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DIFFUSION TRANSFER COLOR PROCESSES

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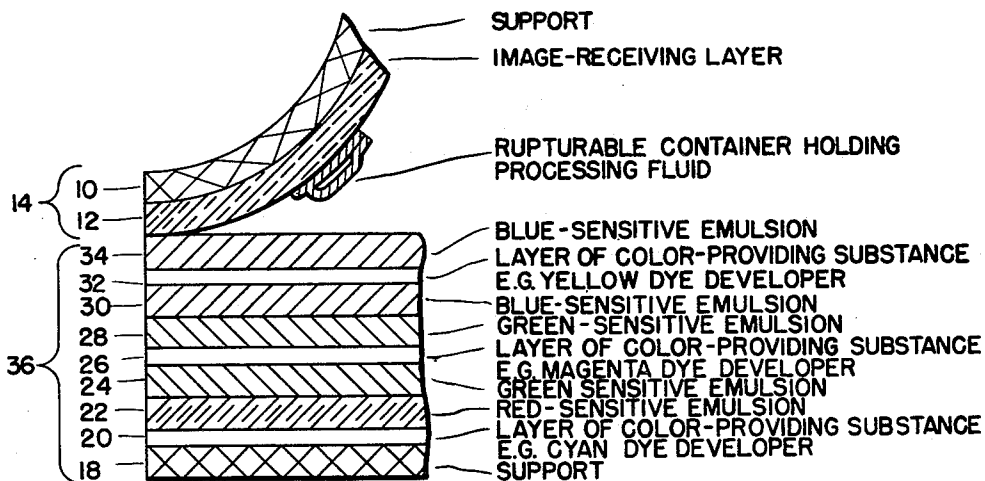


FIG. 1

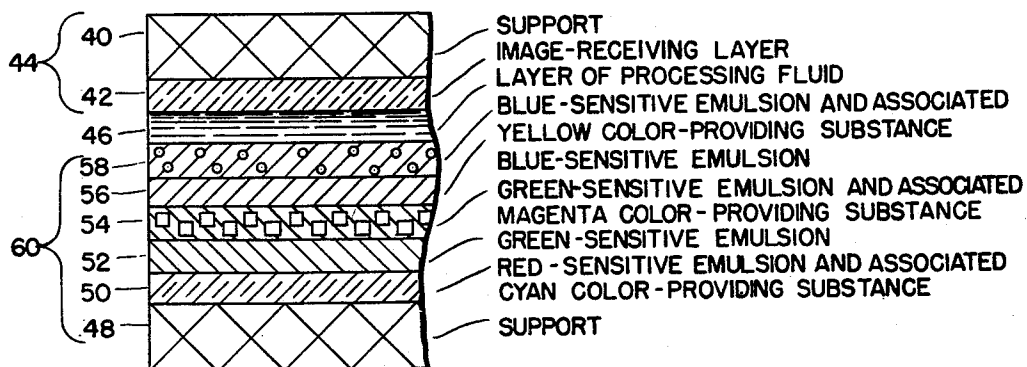


FIG. 2

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3,188,209

DIFFUSION TRANSFER COLOR PROCESSES

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2 Claims. (Cl. 96—3)

This invention relates to photography and more particularly to an improvement in photographic diffusion-transfer processes for obtaining color images and to photographic products for use in such processes.

This application is a continuation-in-part of our copending application, Serial No. 565,135, filed February 13, 1956.

It has been previously proposed to form positive transfer images in color by diffusion-transfer processes wherein an imagewise distribution of color-providing substance is formed and transferred to a superposed image-receiving material. In such processes the formation of the imagewise distribution results from an immobilization of the color-providing substance in exposed areas of a photosensitive emulsion.

In U.S. Patent No. 2,983,606, which issued May 9, 1961, on the copending application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, which is a continuation-in-part of applications Serial No. 415,073, filed March 9, 1954, and Serial No. 518,979, filed June 29, 1955, both now abandoned, said continuation-in-part application having issued on May 9, 1961, as U.S. Patent 2,983,606, there is disclosed and claimed diffusion-transfer processes wherein dye developers are utilized in the development of the latent image present in an exposed photosensitive emulsion; and a positive color image is imparted to a superposed image-receiving layer by diffusion of unreacted dye developer originating from unexposed areas of the exposed photosensitive emulsion. The dye developers of this process are dyes which contain in the same molecule a silver halide developing function and the chromophoric system of a dye.

In our previously mentioned copending application Serial No. 565,135, there is disclosed the use of color-providing substances, particularly dye developers, to form multicolor transfer images using integral multilayer photosensitive elements and a single image-receiving layer. In multicolor processes of this type, it is highly desirable to delay the outward diffusibility or availability for the transfer of nonimmobilized dye developers until after substantial development of the exposed silver halide emulsions has occurred and to control the inward diffusion or penetration of the dye developers. Such control of the unoxidized or nonimmobilized dye developers greatly improves color separation by reducing the possibility of interfering development, i.e., oxidation of a dye developer in a silver halide emulsion other than that with which the dye developer is initially associated. Thus it is desired to control the diffusion of the dye developers so as to insure that the dye developers are reacted to the extent required by the degree of exposure and that the proper dye developer is reacted as a result of the exposure of silver halide of a given sensitivity.

