,5-dihydroxynaphthalene. Development of the photosensitive layer is continued for several minutes after removal from the developer bath. The developed photosensitive layer is then placed in contact with the image-carrying layer to cause the unreacted portions of the developer to migrate to the surface of the image-carrying layer where they couple with the Naphthosol Fast Orange Salt G C to form a positive dye image on the image-carrying layer. This image appears to be intensified by the aerial oxidation of the unreacted developer after the initial positive image is formed. Thus the image appears to be formed by the unreacted portions of the developer which couples, partially in its unoxidized and partially in its oxidized condition, with the color-former. Those portions of the developer oxidized as the result of the development of the latent negative image appear to be trapped within the photosensitive layer and thus cannot spoil the positive image.

In another method of forming a dye positive image from a latent negative image there is utilized a color-former capable of coupling with oxidized, rather than unoxidized, portions of the developer. Such a process where the color-former is contained in the liquid is described in the following nonlimiting example:

Example 2

The photosensitive layer **10**, which may comprise an orthochromatic emulsion of the character described in connection with Example 1, is exposed to actinic light to create therein a latent negative image. This latent negative image is developed using the following developer:

Diethylparaphenylenediamine hydrochloride	grams	6
Sodium sulphite	do	10
Potassium bromide	do	0.5
Sodium carbonate	do	117
Color-former (p-nitrophenylacetonitrile)	grams	0.10
Water	cc	2000
Acetone	cc	10

The negative is removed from the above developing bath after approximately 5 seconds and development is allowed to continue for a minute and a half. The developed negative is then pressed into contact with an image-carrying layer **12** containing an oxidizing agent. Such an image-carrying layer may be prepared by swabbing a sheet of paper, known in the art as imbibition paper, with a 10% solution of sodium perborate. The negative is left in contact with the image-carrying layer for approximately four minutes to permit the sodium perborate to oxidize the unreacted portions of the developer so that they may couple with the color-former. The negative is then separated from the image-carrying layer to reveal the positive dye image on the image-carrying layer. The image obtained by this process is magenta and may be utilized to advantage in three-color photography.

Example 3

A cyan positive image may be obtained in Example 2 by using, as the color-former, 2,4-dichloro-1-naphthol.

Example 4

A yellow positive image may be obtained, in Example 2, by using, as the color-former, ethyl acetoacetic acid.

While the above description of the invention

relates to a process where the color-former is included in the developer liquid, it is equally possible to swab a solution of one or more of the color-formers on the image-carrying layer. This swabbing with a color-former may be accomplished either before or after the unreacted portions of the developer have been transferred to the image-carrying layer. In this case the developer solution is the same except that no color-former is included therein.

In the above specific example, sodium perborate was used as the oxidizing agent for oxidizing those portions of the developer unreacted by the development of the latent negative image. Other nonphotosensitive oxidizing agents such as sodium perchlorate, ammonium dichromate, and ammonium persulfate may also be used.

It is also contemplated to use a photosensitive oxidizing agent on or within the surface of the image-carrying layer. Such a photosensitive material can be a silver halide and is preferably dispersed within the surface of the paper. This photosensitive material can be either exposed or unexposed depending upon the desired type of process. If exposed, it reacts with the developer as soon as it contacts the developer. If unexposed, it must be exposed to actinic light, or otherwise made developable, before it can oxidize the developer. This latter condition has certain advantages since it enables the use of such an unexposed oxidizing agent with a film unit of the type shown in Fig. 5.

In practicing the above modification of the invention it is equally possible to rely on aerial oxidation as the sole means for oxidizing the unreacted portions of the developer as set forth in the following example:

Example 5

The process of Example 2 is modified by eliminating the oxidizing agent from the image-carrying layer **12**. When the image-carrying layer has been imbibed with the developed negative for 4 or 5 minutes it is separated therefrom and the invisible image in unreacted developer on the surface of the image-carrying layer is exposed to aerial oxidation. As the developer oxidizes it couples with the color-former to create a color and thus produces a positive image.

