

Dec. 23, 1969

E. H. LAND

3,485,628

MULTICOLOR DIFFUSION TRANSFER PROCESS EMPLOYING
A MINIMUM AMOUNT OF A PROCESSING COMPOSITION

Filed July 13, 1965

3 Sheets-Sheet 1

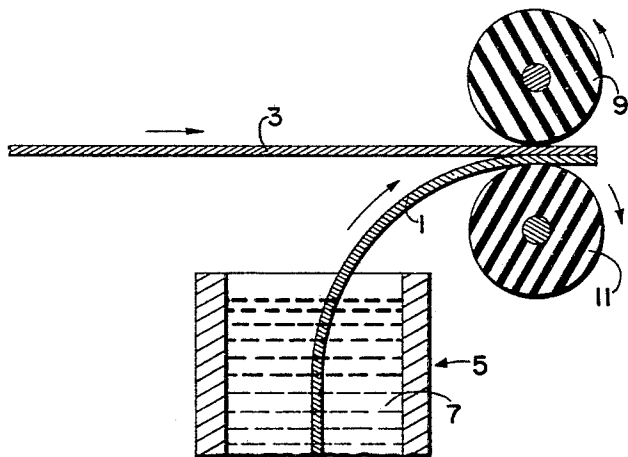


FIG. 1

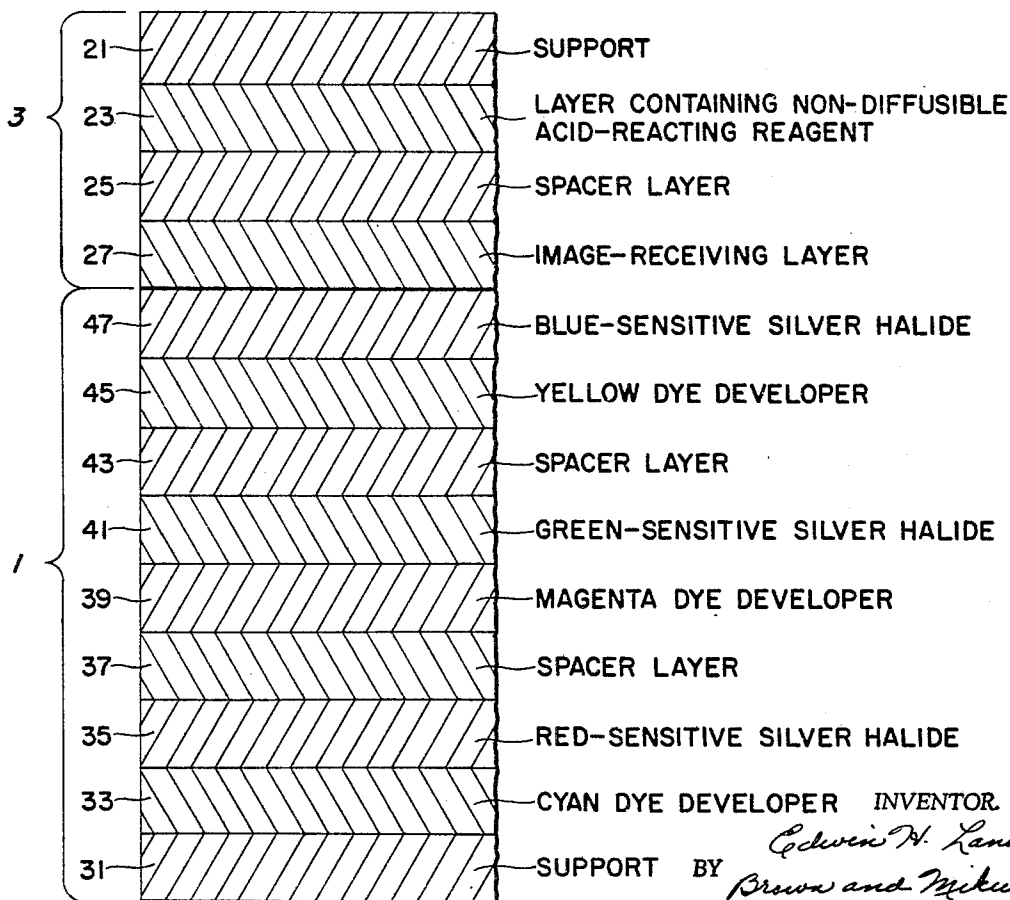


FIG. 2

INVENTOR