It has now been found that the inward and premature outward diffusion of the dye developers can be readily and simply controlled by associating with appropriate dye developers at least two commonly or similarly sensitized silver halide emulsions. For example, in one preferred integral multilayer photosensitive element contemplated by the present invention, there is utilized a layer of a yellow dye developer disposed between two layers of a blue-sensitive emulsion. In such integral multilayer photosensitive elements, the layer of a magenta dye de-

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veloper may also be similarly disposed between two layers of a green-sensitive emulsion. In integral multilayer photosensitive elements where a dye developer is dispersed within an appropriate silver halide emulsion layer, there is preferably associated or employed with such layer at least one additional similarly sensitized silver halide emulsion. For example, there may be utilized with a blue-sensitive emulsion having a yellow dye developer dispersed therein, another blue-sensitive emulsion of a similar sensitivity so located with respect to said yellow dye developer containing emulsion as to be effective in controlling the inward and/or premature outward diffusion of dye developer.

It is a primary object of this invention to provide diffusion-transfer processes wherein a positive multicolor image may be obtained on a single image-receiving layer using an integral multilayer photosensitive element and to provide diffusion-transfer processes and products therefor for the formation of positive multicolor photographs wherein accurate registration of separately formed color records may be readily obtained in a single image-receiving layer.

Still another object of this invention is to provide diffusion-transfer processes and products therefor whereby improved control of the inward and/or premature outward diffusion of unoxidized dye developer may be obtained.

Still another object of this invention is to provide diffusion-transfer processes and products therefor whereby improved control of the diffusion of unoxidized dye developer may be achieved by means of suitably sensitized silver halide emulsions.

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

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

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

FIGURE 1 is a diagrammatic cross-sectional view of one embodiment of a photographic product for use in obtaining multicolor images in accordance with this invention and comprising an integral multilayer photosensitive element, an image-receiving element and a rupturable container holding a liquid processing fluid or composition; and

FIG. 2 is a diagrammatic cross-sectional view of another embodiment of this invention for use in obtaining multicolor images, during processing, and comprising an integral multilayer photosensitive element, an image-receiving element and a processing fluid.

For simplicity the following descriptions are with regard to the use of dye developers, it being understood, however, that such descriptions are intended to be illustrative only.

As stated above, it has been proposed to form multicolor images by a diffusion-transfer process utilizing dye developers. In processes of this type, a photosensitive element containing at least two selectively sensitized silver halide emulsions and at least two suitable dye developers associated therewith is exposed and wetted by a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting on a sheet-like support element which

may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element. The liquid processing composition permeates the emulsions to initiate development of the latent images contained therein. The dye developers are immobilized or precipitated in exposed areas as a consequence of the development of the latent images. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developers upon oxidation and especially as regards their solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsions by oxidized developing agent. In unexposed and partially exposed areas of the emulsions, the dye developers are unreacted and diffusible, and this provides imagewise distributions of unoxidized dye developers, dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsions. At least part of these imagewise distributions of unoxidized dye developers is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developers. Under certain conditions, the layer of the liquid processing composition may be utilized as the image-receiving layer. The image-receiving element receives a depthwise diffusion, from the developed emulsions, of unoxidized dye developers without appreciably disturbing the imagewise distributions thereof to provide reversed or positive multicolor images of the developed images. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developers. If the color or colors of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of a suitable imbibition period.

When the liquid processing fluid or composition is applied to an integral multilayer photosensitive element comprising a plurality of superposed silver halide emulsion layers and a plurality of suitable dye developers associated therewith, it successively permeates each layer of the photosensitive element, solubilizing dye developer as it so permeates. Thus, dye developer associated with at least the outer silver halide layer or layers is solubilized and may in part be carried "backwards" or inwardly by the processing fluid into an inner silver halide emulsion layer or layers other than that with which it is associated where it may participate in the development of the latent color record image therein. This backward or inward movement may be due to osmotic pressure between wet and dry layers, the rate of diffusion from a wet to a dry layer being greater than that of the same reagent within a wet layer itself. Likewise, solubilized nonimmobilized dye developer associated with the inner silver halide emulsion layer or layers may outwardly diffuse or transfer prematurely from exposed areas, that is, before substantial development has taken place in the next outermost silver halide emulsion layer so that it participates in the development of an emulsion layer other than that with which it is associated. It is desirable to avoid participation by a nonimmobilized dye developer in the development of a silver halide emulsion other than that with which it is associated since it may give rise to incomplete color isolation. In the present invention superior multicolor positive images may be imparted to a single image-receiving layer from an integral multilayer photosensitive element comprising a plurality of superposed silver halide emulsion layers which are processed as a unit in conjunction with a common image-receiving element by suitably controlling or restricting the diffusion of solubilized dye