In the process of the type of Example 2, where a color-former couples with the oxidized developer, it is desirable to insure the trapping, within the photosensitive layer, of all the developer that is oxidized by the development of the latent negative image. Such a trapping may be improved by including within the photosensitive layer **10** a color-former that couples with the oxidized developer to form a relatively immobile dye. Thus, as the developer is oxidized by the development of the latent negative image, it immediately couples with the color-former in the photosensitive layer **10** and is converted into an immobile dye, thereby being trapped within the photosensitive layer. This is particularly desirable where the color-former used to create the positive image is placed on the image-carrying layer rather than in the developer solution.

In still another method of forming a dye positive image from a latent negative image, a self-coupling developer is used. This developer may be one of the type known in the art as a direct color-forming developer, i. e., one which couples with itself to form a dye when oxidized, as set forth in the following nonlimiting example:

Example 6

A layer of silver halide photosensitive film **30—36** of Fig. 5, such as orthochromatic copying film of the type described in Example 1, is exposed to a subject image. A preferred form of image-carrying layer **32** comprises a sheet of imbibition paper. A suitable liquid composition contains the following materials:

Water	cc.	476
Sodium carboxymethyl cellulose	grams	42.6
Sodium hydroxide	do	17.5
1,5-dihydroxynaphthalene	do	9.0

With such a liquid composition, the process is preferably carried out by spreading a thin layer of the liquid composition between the exposed photosensitive layer **30** and the image-carrying layer **32**. This spreading may be accomplished by releasing the liquid composition from a container **34** positioned between these two layers and spreading the liquid by means such as a pair of pressure rollers. The 1,5-dihydroxynaphthalene develops the latent negative image and, where development occurs, it self-couples to form an immobile dye. Where development does not occur, the unreacted developer migrates to the surface of the image-carrying layer. The image-carrying layer **32**, with the positive image in terms of unreacted developer on its surface, is then separated from the photosensitive layer **30** and exposed to air so as to oxidize the unreacted developer. This oxidation causes the developer on the image-carrying layer to self-couple, thus creating a color and forming a positive image of the subject image.

It is equally possible to use oxidizing agents on the image-carrying layer of Example 6 rather than relying on aerial oxidation to oxidize the unreacted developer on the image-carrying layer. In such a case the film unit should be of the form of Fig. 6 or 7 and the oxidizing agents may be of the various types discussed in connection with Examples 2 through 4 above.

Where the positive image on the image-carrying layer is formed in terms of a color created by a pigment, as distinguished from a color created by a dye, the unreacted portions of the developer may be used to form this pigment by the reducing action of the developer on a reducible salt, as set forth in the following nonlimiting example:

Example 7

The layer **10** of photosensitive material preferably comprises an orthochromatic emulsion of the copying film type referred to in Example 1. The layer **10** is exposed to actinic light to create therein a latent negative image. This negative image is then developed by placing it in a bath containing:

	Grams
Hydroquinone	25.2
Sodium sulphite	37.8
Sodium hydroxide	36.1
Water	900

The layer **10** is removed from the bath after about 30 seconds and development is allowed to continue for about 2 minutes. The developed negative image, containing an invisible image in unreacted developer, is then placed in intimate contact with an image-carrying layer comprising a sheet of uniformly exposed photosensitive paper such as a relatively fast, conventional enlarging paper having an emulsion comprising silver bromide and silver chloride. The unre-

acted developer permeates and develops the exposed photosensitive grains in the image-carrying layer and thus develops a positive image in silver on the image-carrying layer. The undeveloped grains in the image-carrying layers are then preferably fixed out by bathing in a suitable silver halide solvent, such as a solution of sodium thiosulphate.

The process of Example 7 has been described in connection with a process of the type shown in Figs. 1 through 4. It may equally be used in film units of the type shown in Figs. 6 and 7, or in a film unit like Fig. 5 where the image-carrying layer is sufficiently impermeable so as to delay permeation thereof by the developer. If it is desired to include a silver halide solvent in the liquid composition for the purpose of removing unreduced silver halide from the image-carrying layer of Example 7 the photosensitive material in the photosensitive layer **30** is made of less soluble material than the silver halide in the image-carrying layer. The unreduced silver halide may be removed from the image-receiving layer to a protective colloid film formed between the image-carrying layer and the photosensitive layer by a plastic material such as sodium carboxymethyl cellulose carried in the liquid-processing composition or this unreduced silver halide may be transported to the base which supports the photosensitive layer.