Edwin H. Land
BY *Brown and Mikulka*
and *Stanley H. Mervin*
ATTORNEYS

Dec. 23, 1969

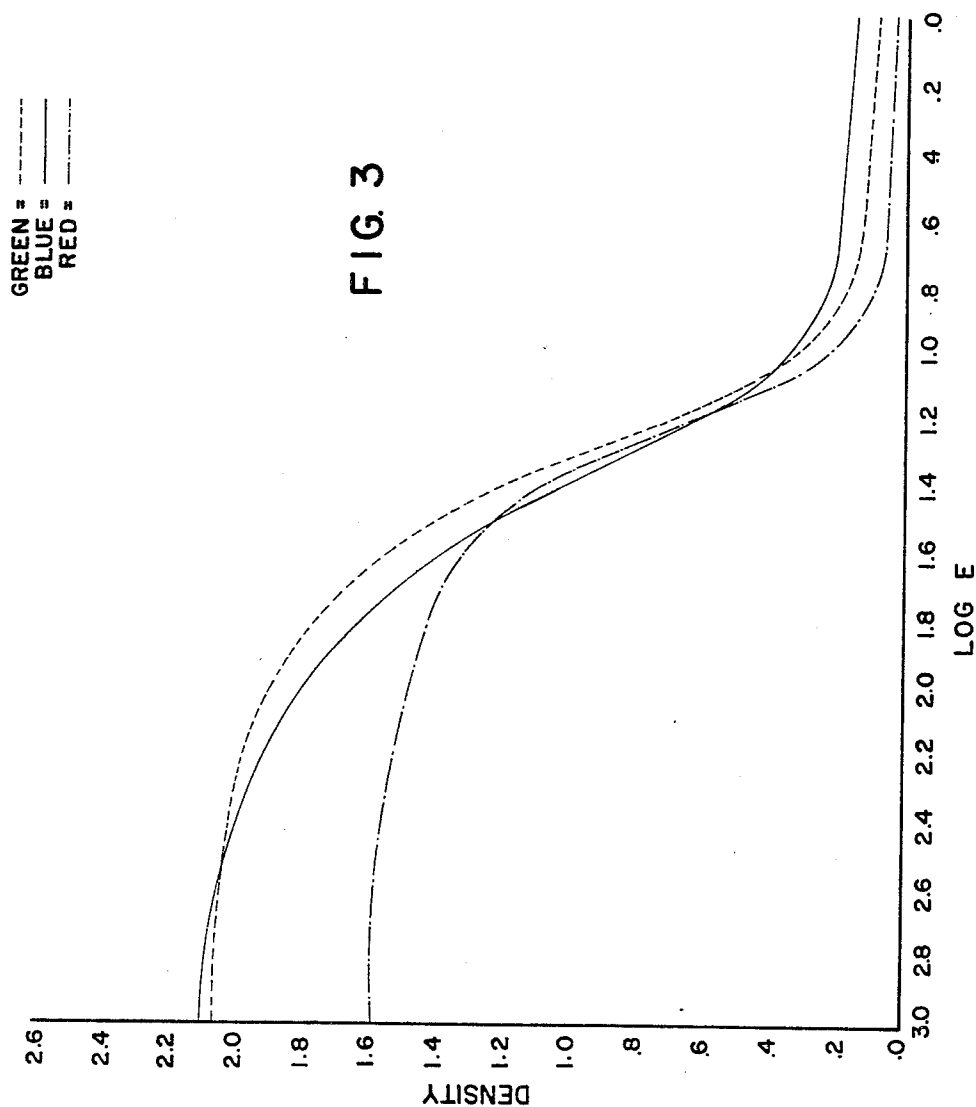
E. H. LAND

3,485,628

MULTICOLOR DIFFUSION TRANSFER PROCESS EMPLOYING
A MINIMUM AMOUNT OF A PROCESSING COMPOSITION

Filed July 13, 1965

3 Sheets-Sheet 2



INVENTOR.