developer, that is, the inward or rearward diffusion of at least dye developer associated with the outer silver halide emulsion layer or layers and which has not been immobilized as a result of development and the premature outward diffusion of at least dye developer associated with the inner silver halide layer or layers and which has not been immobilized as a result of development. This control is preferably achieved by employing behind the outer layer or layers containing dye developer at least one silver halide emulsion layer of the same sensitivity as the photosensitive silver halide emulsion layer with which the dye developer is initially associated. Thus, for example, unoxidized or non-immobilized dye developer being carried or diffused inwardly from an outer layer will become trapped or immobilized by participating in the development of the additional similarly sensitized exposed silver halide emulsion or emulsions and therefore be prevented or restricted from participating in the development of other inner differently sensitized silver halide emulsion layers. It should be noted that the sets or pairs of associated silver halide emulsions of a similar or common sensitivity are such as to be exposed by light of substantially the same wavelength.

In integral multilayer photosensitive elements of the present invention, steps should be taken to permit adequate light to reach all the silver halide emulsions, particularly the inner emulsion or emulsions, so as to obtain proper exposure. This is particularly necessary if one or more of the dye developers utilized possesses a color which absorbs wavelengths which the associated emulsion is intended to record. Several methods may be used to prevent undesired light absorption by a colored dye developer which would reduce the sensitivity of its associated silver halide emulsion. One method of reducing the light-absorbing effect of a colored dye developer is to employ it in the form of low covering power particles. Additionally, the dye developer may be employed in a dichroic state. Another method comprises employing dye developers where the spectral absorption characteristics are beneficially modified to effect a shift in the wavelengths absorbed during exposure of an associated photosensitive emulsion and which, subsequent to exposure, are shifted so as to possess other more desirable absorption characteristics. For example, some dyes exhibit a pH sensitivity such that they absorb at a lower wavelength in neutral or acidic environment and exhibit a bathochromic absorption shift in an alkaline medium. This property may be utilized to reduce or eliminate absorption of light required to expose an emulsion. Likewise, a dye developer may be utilized which does not absorb light but which undergoes a color change after transfer as by forming a metal complex in the image-receiving layer. Another method of obtaining a reduced light absorption in the negative is to attach a group to the chromophoric system of the dye developer which will effect a hypsochromic shift in the color characteristics of the dye developer. Removal of such a group, as by hydrolysis, will effect a bathochromic color shift to provide the desired dye color. In the present invention, the dye developers utilized are preferably those which exert a negligible absorption upon light to expose the photosensitive element.

The expression "integral multilayer photosensitive element" as used herein is intended to include photosensitive elements comprising at least two separate, superposed layers of photosensitive material, each layer being selectively sensitized to an appropriate portion of the spectrum, at least the inner layer or layers having associated therewith appropriate dye developers. The integral multilayer photosensitive element is intended to be processed without separation of the layers. The imagewise distribution of dye developers present in each layer as a result of the development of latent images therein is transferred to a single, common image-receiving element to provide the desired multicolor image.

The expression "color-providing substances" as used

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herein is intended to include all types of reagents which may be utilized to produce a color image, and such reagents may initially possess the desired color or may undergo a reaction after transfer to give the desired color. In a preferred embodiment the color-providing substances are dye developers, that is, complete dyes which have a silver halide developing function, as disclosed in the aforementioned U.S. Patent No. 2,983,606. The nature of these and other color-providing substances will be referred to in more detail hereinafter.

Several embodiments wherein this invention may be practiced are illustrated in the accompanying drawing. References to particular dye developers in the description of these embodiments are intended to be illustrative only. While the preferred color-providing substances are dye developers and the several embodiments are illustrated by the use of dye developers, it is to be understood that other types of color-providing substances also may be employed.

One process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element such as disclosed and claimed in our previously mentioned copending application, Serial No. 565,135, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, e.g., in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion layers. In the photosensitive elements of the present invention each set of silver halide emulsion and associated dye developer strata may be separated from the other sets by additional suitably sensitized silver halide emulsions as heretofore disclosed.

FIGURE 1 of the accompanying drawing diagrammatically illustrates in cross section one example of an integral multilayer photosensitive element constructed in accordance with this invention. Photosensitive element 36 comprises: a support 18; a layer 20 of a cyan dye developer; a layer 22 of a red-sensitive silver halide emulsion; a layer 24 of a green-sensitive silver halide emulsion; a layer 26 of a magenta dye developer; a layer 28 of a green-sensitive silver halide emulsion; a layer 30 of a blue-sensitive silver halide emulsion; a layer 32 of a yellow dye developer; and a layer 34 of a blue-sensitive silver halide emulsion. As shown in the particular embodiment depicted in FIG. 1, the photosensitive element 36 is shown in a spread-apart relationship with an image-receiving element 14 having mounted thereon a rupturable container 16 holding a processing fluid or composition. The image-receiving element 14 comprises a support 10 and an image-receiving layer 12. After exposure, the image-receiving element 14 is brought into superposed relationship with the photosensitive element 36; the rupturable container 16 is ruptured by application of suitable pressure, e.g., by advancing between a pair of rollers (not shown); and a layer of the liquid processing fluid is spread between the superposed elements. The processing fluid permeates into the photosensitive element 36 whereby the dye developers are rendered effective to develop the latent images in the respective silver halide emulsions. Dye developer, for example, from outer layer 32 carried inwardly by the processing fluid, will be prevented from immediate contact with inner green-sensitive silver halide layer 28 since it will participate in the development of silver halide emulsion layer 30. Likewise, dye developer from middle layer 26 carried inwardly by the processing fluid will also