In still another modification of the invention, a nonphotosensitive salt is added to the image-carrying layer for the purpose of making available a material which can be reduced to a pigment by unreacted portions of the developer. This salt may be added after the invisible image in unreacted developer has been formed on the surface of the image-carrying layer. One method of practicing this feature of the invention is set forth in the following nonlimiting example:

Example 8

A copying film, of the type heretofore described, is used as the photosensitive layer **10**, and a sheet of inbibition paper is used as the image-carrying layer **12**. The photosensitive layer is then exposed to a subject image and developed with a liquid composition **14** comprising a mixture of solutions A and B as follows:

Solution A:		
Sodium carboxymethyl cellulose	grams	20
Water	cc	100
Sodium hydroxide	grams	3
Solution B:		
Sodium sulphite	grams	13
Sodium hydroxide	do	7.50
Hydroquinone	do	9
Water to make	do	300

This development is preferably accomplished by spreading the liquid composition in a uniform thin layer between the photosensitive layer **30** and the image-carrying layer **32** of Fig. 5. This spreading is preferably accomplished by releasing the liquid composition from a container **34** therefor positioned between the two layers. After several minutes the image-carrying layer **32** is separated from the photosensitive layer **30** and there is seen an extremely faint yellowish image, which apparently is an image in unreacted developer which has started to oxidize. The image-carrying layer **32** is next swabbed with a dilute solution of silver nitrate and a gray positive image is developed as the result of the reduction of the silver nitrate by the unreacted developer.

Example 9

A yellow positive image can be obtained in the process of Example 8 by swabbing the image-carrying layer **32**, containing an invisible positive image in unreacted developer, with a salt such as ferric chloride, chromic trioxide or platinum chloride.

In another modification of the invention wherein unreacted portions of the developer are utilized for creating a color in terms of a pigment, a nonphotosensitive salt is selectively reduced to colloidal particles by these unreacted portions of the developer, as set forth in the following example:

Example 10

An image-carrying layer **32** of Fig. 5 is formed of baryta paper and is prepared by swabbing with a 2% solution of chloroplatinic acid. The photosensitive layer **30** and the base layer **36** may comprise a sheet of the heretofore described copying film. With such materials the liquid composition in the container **34** preferably comprises:

Water	cc	476
Sodium sulphite	grams	9
Sodium hydroxide	do	19.6
Sodium carboxymethyl cellulose	do	42.6
Hydroquinone	do	9

The film unit is processed by exposing the photosensitive layer **30** to actinic light and then passing it through a wringer. The layers are kept together for a few minutes and then separated to reveal a yellow positive image on the image-carrying layer.

Example 11

An image-carrying layer **32** of Fig. 5 is formed of baryta paper and is prepared by swabbing with a 2% solution of palladium chloride. The photosensitive layer **30** and the base layer **36** may comprise a sheet of the heretofore described copying film. With such materials the liquid composition in the container **34** preferably comprises:

Water	cc	476
Sodium sulphite	grams	9
Sodium hydroxide	do	4.9
Sodium carboxymethyl cellulose	do	28.4
Hydroquinone	do	9

The film unit is processed by exposing the photosensitive layer **30** to actinic light and then passing it through a wringer. The layers are kept together for a few minutes and then separated to reveal a yellow positive image on the image-carrying layer.

Example 12

The contrast of the positive image obtained by the process of Example 11 may be improved by treating the prepared image-carrying layer with (*a*) ammonium hydroxide or (*b*) ammonium hydroxide and hydrochloric acid to form colorless palladium complexes in place of the palladium chloride.

Other reducible salts, which may be nonphotosensitive or only slightly photosensitive, such as a silver salt of sodium carboxymethyl cellulose, may also be used as the reducible metallic salt on the image-carrying layer **32**.