Edwin H. Land

BY *Brown and Mikulka*

and
Stanley H. Mervin

ATTORNEYS

Dec. 23, 1969

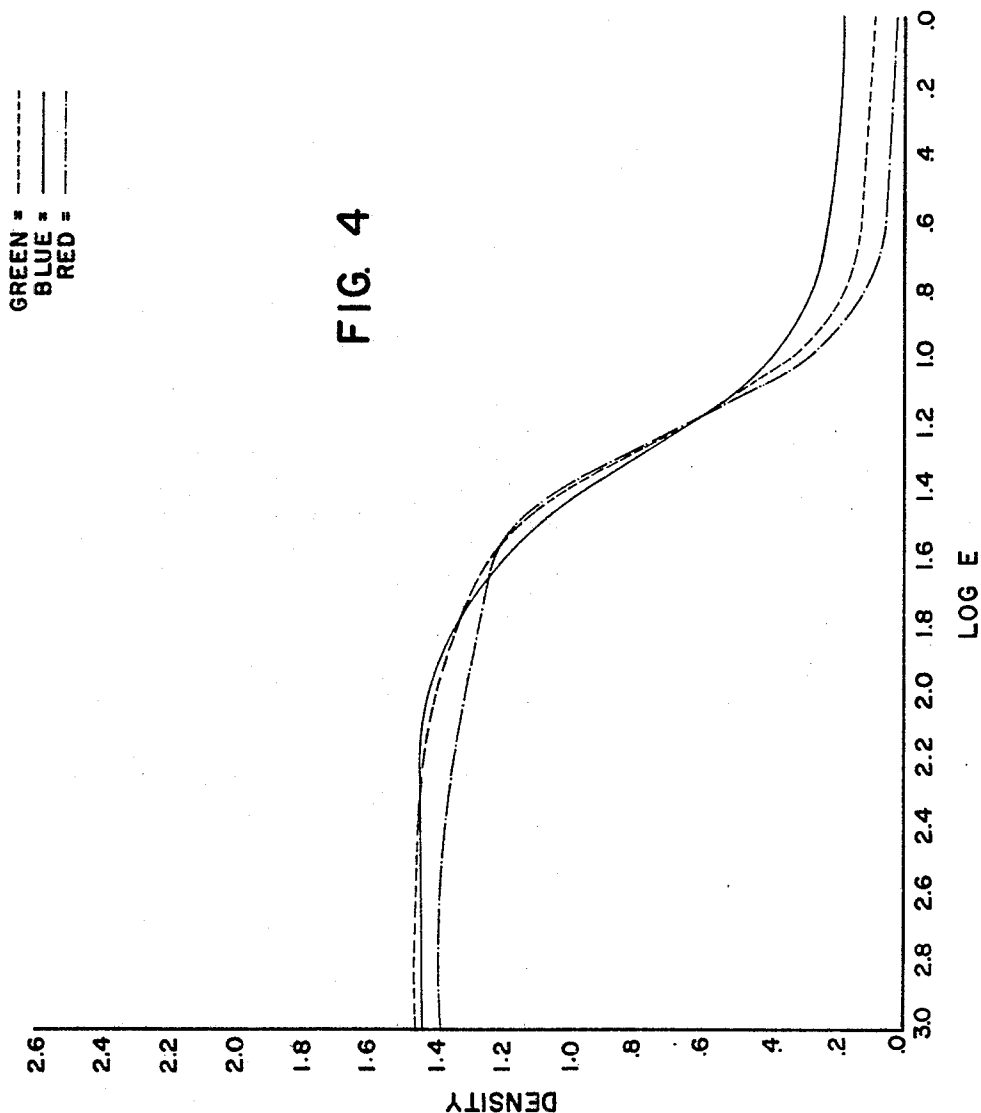
E. H. LAND

3,485,628

MULTICOLOR DIFFUSION TRANSFER PROCESS EMPLOYING
A MINIMUM AMOUNT OF A PROCESSING COMPOSITION

Filed July 13, 1965

3 Sheets-Sheet 3



INVENTOR

Edwin H. Land

BY

Brown and Mikulka

and

Stanley H. Mervin

ATTORNEYS

1

2

3,485,628

MULTICOLOR DIFFUSION TRANSFER PROCESS EMPLOYING A MINIMUM AMOUNT OF A PROCESSING COMPOSITION

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

Filed July 13, 1965, Ser. No. 471,665

The portion of the term of the patent subsequent to

Jan. 9, 1985, has been disclaimed

Int. Cl. G03c 5/54, 7/00

U.S. Cl. 96—29

12 Claims

ABSTRACT OF THE DISCLOSURE

Diffusion transfer color images are formed by a process wherein a small quantity of processing liquid is absorbed into an exposed photosensitive element, and the wetted photosensitive element is then superposed on a dry image-receiving element which includes a non-diffusible, acid-reacting reagent positioned in a layer adjacent the image-receiving layer. The quantity of processing liquid absorbed by the exposed photosensitive element is sufficient to effect development and transfer.

This invention relates to photography and, more particularly, to a method of forming improved photographic images in dyes by diffusion transfer processes.