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be prevented from immediate contact with the innermost silver halide emulsion layer 22 since it will participate in the development of silver halide emulsion layer 24. In exposed areas of each of the emulsions, the dye developers will be reacted and become immobilized. In unexposed areas of each of the emulsions, the dye developers will be mobile and diffuse to the superposed image-receiving layer 12. After a suitable imbibition period the photosensitive element 36 and image-receiving element 14 are separated to reveal the positive multicolor image.

FIG. 2 of the accompanying drawing diagrammatically illustrates in cross section, during processing, another example of an integral multilayer photosensitive element constructed in accordance with this invention. In this embodiment exposed photosensitive element 60 comprises: a support 48; a layer 50 of a red-sensitive silver halide emulsion containing a cyan dye developer; a layer 52 of a green-sensitive silver halide emulsion; a layer 54 of a green-sensitive silver halide emulsion containing a magenta dye developer; a layer 56 of a blue-sensitive silver halide emulsion; and a layer 58 of a blue-sensitive silver halide emulsion containing a yellow dye developer. Instead of being contained within the red-sensitive silver halide emulsion as shown in layer 50, the cyan dye developer can also be employed in a separate layer behind the red-sensitive silver halide emulsion. As illustrated, photosensitive element 60 is in superposed relationship with an image-receiving element 44 which comprises a support 40 and an image-receiving layer 42. Between the two elements is a uniform layer of processing fluid 46. The processing of the photosensitive element 60 is as described in FIG. 1.

Although the structure of the integral, multilayer photosensitive element has been illustrated as having emulsion layers from top to bottom sensitized to blue, green and red portions of the spectrum, respectively, it is to be understood that the order of these emulsions may vary in accordance with well-known practices in the art. Likewise, the sensitivities of the several emulsions may be selected in accordance with well-known photographic principles. Moreover, the techniques of this invention may be utilized in two-color processes as well as the three-color photographic processes illustrated. Thus, although an integral multilayer photosensitive element for three-color processes has been shown, an integral multilayer photosensitive element for use in two-color processes may also be constructed and processed in a similar manner. For example, an integral multilayer photosensitive element suitable for use in two-color processes may have at least two silver halide emulsion layers similarly sensitized to the blue and green portions of the spectrum and a single silver halide emulsion layer sensitized to the orange and red portions of the spectrum. The dye developers associated with such two-color photosensitive elements are, respectively, orange and cyan or red and green. In other words, the above photosensitive element may comprise in the following sequence a support, a cyan dye developer layer, a silver halide emulsion layer sensitized to orange and red, a silver halide emulsion layer sensitized to blue and green and an orange dye developer associated with another silver halide emulsion also sensitized to blue and green. The orange dye developer may be behind the outermost blue-green sensitized silver halide emulsion as a distinct layer, or it may be contained within the outermost emulsion layer itself. In some instances it may be desirable to utilize a yellow filter layer over the emulsion layers in accordance with known principles. Obviously, the sensitivities of the several emulsions may be selected in accordance with well-known photographic principles and the above sensitivities are given by way of example only.

It is also apparent that many variations in the three-color integral multilayer photosensitive elements illustrated are possible without departing from the scope of this invention. For example, the photosensitive element may employ only a blue-sensitive silver halide emulsion

behind a layer containing yellow dye developer, that is, the use of a green-sensitive silver halide emulsion layer behind a layer containing magenta dye developer as illustrated in the drawing may be omitted. Likewise, the photosensitive element may employ only a green-sensitive silver halide emulsion layer behind a layer containing magenta dye developer and the yellow dye developer to be associated with the blue-sensitive silver halide emulsion layer may be introduced as an ingredient of the liquid processing fluid.

Suitable three-color integral multilayer photosensitive elements may comprise outer blue-sensitive emulsions separated by a yellow filter layer from inner red-sensitive and green-sensitive emulsion layers. Where a yellow dye developer is utilized in processing the blue-sensitive outer emulsion layer, a layer of such dye developer behind the blue-sensitive emulsion may be utilized as an efficient yellow filter. Where the dye developer associated with the blue-sensitive emulsion is dispersed therein or otherwise utilized in such a way as to be incapable of effectively functioning as a yellow filter, a suitable yellow filter layer may be used. In a preferred embodiment, a yellow filter layer may be prepared using a pigment comprising a suspension of a benzidine yellow, such as that commercially available under the name of "Padding Yellow GL" from Textile Colors Division, Interchemical Corporation, Hawthorne, N.J.