Another modification of the invention wherein the reaction of the developer with the negative image is inherently faster than the color-

forming reaction is described in the following non-limiting example:

Example 13

The photosensitive layer **30** and the base layer **36** of Fig. 5 may comprise a silver halide photographic film such as the heretofore described copying film. For use with this photosensitive layer **30** the liquid composition in the container **34** preferably comprises:

	Grams
5% water solution of sodium carboxymethyl cellulose	40
Sodium hydroxide	1
Sodium sulphite	2.5
Pyrocatechin	0.5

The image-carrying layer **32** is preferably formed of a sheet of baryta paper which has been swabbed with a color-former capable of coupling with unreacted portions of the pyrocatechin. Such a color-former may be applied by making an alcohol and water solution of Naphthosol Fast Orange Salt G C. The photosensitive layer **30** is exposed to actinic light, and the developer is then spread between the exposed photosensitive layer **30** and the image-carrying layer **32** by the use of pressure rollers or other suitable means. The pyrocatechin appears to react first with the latent negative image in the photosensitive layer **30**, and then the unreacted portions thereof migrate to the image-carrying layer where they couple with the color-former on the image-carrying layer to give a positive image.

In still another modification of the embodiment of Fig. 5 wherein a dye positive image is obtained, a process is used which is similar to that described in Example 2. In the following example there is shown a method of practicing this feature of the invention with the modification of Fig. 5 wherein the proper sequence of reactions is assured by using an oxidizing agent which oxidizes the developer more slowly than the developer develops the latent negative image:

Example 14

The photosensitive layer **30** and the base layer **36** preferably comprise a sheet of the copying film of the preceding examples, and the image-carrying layer **32** comprises a sheet of baryta paper which has been swabbed with a 10% solution of sodium perborate. A preferred liquid composition comprises:

	Grams
Diethylparaphenylenediamine hydrochloride	.75
Sodium sulphite	1.5
Potassium bromide	0.6
5% water solution of sodium carboxymethyl cellulose	131
Sodium carbonate	14.62
2,4-dichloro-1-naphthol (color-former)	.1

After exposure of the photosensitive layer to actinic light to create therein a latent negative image, the film unit is processed to release the liquid composition from the container **34** and to spread the liquid in a uniform thin layer between the photosensitive layer **30** and the image-carrying layer **32**. The developer (diethylparaphenylenediamine hydrochloride) develops the latent negative image and, where development occurs, it couples with the color-former and apparently is trapped within the negative by forming a relatively immobile dye. The unreacted portions of the developer are then slowly oxidized by the sodium perborate on the image-carrying layer. As these portions are oxidized they couple with the color-former to create a color on the image-carrying layer constituting the positive image.

A specific modification of the embodiment of Fig. 6 is described in the following nonlimiting example wherein a metallic salt is selectively reduced by unreacted portions of a developer and a slowly permeable polyvinyl alcohol coating is placed over the metallic salt to assure a proper sequence of reactions.

Example 15

A solution is prepared by adding 20 grams of mercurous nitrate to 200 cc. of a 3 per cent nitric acid solution. A sheet of baryta paper, for use as the image-carrying layer **32**, is placed in this solution for two minutes and the excess solution is removed from the sheet by the use of a squeegee. The sheet is then soaked in a 10 per cent solution of sodium chloride for two minutes, thus forming mercurous chloride in the surface of the baryta paper. The sheet is then dried in air at room temperature. To one surface of a sheet prepared as above there is laminated a layer **38** of polyvinyl alcohol. This layer **38** of polyvinyl alcohol is preferably in the neighborhood of .0006 inch thick and is laminated to the baryta sheet by using a water solution of polyvinyl alcohol.

For use with the above described composite sheet **32—38** a liquid composition in the container **34** preferably comprises the following ingredients:

	Grams
Water	1860
Sodium carboxymethyl cellulose	116
Sodium sulphite	78
Sodium hydroxide	74.6
Citric acid	38.5
Hydroquinone	52

In preparing this liquid composition, the water and sodium carboxymethyl cellulose are mixed for two hours. Then all of the other elements, except the hydroquinone, are added and mixed for 5 minutes. Lastly the hydroquinone is added and the whole batch is mixed for two hours at 50° C. under an atmosphere of nitrogen.

For the negative photosensitive layer **30—36** a preferred material is a sheet of the previously mentioned copying film. The photosensitive layer **30** is exposed to a subject image and the film unit is processed, as by passing it through a pair of pressure rollers to release the liquid composition from the container **34** and to spread the liquid in a uniform thin layer between the photosensitive layer **30** and the polyvinyl alcohol coating **38**. When the above described liquid composition is spread between the exposed photosensitive layer **30** and the polyvinyl alcohol coating **38** on the image-carrying layer **34**, the developer develops the latent negative image in the photosensitive layer, this development being substantially completed before any substantial permeation of the polyvinyl alcohol layer **38** takes place. Where the developer is unreacted by this development, it permeates through the polyvinyl alcohol coating and reduces the mercurous chloride on the surface of the image-carrying layer to colloidal black particles forming a positive image of the latent negative image.