U.S. Patent No. 2,983,606, issued May 9, 1961 to Howard G. Rogers, discloses diffusion transfer processes employing dye developers to form color transfer images. The copending application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956 (now U.S. Patent No. 3,345,163 issued Oct. 3, 1967), discloses the use of such dye developers in integral multilayer negatives to give multicolor transfer images. This invention is particularly concerned with an improvement in such dye developer diffusion transfer processes and, it is a primary object of this invention to provide novel diffusion transfer processes whereby dye developer transfer images are obtained which exhibit unobvious and superior photographic quality.

It is a further object of this invention to provide a novel diffusion transfer process employing a nonviscous processing composition.

A further object of this invention is to provide diffusion transfer processes wherein a processing composition is allowed to act upon an exposed photosensitive element for a predetermined period prior to superposing said exposed photosensitive element on a dry image-receiving element, which image-receiving element includes a non-diffusible, acid-reacting reagent positioned in a layer adjacent the image-receiving layer.

Yet another object of this invention is to provide diffusion transfer processes wherein a minimum quantity of processing composition is employed to effect development and transfer.

A further object of this invention is to provide diffusion transfer processes for forming multicolor transfer images having increased dye density and improved color reproduction.

Still another object of this invention is to provide a novel diffusion transfer process which employs a highly alkaline, nonviscous processing composition, and wherein the pH of the color transfer image is substantially reduced very rapidly prior to exposing the image dyes to air.

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

The invention accordingly comprises the processes in-

volving 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 and the scope of the application of which will be indicated in the claims.

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

FIGURE 1 is a diagrammatic enlarged cross-sectional view illustrating the processing of a photosensitive element in a preferred embodiment of this invention;

FIG. 2 is a diagrammatic enlarged cross-sectional view of a photosensitive element in face-to-face contact with an image-receiving element in a preferred embodiment of this invention;

FIG. 3 is a graphic illustration of the transfer density versus exposure relationship of each dye in a multicolor dye developer transfer image obtained in accordance with this invention, wherein the image-receiving element contains a layer of a polymeric acid; and

FIG. 4 is a graphic illustration of the transfer density versus exposure relationship of each dye in a multilayer dye developer transfer image formed in the same manner as the image from which the curves reproduced in FIG. 3 were obtained, except that the image-receiving element did not contain a layer of a polymeric acid.

The above-mentioned U.S. Patent No. 2,983,606 and copending application Ser. No. 565,135, disclose highly useful diffusion transfer processes which employ dye developers. As set forth therein, and in numerous other patents, a dye developer is a compound which is both a dye and a silver halide developing agent. Particularly useful and preferred dye developers are azo and anthraquinone dyes which contain one or more hydroquinonyl groups. Numerous examples of useful dye developers and syntheses for preparing dye developers have been set forth in the literature and such information, therefore, is omitted from this application.

The dye developer diffusion transfer process has been embodied in commercially available films intended for use in self-developing cameras to obtain a full color transfer image in approximately one minute. In these films, the processing composition is supplied in a highly viscous form, and it is applied to the exposed photosensitive element by being spread between said exposed photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element contains a non-diffusible, acid-reacting reagent positioned in a layer adjacent the image-receiving layer; image-receiving elements of this type and color diffusion transfer processes employing such image-receiving elements are disclosed and claimed in the copending application of Edwin H. Land, Ser. No. 234,864, filed Nov. 1, 1962 (now U.S. Patent No. 3,362,819 issued Jan. 9, 1968). The aforementioned non-diffusible, acid-reacting reagent is effective to substantially reduce the pH of the color transfer image prior to the time at which the photosensitive element and the image-receiving element are separated from their superposed relationship, thereby eliminating post-treatment of said separated image-receiving element to avoid color changes due to exposing the image dyes to the air. Diffusion transfer images formed on image-receiving elements containing such a non-diffusible, acid-reacting reagent exhibit high optical clarity and luminosity.

The aforementioned U.S. Patent No. 2,983,606 and copending application Ser. No. 565,135, recognize that the processing composition may be applied to the exposed photosensitive element before said exposed photosensitive element is brought into superposed relationship with the

image-receiving element. In addition, it is disclosed that such diffusion transfer processes may be practiced without the use of a film-forming, i.e., viscosity-increasing material, such as sodium carboxymethyl cellulose or hydroxyethyl cellulose, in the processing composition.