The present invention may be used alone or in combination with other various mechanisms that may also be utilized to control the premature outward diffusion of dye developer. Many of such means for suitably controlling the diffusibility or availability for diffusion of dye developers associated with the inner photosensitive layer or layers to other photosensitive layers of an integral multilayer photosensitive element or to the image-receiving layer are described and claimed in the above-mentioned copending application, Serial No. 565,135.

The liquid processing composition utilized to process the exposed photosensitive element comprises at least an aqueous solution, and may contain an alkaline reagent. If the liquid processing composition is to be applied to the exposed photosensitive element by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting a film-forming material of the type which, when said composition is spread and dried, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric water-soluble ether which is inert to an alkaline solution as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. Illustrations of suitable liquid processing compositions may be found in the several patents and copending applications herein mentioned, and also in the example hereinafter given. Under certain circumstances, it may be desirable to apply the liquid processing composition to the integral multilayer photosensitive element prior to exposure in accordance with the technique described in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955 (now U.S. Patent No. 3,087,816).

The following example describes the preparation and processing of a single-color, multilayer photosensitive element and is given only to illustrate the techniques by which this invention may be practiced.

Example

A photosensitive element is prepared as follows: an image-receiving layer is applied to a polyvinyl butyral-

coated support using an aqueous 80% isopropanol solution containing 4% N-methoxymethyl polyhexamethylene adipamide. This is followed by coating, sequentially, with (1) an aqueous solution containing 0.5% sodium carboxymethyl cellulose (high viscosity), (2) an aqueous solution containing 2% polyvinyl alcohol, and (3) an acetone solution containing 2% cellulose acetate hydrogen phthalate and 0.5% cellulose acetate. A blue-sensitive silver iodobromide emulsion containing a small amount of potassium chrome alum is then applied. After this layer has dried, a coating of dye developer is applied using a solution prepared by dissolving 0.4 gram of 1-phenyl-3-n-hexyl-carboxamido-4-(p-2',5'-dihydroxyphenethyl)-phenylazo-5-pyrazolone (prepared in accordance with the disclosure in the copending application of Elkan R. Blout et al., Serial No. 612,045, filed September 25, 1956, which application has been abandoned in favor of a continuation-in-part thereof, Serial No. 144,816, filed October 18, 1961 and now U.S. Patent No. 3,134,672, issued May 26, 1964) in 4 cc. of tetrahydrofuran and adding this solution to 15 cc. of methanol containing 4% of o-benzene sulfonyl acetal of polyvinyl alcohol. Another layer of the blue-sensitive silver iodobromide emulsion containing potassium chrome alum is then applied. The photosensitive element is then exposed and an aqueous processing composition comprising:

	Percent
Sodium hydroxide -----	3.0
Sodium carboxymethyl cellulose -----	4.5
1-phenyl-3-pyrazolidone -----	0.8
2,5-bis-ethyleneimino-hydroquinone -----	0.6

is applied thereto as said photosensitive element is brought into superposed relationship with an image-receiving element prepared by coating a 4% solution of N-methoxymethyl polyhexamethylene adipamide on a cellulose acetate-coated baryta paper. After an imbibition period of one minute, the superposed elements are separated and the emulsion layer is removed from the first image-receiving layers. Each of the image-receiving layers carries a yellow, positive dye image. The first positive image has a D_{max} of 1.2 and the second positive image has a D_{max} of 1.0.

In the above example a layer of dye developer is disposed between two layers of a blue-sensitive emulsion. As shown, by casting the layer of dye developer between two layers of a commonly sensitized emulsion, the innermost of the two emulsion layers acts as a barrier layer to reduce the inward diffusion of the dye developer. Such control of the nonimmobilized dye developer was effected by causing the inwardly diffusing dye developer to participate in the development of the latent color record image in the innermost of the two emulsion layers. Thus the use of a silver halide emulsion layer behind a layer containing dye developer, said emulsion having the same sensitivity as that of the silver halide emulsion with which the dye developer is associated, will function as an effective barrier layer to reduce or eliminate inward diffusion of the dye developer.

Dye developers, as noted above, are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a group- ing adapted to develop exposed silver halide. A preferred silver halide developing function is a hydroquinonyl group. Other suitable developing functions include o-dihydroxyphenyl and o- and p-amino substituted hydroxyphenyl groups. In general, the developing function includes a benzenoid developing function. Preferred dye systems are azo and anthraquinone dye systems. Examples of representative dye developers are given in the previously mentioned application of Howard G. Rogers, Serial No. 748,421. Additional useful dye developers are described in the following copending applications:

Serial Nos. 1,442 and 1,443, both filed January 11,

1960, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, as continuations-in-part of, and replacements for Serial No. 471,542, filed November 26, 1954 (now abandoned).