While the above modification of the invention

describes a preferred form thereof, numerous other materials and processes may be utilized. The slowly permeable layer **38** may comprise plastics other than polyvinyl alcohol, and reducible salts other than mercurous chloride may be used. The liquid composition is also susceptible of wide variations without departing from the scope of the invention.

While the slowly permeable layer **38** of polyvinyl alcohol is preferably applied in the form of a sheet by laminating to the image-carrying layer, it is equally possible to cast, from an aqueous solution, a layer **38** of polyvinyl alcohol directly on the surface of the prepared image-carrying layer **32** by the use of a doctor blade or other coating techniques.

The slowly permeable barrier layer **38** may equally be formed of a plastic such as cellulose nitrate, as set forth in the following example:

Example 16

In this case a sheet of baryta paper, containing mercurous chloride, is dipped in a bath containing a 2% one-half second cellulose nitrate solution in equal parts of butyl alcohol and butyl acetate. The sheet is dried, and the layer of cellulose nitrate is found to be approximately .0001 to .0002 inch thick over the mercurous chloride. Such a sheet is preferably used with a developer of the type mentioned above.

In the embodiment of the invention of Figs. 5, 6 and 7, the material which reacts with the developer on the image-carrying layer **32** may be situated on the surface thereof nearest the photosensitive layer. If such be the case with respect to Fig. 7, the photosensitive layer **30** is preferably so formed that it may be readily separated from the image-carrying layer **32**. This separation may be assisted by including within the liquid composition a film-forming material, such as sodium carboxymethyl cellulose, which is capable of forming a strong adhesive bond between the photosensitive layer **30** and the backing layer **40**. Thus when the image-carrying layer **32** is separated from the backing layer **40**, the photosensitive layer **30** adheres to the backing layer **40**. The photosensitive layer of Fig. 7 may, if desired, be carried by a suitable permeable base material such as a sheet of gelatin, in which case the base can be mounted with respect to the image-carrying layer so as to be readily separable therefrom as in the manner of conventional stripping film.

In another modification of Figs. 5, 6 and 7, the material which reacts with the unreacted portions of the developer is situated on the surface of the image-carrying layer farthest from the photosensitive layer. In this case no separation of the various layers of the film unit is required in order to view the positive image. Visibility of the negative image, in instances where the layers of the firm unit are to remain unseparated after positive image formation, may be prevented by the use of a suitable opaque material, for example baryta paper, for the image-carrying layer.

In still another modification of the embodiment of Figs. 5, 6 and 7 there may be one reactive material on one surface of the image-carrying layer and another reactive material on the other surface of the image-carrying layer. As an example of such an arrangement, as applied to Fig. 7, an oxidizing agent may be included on the upper surface of the image-carrying layer in a position to oxidize unreacted portions of the developer as it permeates through the composite film unit. On the lower surface of the image-carrying layer there may be a color-former capable of coupling with the oxidized developer. As the developer reaches the color-former on the lower surface it couples therewith to form a positive dye image.

In the physical embodiments of the invention represented by Figs. 5, 6 and 7, the container **34** preferably comprises a paper-backed metal foil coated on its inner surface with a resin, such as polyvinyl butyral, which is inert to alkalies, although it may take numerous other forms.

The liquid composition in the container **34** preferably comprises an aqueous solution of the reactive substance. For assisting in spreading the liquid in a uniform film, the liquid preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm, dimensionally stable film. Where the aqueous solution is alkaline, the film-forming material is preferably one which is not hydrolyzed in an alkaline solution. A preferred film-forming material is a high molecular weight polymer as, for example, a polymeric, water-soluble ether inert to an alkali solution, such as hydroxyethyl cellulose or a metal salt of carboxymethyl cellulose, e. g., sodium or aluminum carboxymethyl cellulose. Other film-forming materials or thickening agents can be used for the conversion of nonviscous solution to viscous solutions where the conditions are such that their ability to increase the viscosity of the solution is not destroyed when left in solution for a considerable length of time. The viscosity of the liquid composition is preferably in the neighborhood of 20,000 centipoises, although it may be as low as 8 centipoises. The high viscosities are preferred, since they give a more accurate control of spreading of the liquid composition.