It now has been discovered that the efficiency of such diffusion transfer processes as well as the quality of the resulting color transfer image may be substantially improved by treating the exposed photosensitive element with a processing composition for a predetermined period, during which period the photosensitive element absorbs a relatively small quantity of processing solution, and thereafter bringing said exposed photosensitive element into face-to-face contact with a dry image-receiving element containing a non-diffusible, acid-reacting reagent positioned in a layer adjacent the image-receiving layer. Multicolor transfer images formed in accordance with this invention have been found to exhibit improved density and color quality as compared with multicolor transfer images obtained by use of the nonviscous processing composition with a dry image-receiving element which does not contain said nondiffusible, acid-reacting reagent. The diffusion transfer processes of this invention are characterized by the fact that an extremely small quantity of processing solution is employed to process each frame or negative.

In the preferred embodiments of this invention, the processing solution is absorbed into the exposed photosensitive element from a nonviscous processing solution, e.g., by passing the exposed photosensitive element through a container of said processing solution. Other techniques capable of supplying the requisite small quantity of processing solution substantially uniformly over the negative area also may be used, e.g., a liquid applicator which provides a capillary interspace through which the processing solution is applied, as disclosed in my copending application Ser. No. 242,271, filed Nov. 8, 1962 (now U.S. Patent No. 3,194,138 issued July 13, 1965). It is also possible to have the photosensitive element absorb the requisite quantity of processing solution from a viscous processing composition, provided it is applied in such a way that no layer of polymer or processing composition is present between the subsequently superposed photosensitive element and image-receiving element. The use of a nonviscous processing solution, however, is preferred, since it permits one to employ very simple processing apparatus and handling techniques. It will be noted that, regardless of the particular technique of supplying the processing solution to the photosensitive element, the image-receiving element is kept dry until it is brought into face-to-face contact with the wetted photosensitive element, and thus the image-receiving element is wetted essentially only by processing solution extracted from the photosensitive element.

The expression "face-to-face contact" is used herein to denote the absence of any layer of processing composition between the superposed photosensitive element and image-receiving element.

As used herein, the expressions "nonviscous processing solution" and "nonviscous processing composition" are intended to refer to processing solutions or compositions having a viscosity substantially the same as that of water. The nonviscous processing composition does not contain a polymeric film-forming material or other viscosity-providing component such as that employed in the commercially practiced color diffusion transfer process. In general, one may obtain nonviscous processing solutions suitable for use in this invention by simply omitting the film-forming reagent from processing compositions of the types heretofore described in the literature; in certain instances such viscous processing compositions also may contain a reagent whose primary function is to facilitate the adherence of the partially solidified layer of processing composition to either the exposed photosensitive element or image-receiving element when said elements are separated from their superposed relationship, and such re-

agent also may be omitted since this function is not utilized in the process of the instant invention. In some instances, the novel processing techniques of this invention have permitted a reduction in the concentration of one or more reagents of the processing composition as compared with the concentration of said reagent which would be employed in a viscous processing composition. The particular concentration of a given reagent which should be employed in a nonviscous processing composition may be readily determined by one skilled in the art by performing routine concentration tests.

As noted above, a nonviscous processing composition may be applied to the photosensitive element by a number of techniques, e.g., by use of a porous applicator block or head, by dipping the exposed photosensitive element into a container of the nonviscous processing composition or by passing the exposed photosensitive element through a container of said nonviscous processing composition. Particularly useful apparatus for practicing the processes of this invention and embodying the latter two techniques are disclosed in the copending application of Edwin H. Land and Vaito K. Eloranta, Ser. No. 509,957 filed Nov. 26, 1965, and the copending application of Edwin H. Land and Albert J. Bachelder, Ser. No. 509,713 filed Nov. 26, 1965.

Referring to the drawing, FIG. 1 shows an exposed photosensitive element 1 (containing absorbed processing solution) being removed from a container 5 of a nonviscous processing solution 7 and being brought into face-to-face contact with a dry image-receiving element 3 by passing said elements between pressure rolls 9 and 11. It will be noted that the pressure rolls 9 and 10 may be of much simpler construction and mounting than would be the case if the rolls were required to distribute a viscous processing liquid between the two sheets, since the pressure rolls 9 and 11 are required only to press the photosensitive element 1 and the image-receiving element 3 into face-to-face contact with each other. Squeegees or other means (not shown) may be provided to remove excess processing solution adhering to the front and/or back of the photosensitive element as it is withdrawn from the processing solution 7 prior to being superposed on the dry image-receiving element.