Serial Nos. 144,816 and 145,978 (now U.S. Patents Nos. 3,134,672 and 3,134,764, respectively, issued on May 26, 1964), both filed October 18, 1961 in the names of Elkan R. Blout, Milton Green and Howard G. Rogers, as continuations-in-part of, and replacements for, Serial No. 612,045, filed September 25, 1956 (now abandoned).

Serial Nos. 165,930 and 165,940 (now U.S. Patents Nos. 3,135,604 and 3,135,734, respectively, issued June 2, 1964), both filed January 12, 1962 in the names of Milton Green and Howard G. Rogers as continuations-in-part of, and replacements for, Serial No. 612,052, filed September 25, 1956 (now abandoned).

Serial Nos. 196,523 and 196,524 (now U.S. Patent No. 3,134,765, issued May 26, 1964), both filed May 21, 1962, in the name of Myron S. Simon, as continuations-in-part of, and replacements for, Serial No. 612,053, filed September 25, 1956 (now abandoned).

Serial Nos. 197,283 and 197,259 (now U.S. Patent No. 3,134,763, issued May 26, 1964), both filed May 24, 1962, in the names of Helen P. Husek and Myron S. Simon, as continuations-in-part of, and replacements for, Serial No. 612,054, filed September 25, 1956 (now abandoned).

Serial Nos. 192,355 and 192,354 (now U.S. Patent No. 3,134,762, issued May 26, 1964), both filed May 4, 1962, in the name of Helen P. Husek, as continuations-in-part of, and replacements for, Serial No. 612,055, filed September 25, 1956 (now abandoned).

Application Serial No. 755,804, filed August 18, 1958, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green and Myron S. Simon (now abandoned).

Serial No. 233,461, filed October 26, 1962, in the names of Elkan R. Blout, Marilyn R. Cohler, Milton Green, Myron S. Simon and Robert B. Woodward (now U.S. Patent No. 3,135,606, issued June 9, 1964), as a continuation-in-part of, and a replacement for, Serial No. 824,785, filed July 3, 1959 (now abandoned), which application was a continuation-in-part of Serial No. 478,922, filed December 20, 1954 (now abandoned).

Serial No. 318,827, filed October 25, 1963, in the names of Elkan R. Blout, Marilyn R. Cohler, Milton Green, Myron S. Simon and Robert B. Woodward, as a continuation-in-part of, and a replacement for, Serial No. 824,786, filed July 3, 1959 (now abandoned), which application was a continuation-in-part of Serial No. 478,922, filed December 20, 1954 (now abandoned).

Serial No. 849,727, filed October 30, 1959 (now abandoned), in the names of Elkan R. Blout and Myron S. Simon, as a continuation-in-part of, and as a replacement for, Serial No. 449,514, filed August 12, 1954 (now abandoned).

As examples of suitable dye developers, mention may be made of 2-naphthylazohydroquinone, 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenethyl) - phenylazo-5-pyrazolone and phenylazohydroquinone, for yellow; 2-hydroxynaphthylazohydroquinone, 2 - [p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol and 1-amino-4-phenylazo-2-naphthol, for magenta; 1,4-bis-(2',5'-dihydroxyanilino)-anthraquinone, 1,4-bis-[β -(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone and 1,4-bis-[β -(2',5'-dihydroxyphenyl)-propylamino]-anthraquinone, for cyan.

It is also contemplated to use dye developers initially in the form of a hydrolyzable derivative, particularly the form of a hydrolyzable ester or salt and wherein said hydrolyzable derivative is subjected to hydrolysis conditions during processing. Such hydrolyzable dye developers are dye developers containing a grouping removable by hydrolysis, which grouping renders the dye developer substantially less mobile and/or less soluble until such grouping is removed by alkaline hydrolysis. Examples of such dye developers are given in our copending application,

Serial No. 609,542, filed July 2, 1957 (now abandoned in favor of Serial No. 194,359, filed May 14, 1962). Hydrolyzable dye developers of the above type are particularly useful in the present invention in view of the deferred mobility or diffusibility afforded thereby.

In all embodiments of this invention, it is contemplated that the color-providing substance may be present in an emulsion layer or in a layer behind an emulsion. If the color-providing substance is of a color which absorbs wavelengths which the associated emulsion is intended to record, suitable steps should be taken to prevent undesired light absorption by the color-providing substance which would thus reduce such sensitivity of the emulsion. One method of reducing the light-absorbing effect of a dye developer is to have said substance present in a dichroic state, as by utilizing it in the form of polarizing crystals which, preferably, are oriented. If a polyvinyl alcohol is used as the emulsion medium, the photosensitive portions may be stretched as applied to give an oriented, dichroic emulsion. The use of dye developers in a dichroic state is disclosed and claimed in the copending application of Edwin H. Land, Serial No. 607,820, filed September 4, 1956 (now U.S. Patent No. 3,039,969, issued June 19, 1962). In addition to using dye developers in a dichroic state, one may employ the dye developer in the form of low covering power particles. Some dyes exhibit a pH sensitivity such that they absorb at lower wavelengths in a neutral or acidic environment and exhibit a bathochromic absorption shift in an alkaline environment. This property may also be utilized to reduce or eliminate absorption of light required to expose an emulsion. Dye developers which are color-shifting or with temporarily shifted spectral absorption characteristics as mentioned above are particularly applicable.