In the various physical embodiments of the invention, the liquid composition in the container **34** preferably comprises an aqueous solution of the reactive substance. In some cases, however, it is desirable to include the reactive substance, such as a developer, in or on one of the layers of the film unit and for the liquid composition to include only water, possibly an alkali, and possibly a film-forming material to aid in accurate spreading. In other cases, the liquid composition may, for example, comprise only an aqueous solution of the developer, and there may be included in solid form in one of the layers of the film unit any alkali which may be required.

In still another modification of the physical embodiment of the invention the film unit may contain no liquid and may contain, in solid form, all of the various materials ordinarily carried in solution within the film unit. Such a modification of the invention is not as preferred as those described, since it requires the addition of a solvent to the film unit and thus cannot be processed by the mere application of mechanical stress to the film unit. Such a modification of the invention is, however, included within the scope of the present application.

The image-carrying layer, while being preferably formed of papers such as those known in the art as baryta paper or imbibition paper, may be formed of numerous other materials such as a water-permeable plastic or a water-permeable, reversible, film-forming organic colloid capable of having high viscosity characteristics and appreciable jelly strength, in which dye bases or salts may be suspended.

Examples of other suitable image-carrying lay-

ers are regenerated cellulose; polyhydroxy alkanes, such as polyvinyl alcohol; sodium alginate; cellulose ethers, such as methyl cellulose, or their derivatives, such as sodium carboxymethyl cellulose or hydroxyethyl cellulose; papers; proteins, such as glue or gelatin; carbohydrates, such as gums and starch; and mixtures of these materials where the latter are compatible. Where the above materials are transparent they may be mounted on an opaque base if desired, or have incorporated therein a celloidal pigment to render them opaque.

Throughout the specification and appended claims the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive layer. As an example of an alternative meaning for "positive image," assume that the photosensitive layer is exposed to actinic light through a negative transparency. In this case the latent image in the photosensitive layer will be a positive and the image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of three colors to obtain black.

Throughout the specification and claims the expression superimposing has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in separated condition and including between them at least one layer or stratum of a material which may be a viscous liquid.

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

What is claimed is:

1. A process of forming positive transfer images in color wherein a single application of liquid to the exposed silver halide emulsion of a photosensitive element produces the necessary sequences of reactions for giving the finished positive print, said process comprising the steps of: permeating said silver halide emulsion with a liquid composition, and, during said permeation, having said silver halide emulsion so superposed on an image-receiving layer that said liquid has access to the latter layer; providing within the lamination comprising said photosensitive element and said image-receiving layer a pair of reagents capable of reacting with one another in the presence of an oxidizing agent to give a dye, one of said reagents being a color forming silver halide developer and the other a coupler, and said reagents being so distributed throughout said lamination as to have a substantially constant depthwise concentration per unit surface area of said lamination and at least one of said reagents being present per each said unit area substantially only in such quantity as to cause said reagent to be substantially completely reacted in the emulsion in the event of the full development of the silver halide of said unit area, said reagents being dissolvable in said composition when contacted thereby and when dissolved therein being mobile in said lamination; developing the latent image in the silver halide emulsion by means of said developer and causing so much of the said developer as is oxidized by this development to be substantially fully reacted with the coupler to produce a dye image in the emulsion and to there effect, by reason of said reaction, the exhaustion of the said reagent present in limited quantity in proportion to the development of silver per each said unit area of said lamination; transferring to said image-receiving layer in solution in said composition at least a part of the unexhausted portions of said reagents; thereafter, causing the transferred unexhausted portions of the said reagents to react in the image-receiving layer in the presence of an oxidizing agent to produce a dye image in said layer; and, throughout said process, maintaining said image-receiving layer free of appreciable amounts of silver, silver salts and material which, during said process or in the presence of light and air, will impart to said image-receiving layer a color that will adversely affect the visability of the said image in the image-receiving layer.

2. In a process of forming positive transfer images in color as defined in claim 1, the step of separating the image-receiving layer and said photosensitive element from their superposed relationship at some stage of said process after the unexhausted portions of said reagents have been transferred to said image-receiving layer.