The preferred structures of the image-receiving element and the photosensitive element are shown in superposed relationship and in greater detail in FIG. 2. Image-receiving element 3 comprises a support 21 bearing a layer 23 containing a non-diffusible, acid-reacting reagent, a spacer layer 25, and an image-receiving layer 27. The photosensitive element 1 comprises a support 31 carrying a layer 33 of a cyan dye developer, a layer 35 of a red-sensitive silver halide emulsion, a spacer layer 37, a layer 39 of a magenta dye developer, a layer 41 of a green-sensitive silver halide emulsion, a spacer layer 43, a layer 45 of a yellow dye developer, and a layer 47 of a blue-sensitive silver halide emulsion. In certain instances, the blue-sensitive emulsion layer may be overcoated with a layer containing an auxiliary silver halide developing agent, as disclosed and claimed in U.S. Patent No. 3,192,044 issued June 29, 1965 to Howard G. Rogers and Harriet W. Lutes.

By way of recapitulation, this invention provides a transfer process wherein a photosensitive element is allowed to absorb a predetermined, small quantity of processing solution, after which it is brought into face-to-face contact with a dry image-receiving element containing a non-diffusible, acid-reacting reagent in a layer of the image-receiving element adjacent to the image-receiving layer. The requisite quantity of processing solution is absorbed by allowing the photosensitive element to be in contact for a predetermined period with an appropriate quantity of processing composition, e.g., a container of a nonviscous processing solution. This predetermined period constitutes, as a minimum, a period of time sufficient for the permeable layers of said photo-

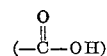
sensitive element, or at least some of such permeable layers, to absorb from said processing composition a quantity of processing solution sufficient to effect diffusion transfer processing of said photosensitive element, and, as a maximum, a period of time after which the unoxidized dye developers would begin to diffuse laterally and/or out of the photosensitive layer, prior to being superposed on the dry image-receiving element, to an extent such that the photographic quality of the transfer image (particularly such elements of photographic quality as maximum density, color saturation and color separation) would be adversely affected. It will be recognized that the practical limits of this predetermined period will vary as a function of the permeability and swellability of the various layers and hence the rate at which the processing solution or liquid is absorbed, the diffusion rates of the dye developers, etc., and may be readily and quickly determined by one skilled in the art for any given combination of photosensitive element, image-receiving element and viscous processing liquid. It will also be recognized that it is within the ability of one skilled in the art to vary such permeability and/or diffusibility to facilitate practice of this processing technique. Thus, for example, one may reduce the initial rate of diffusion by employing hydrolyzable derivatives of dye developers, as disclosed and claimed in the copending application of Edwin H. Land and Howard G. Rogers, Ser. No. 194,359, filed May 14, 1962 (now U.S. Patent No. 3,230,082 issued Jan. 18, 1966).

While the precise reasons for the improved efficiency and color quality obtained in the processes of this invention are not fully understood, certain factors may be identified. Initially, it will be noted that a very small quantity of processing solution is absorbed into the negative, and that absorbed liquid is allowed to act only upon the exposed negative for a controlled period prior to the superpositioning thereon of the dry image-receiving element. Because the image-receiving element is dry, it acts as a sink, i.e., it starts to extract processing solution from the negative at a rapid rate. There is no reservoir of processing solution between the superposed negative and image-receiving element, as there is when a viscous processing solution is employed. The rapid extraction absorption of processing solution from the negative by the dry image-receiving element, together with the attraction of the diffusible dye developers to the mordant and/or dyeable materials of the image-receiving layer, accelerates the transfer of diffusible dye to the image-receiving element. In addition, the time controlled changes in concentration gradients which are created by this processing technique minimize the natural tendency of the yellow and magenta dye developers to diffuse inwardly towards the base of the photosensitive element, thus reducing the loss of transfer density and the creation of undesirable inter-image effects which flow from such inward diffusion of dye developers. Because the image-receiving element is not brought into superposed relationship with the wetted negative until after the requisite quantity of processing solution has been absorbed into the negative, there is a delay before the acid-reacting reagent is available to react with alkali dissolved in the processing solution, without a corresponding delay in the ability of the processing solution to initiate development of the photosensitive element. Once the acid-reacting reagent does have access to the alkaline components of the processing solution, it is effective to reduce the pH at a more rapid rate, in view of the small total quantity of processing solution being used, than if it is used with a viscous processing composition applied simultaneously to both the negative and the image-receiving element. Thus, the pH-reducing action of the acid-reacting reagent is deferred without having to lower the rate at which pH reduction is effected once it is initiated. In addition, the reaction of the alkali with a polymeric acid, as in the preferred embodiments, releases a quantity of water

which, though quite small, is significant in relation to the total quantity of processing solution originally absorbed into the photosensitive element. This released "water of reaction" is formed imagewise and is believed to aid in the desired transfer of the diffusible dyes. One other factor may be mentioned: image-receiving elements containing a polymeric acid layer are appreciably thicker than similar elements which do not contain such a polymeric acid layer; this added thickness of permeable layers of the image-receiving element also is believed to have an effect in creating the desired time controlled changes in the concentration gradients of the various reagents, including the alkali and the diffusible dye developers.