Mention should also be made of the applicability in the present invention of dye developers where the spectral absorption characteristics are modified to effect a temporary shift in the wavelengths absorbed during exposure of an associated photosensitive emulsion and which, subsequent to said exposure, are restored to their original absorption characteristics. Such dye developers are described in the copending application of Howard G. Rogers, Serial No. 789,080, filed January 6, 1958.

When dye developers are employed, the liquid processing composition may contain an auxiliary or accelerating developing agent. A preferred accelerating developing agent is 3-pyrazolidone developing agent and preferably 1-phenyl-3-pyrazolidone which is available under the trade name "Phenidone" from Ilford Limited. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed and claimed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 654,781, filed April 24, 1957 (now U.S. Patent No. 3,039,869, issued June 19, 1962). As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethyleneimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in the silver halide emulsion layers or the layers containing the dye developers. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

The dye developers employed should be diffusible, but is, dye developers which undergo diffusion if not reacted by development. The dye developers are preferably se-

lected for their ability to provide colors that are useful in carrying out subtractive color photography, i.e., cyan, magenta and yellow. It should be noted that it is within the scope of this invention to use mixtures of dye developers to obtain a desired color, e.g., black. Thus, it is to be understood that the expression "color" as used herein is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

The dye developers are used in a quantity per unit portion of emulsion sufficient to be completely immobilized by the development reaction as said unit portion is fully exposed. The dye developers are intended to be so distributed as to have a substantially uniform concentration for each unit surface area of the emulsion layer with which they are associated.

Although the invention has been described in connection with the use of dye developers, the concepts are also applicable when other color-providing substances are employed to create multicolor positive images. As examples of other methods of forming color transfer images, mention may be made of the use of color couplers and color developing agents, as disclosed, for example, in U.S. Patent No. 2,661,293, issued December 1, 1953, to Edwin H. Land. In such processes, the color coupler is immobilized in exposed areas by the formation of a non-diffusible product by reaction with oxidized color developer. The unreacted color coupler in unexposed areas is transferred to the image-receiving layers and reacted to form the desired color image, as by coupling with an oxidation product of a color developer.

As examples of complete dyes other than dye developers which may be used to form a color transfer image, mention may be made of coupling dyes such as disclosed in U. S. Patent No. 2,774,668, issued to Howard G. Rogers on December 18, 1956, and in the copending application of Howard G. Rogers, Serial No. 613,691, filed October 3, 1956, as a continuation-in-part thereof (now U.S. Patent No. 3,087,817, issued April 30, 1963). The coupling dye is immobilized in exposed areas by reaction with the oxidation product of a color developer. The unreacted coupling dye present in unexposed areas is transferred to the image-receiving layer and may be used to provide a positive color image without further reaction.

In all products employed in the practice of this invention, it is preferable to expose the integral, multilayer, photosensitive element from the emulsion side. It is, therefore, desirable to hold said photosensitive element and the image-receiving element together at one end thereof by fastening means not shown but comprising hinges, staples, or the like in such manner that the photosensitive element and the image-receiving element may be spread apart from their processing positions illustrated in FIG. 1. Where the film unit is of the roll film type, said photosensitive element and image-receiving element are wound into separate rolls and the free ends of said rolls are connected together in the manner described. A camera apparatus suitable for processing roll film of the type just mentioned is provided by the Polaroid Land Camera Model 95A, sold by Polaroid Corporation, Cambridge, Mass., or similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof, as well as individual processing of an exposed frame, by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which rupture a container associated therewith and effect the spreading of the processing liquid, released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

The nature and construction of rupturable containers, such as container 16 of FIG. 1, are well understood in the art; see, for example, U.S. Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, and U.S. Patent No. 2,634,886, issued to Edwin H. Land on April 14, 1953.

The image-receiving element comprises an image-receiving layer of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions. This element may comprise a single sheet of permeable material, for example, paper, or it may comprise a support upon which at least one liquid-permeable and dyeable layer is mounted. The support layer may have a water-impermeable subcoat over which the stratum of permeable and dyeable material is applied. In certain instances, the dyeable layer may comprise a layer of liquid processing composition which is adapted to remain adhered to the support layer upon stripping.