3. A process of forming positive transfer images in color as defined in claim 1 wherein one of said reagents is contained in said liquid composition when the liquid composition is permeated into said silver halide emulsion.

4. A process of forming positive transfer images in color as defined in claim 1 wherein both said reagents are contained in said liquid compositions and the image-receiving layer is part of a separate element, and wherein said process includes the step of retarding the contact of said liquid composition with said image-receiving layer by causing said liquid composition before coming into contact with said image-receiving layer to pass through a stratum of material which is located between said emulsion and said image-receiving layer and which is characterized by being slowly permeable to said liquid composition.

5. A process of forming positive transfer images in color as defined in claim 1 wherein the permeation of said emulsion with said liquid composition is effected by the step of providing a layerwise distribution of said liquid composition between said photosensitive element and another element, the latter element supporting said image-receiving layer.

6. In a process of forming positive transfer images in color as defined in claim 5, the step of separating said image-receiving layer and said photosensitive element from their superposed relationship at some stage of said process after the unexhausted portions of said reagents have been transferred to said image-receiving layer.

7. A process for forming positive transfer images in color as defined in claim 1 and including the steps of providing a layerwise distribution of liquid composition having both reagents dissolved therein between said emulsion and a stratum of material which is located on said image-receiving layer and is characterized by being less permeable to said liquid composition

than said emulsion and permeating said emulsion with liquid composition from said layer-wise distribution while retarding contact of liquid composition with said image-receiving layer until said liquid composition has passed through the stratum of lesser permeability.

8. A process of forming positive transfer images in color as defined in claim 1 and including the step of effecting the oxidation of the unexhausted portion of said developer which is transferred to said image-receiving layer with an oxidizing agent substantially uniformly distributed throughout at least a stratum of said image-receiving layer adjacent the surface thereof to which said reagent is transferred.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,055,155	Fischer	Mar. 4, 1913
1,102,028	Fischer	June 30, 1914
1,900,870	Seymour	Mar. 7, 1933
1,993,576	Troland	Mar. 5, 1935
2,054,261	Lierg	Sept. 15, 1936
2,059,884	Mannes	Nov. 3, 1936
2,059,887	Mannes	Nov. 3, 1936
2,137,336	Gaspar	Nov. 22, 1938
2,172,307	Gaspar	Sept. 5, 1939
2,206,126	Schinzel	July 2, 1940
2,252,718	Mannes	Apr. 19, 1941
2,289,714	Land	July 14, 1942
2,315,966	Knott	Apr. 6, 1943
2,328,034	Sease et al.	Aug. 31, 1943
2,336,327	Weissberger	Dec. 7, 1943
2,342,620	Woodward	Feb. 22, 1944
2,347,119	Michaelis	Apr. 18, 1944
2,350,380	White	June 6, 1944
2,352,014	Rott	June 20, 1944
2,363,764	White	Nov. 28, 1944
2,386,167	Murray	Oct. 2, 1945
2,388,894	Yackel	Nov. 13, 1945
2,397,015	Kendall	Mar. 19, 1946
2,397,452	White	Mar. 26, 1946
2,410,644	Fierke	Nov. 5, 1946
2,500,421	Land	Mar. 14, 1950
2,543,181	Land	Feb. 27, 1951

FOREIGN PATENTS

Number	Country	Date
382,975	Germany	July 14, 1922
716,428	France	Oct. 6, 1931
879,995	France	Mar. 10, 1943
900,266	France	Sept. 25, 1944
53,513	France Add.	July 16, 1945
53,515	France Add.	July 16, 1945
449,750	Great Britain	June 29, 1936
451,190	Great Britain	July 31, 1936
503,824	Great Britain	Apr. 11, 1939
503,752	Great Britain	Apr. 11, 1939
503,873	Great Britain	Apr. 17, 1939

OTHER REFERENCES

Stenger, Zeitschrift fur wiss Photographie, vol. 22, 1923, pp. 195–200.

Ricketts, "British Journal of Photography," vol. 61, June 5, 1914, page 446.

Clerc "Photography" Pitman, N. Y. 1937, pps. 231–232.

Friedman American Photography, Jan. 1939, vol. 53, pages 59–61.