The several patents and copending applications referred to herein, in addition to other issued patents, disclose a number of integral multilayer negatives which may be employed in the practice of this invention. In general, these multilayer negatives have a structure of the type shown in FIG. 2. The dye developer layers are prepared by dissolving each dye developer in a water-immiscible solvent and dispersing the resulting solution in gelatin. Unless otherwise indicated, the negatives employed in the examples given herein also contain a small quantity of 4'-methyl-phenyl-hydroquinone dispersed in a layer of gelatin coated over the blue-sensitive silver halide emulsion.

As noted above, the image-receiving element includes a layer containing a non-diffusible, acid-reacting reagent. In the preferred embodiments of this invention, a layer containing an acid-reacting polymer, and particularly a polymer containing free carboxyl



groups, is provided between the image-receiving layer [i.e., the layer in which the dye image is formed, and frequently referred to simply as the image layer] and the support. For simplicity, this layer is sometimes referred to herein as a "polymeric acid layer" or as an "acid polymer layer."

The pH of the processing composition preferably is at least 12, and more preferably is of the order of at least 13 to 14. The acid polymer layer contains at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 or 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer should be kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH should be reduced very rapidly to at least about pH 11, and preferably about pH 8 to 10, before the positive image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium, potassium or other alkali salt. The diffusion rate of such dye developers thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye developer has been accomplished. The subsequent pH reduction serves a highly valuable photographic function by substantially terminating further dye transfer, thus effectively minimizing changes in color balance as a result of longer imbibition times in multicolor processes using multilayer negatives.

In order to prevent premature pH reduction evidenced, for example, by an undesired reduction in positive image density, the acid groups are so distributed in the acid polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer, which rate in turn has a

direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments may be illustrated, respectively, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

The layer containing the polymeric acid thus may also contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use in this invention, mention may be made of cellulose acetate, cellulose acetate butyrate, etc. Such a polymer also may be added to provide increased wet adhesion to prevent separation of the image-receiving layer or other layers of the image-receiving element during processing. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength. Where necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

As used herein, the term "polymeric acid" is intended to mean polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, non-diffusible from the acid polymer layer. In the preferred embodiments, the acid polymer contains free carboxyl groups and the processing composition contains a large concentration of sodium or potassium ions. The acid polymers found to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium salts. One may employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids contemplated as being used in this invention, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydrides; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy- or sulfo-substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleic anhydride copolymers; etc.

It has also been found that the provision of an inert interlayer between the image layer and the polymeric acid layer substantially improves the control of the pH reduction by the polymeric acid layer. While this spacer layer preferably is composed of a polymer such as polyvinyl alcohol, other polymers, such as gelatin, which are

inert to alkali but through which the alkali may diffuse to the polymeric acid layer, may be used. The presence of such an interlayer has been found quite effective in evening out the various reaction rates over a wide range of temperatures, e.g., by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, e.g., at 95–100° F. By providing an inert interlayer, the rate at which alkali is available for capture in the polymeric acid layer becomes a function of alkali diffusion rates. The pH reduction thus is made relatively independent of chemical reaction rates which would show a greater variation over similar wide changes in imbibition temperature.

In a particularly useful embodiment, the spacer layer referred to above comprises a polymer which exhibits a permeability to alkali ions which is inversely temperature dependent, i.e., it exhibits decreasing permeability to solubilized alkali ions, such as alkali metal and quaternary ammonium ions, under conditions of increasing temperature. The use as spacer layers of polymers which exhibit such inverse temperature dependent permeability to alkali is disclosed and claimed in the copending application of Leonard C. Farney, Howard G. Rogers and Richard W. Young, Ser. No. 447,100, filed Apr. 9, 1965 and now abandoned. As examples of such polymers, mention may be made of hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methylcellulose, and partial acetals of polyvinyl alcohol, such as the partial acetals, butyrals, formals and propionals of polyvinyl alcohol. Particularly useful partial acetals of polyvinyl alcohol have molecular weights of about 1000 to 50,000 and have from about 10 to 80% of the available hydroxyl groups acetalized. Mixed acetals also may be used, and the aldehyde may itself be substituted, e.g., methoxypropionaldehyde. Mixtures of such polymers, e.g., hydroxypropyl methylcellulose and a partial polyvinyl butyral, also may be used. The use of this type of polymeric spacer layer has resulted in improved processing results, particularly with respect to pH control and dye densities, over a wider temperature range, and especially at lower temperatures.