A preferred material for the image-receiving layer is a nylon and preferably a nylon such as N-methoxymethyl polyhexamethylene adipamide. Other materials suitable for image-receiving layers comprise a partially hydrolyzed polyvinyl acetate such as that commercially available under the trade name of Vinylite MA-28-18 from Bakelite Division, Carbide and Carbon Chemicals Co.; polyvinyl alcohol with or without plasticizers; baryta paper, i.e., a support having a baryta coating thereon; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid, and other materials of a similar nature, as is well known in the art.

While a rupturable container 16, such as has been illustrated with the film unit of FIG. 1, provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, an integral, multilayer, photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on said photosensitive element or otherwise wetting said element with the composition, following which the permeated, exposed, photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

It is also to be understood that the invention may be successfully practiced without the use of a film-forming material in the liquid processing composition. As an illustration, a nonviscous liquid processing composition is particularly applicable with the processing technique last mentioned above and may be applied to the exposed photosensitive element by imbibition or coating practices and may be similarly applied to the image-receiving element before said elements are brought into superposed relation or contact for carrying out the transfer of nonimmobilized color-providing substances.

In the example of the specification, percentages of components are given by weight unless otherwise indicated.

Although the present invention is particularly applicable to multilayer photosensitive elements for the production of multicolor prints, it may also be applied to photosensitive elements for the production of monochrome prints. Likewise, although the invention has been described in connection with what is termed one-step processing, it may also be employed in multistep processing such as described in our copending application, Serial No. 665,807, filed June 14, 1957 (now abandoned in favor of Serial No. 298,539, filed July 30, 1963).

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 element. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case the latent image in the photosensitive element 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.

This invention may be practiced in connection with processes employing direct reversal, internal latent image emulsions which are processed to obtain positive images by reversal development. In such processes, development occurs in portions of the emulsion corresponding to the unexposed areas. Development is effected in the presence of a reagent capable of fogging the emulsion. Internal latent image emulsions are known in the art, as are fogging agents, for effecting development of such latent image emulsions to obtain a positive image. As an example of suitable fogging agents, mention may be made of hydrazines.

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 products and processes 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 drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process for forming multicolor dye images by diffusion transfer including the steps of exposing a multilayer photosensitive element comprising a support having thereon in superposed relationship a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a blue-sensitive silver halide emulsion layer, a layer contiguous with each of said red-sensitive, green-sensitive, and blue-sensitive silver halide emulsions containing, respectively, a cyan dye developer, a magenta dye developer, and a yellow dye developer, each of said dye developers being a compound which is both a dye and a silver halide developing agent, applying an aqueous alkaline processing composition to said photosensitive element, each said dye developer where unoxidized being diffusible in said processing composition, developing said exposed photosensitive element, oxidizing said dye developer in developed areas thereby forming in undeveloped areas of each of said silver halide emulsions an imagewise distribution of each said associated dye developer in unoxidized condition, and transferring, by diffusion, at least part of each of said imagewise distributions of said dye developers to a superposed image-receiving layer to provide said multicolor dye transfer image, the improvement wherein said yellow dye developer is positioned, prior to said exposure, in a layer which is substantially free of silver halide, said layer of yellow dye developer being positioned

between and contiguous with two layers containing blue-sensitive silver halide emulsion, said yellow dye developer being present during exposure in a form transmitting blue light whereby both of said blue-sensitive silver halide emulsion layers are exposed by blue light during said exposure, whereby said yellow dye developer diffusing inwardly toward said green-sensitive silver halide emulsion is oxidized by development of silver halide exposed by blue light thereby providing improved control of the imagewise diffusion of said dye developers and said multicolor transfer image exhibits improved color separation.

2. In a process for forming multicolor dye images by diffusion transfer including the steps of exposing a multilayer photosensitive element comprising a support having thereon in superposed relationship a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a blue-sensitive silver halide emulsion layer, a layer contiguous with each of said red-sensitive, green-sensitive and blue-sensitive silver halide emulsions containing, respectively, a cyan dye developer, a magenta dye developer, and a yellow dye developer, each of said dye developers being a compound which is both a dye and a silver halide developing agent, applying an aqueous alkaline processing composition to said photosensitive element, each said dye developer where unoxidized being diffusible in said processing composition, developing said exposed photosensitive element, oxidizing said dye developer in developed areas thereby forming in undeveloped areas of each of said silver halide emulsions an imagewise distribution of each said associated dye developer in unoxidized condition, and transferring, by diffusion, at least part of each said imagewise distributions of said dye developers to a superposed image-receiving layer to provide said multicolor dye transfer image, the improvement wherein said magenta dye developer is positioned, prior to said exposure, in a layer which is substantially free of silver halide, said layer of magenta dye developer being positioned between and contiguous with two layers containing green-sensitive silver halide emulsion, said magenta dye developer being present during exposure in a form transmitting green light whereby both of said green-sensitive silver halide emulsion layers are exposed by green light during said exposure, whereby said magenta dye developer diffusing inwardly toward said red-sensitive silver halide emulsion is oxidized by development of silver halide exposed by green light thereby providing improved control of the imagewise diffusion of said dye developers and said multicolor transfer image exhibits improved color separation.

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