The inert spacer layer, e.g., the polyvinyl alcohol or partial polyvinyl butyral interlayers, acts to "time" control the pH reduction by the polymeric acid layer. This timing is a function of the rate at which the alkali diffuses through this inert spacer layer. It has been found that the pH does not drop until the alkali has passed through this spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion of alkali into the polyvinyl alcohol interlayer, but the pH drops quite rapidly once the alkali diffuses through the polyvinyl alcohol layer.

It is an important feature of the preferred embodiments of this invention that the reaction of the polymeric acid with the diffusing alkali releases water. This water of reaction appears to have an accelerating effect upon the rate at which the pH is reduced. Prior to permeation of the alkali through the inert spacer layer, the equilibria favor the alkali remaining close to the negative and close to the image layer. Once alkali has permeated through to the polymeric acid layer, the equilibria are shifted by the trapping of that alkali. In addition, the water formed by reaction of the acid polymer with the alkali helps to remove alkali ions from the image layer and helps swell the insert polymer, thereby increasing the rate at which the alkali diffuses through the inert layer to the polymeric acid layer. These factors help to keep the pH high until the image is formed, and then to cause the pH to drop rapidly after the image has been formed. Thus, the pH may be kept high during development and transfer, and rapidly dropped after the transfer image has been formed. This also helps to effect the pH reduction within the same imbibition periods which otherwise would be employed. In addition, the released water of reaction permits the

positive and negative to remain in superposed relationship for much longer imbibition times without sticking which is caused by drying out. In turn, this released water permits one to continue imbibition for periods long enough to assure more than the minimum desired pH reduction. The fact that the pH reduction also acts to create a self-limiting transfer density permits such continued imbibition to proceed without undesired color balance changes.

Particularly good results have been obtained using image-receiving layers comprising polyvinyl alcohol and poly-4-vinylpyridine in ratios, by weight, for example, of from 1:3 to 3:1.

Although a preferred image-receiving layer is such a mixture of polyvinyl alcohol and poly-4-vinylpyridine (such receiving layers are disclosed and claimed in U.S. Patent No. 3,148,061 issued to Howard C. Haas on Sept. 8, 1964), the invention is not limited thereto. Other image-receiving layers, such as the partial acetals of polyvinyl alcohol with trialkylammonium benzaldehyde quaternary salts, e.g., the p-trimethylammonium benzaldehyde p-toluene sulfonate partial acetal of polyvinyl alcohol [as disclosed and claimed in the copending application of Howard C. Haas, Ser. No. 71,424, filed Nov. 25, 1960] (now U.S. Patent No. 3,239,337 issued March 8, 1966), are known in the art and may be employed. Similarly, while the preferred embodiment effects developments in the presence of a quaternary ammonium compound (as disclosed and claimed in U.S. Patent No. 3,173,786 issued to Milton Green and Howard G. Rogers on Mar. 16, 1965), and particularly a quaternary ammonium compound capable of forming an active methylene base in alkali, the invention is not so limited, even though the advantages are most dramatic when such an active methylene quaternary ammonium salt is used.

The polymeric acid layer is preferably relatively thick as compared, e.g., with the image-receiving layer. The image-receiving layer is preferably about 0.25 to 0.4 mil thick, and the polymeric acid layer is preferably 0.5 to 1.5 mil thick. If an inert spacer layer is present, that layer is preferably about 0.1 to 0.7 mil thick. Plasticizers may be added to one or more layers to increase flexibility, and subcoats may be employed to facilitate adhesion of various of the layers.

Processing preferably is effected in the presence of an auxiliary or accelerating silver halide developing agent which is substantially colorless, at least in the unoxidized form. Particularly useful are substituted hydroquinones, such as phenylhydroquinone, 4'-methylphenyl-hydroquinone, toluhydroquinone, tertiary-butyl-hydroquinone, and 2,5-triptycene diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative. Particularly useful results are obtained when 4'-methylphenylhydroquinone is dispersed in one or more of the gelatin interlayers of the negative and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

Where desired, the support for the image-receiving layer may be transparent or opaque. Suitable opacifying agents may be incorporated in the negative and/or positive to permit imbibition to be completed outside of a camera, i.e., in an area exposed to light actinic to the silver halide emulsion. In particularly useful embodiments, the addition of small quantities of a white pigment, such as titanium dioxide, to the polymeric acid layer, spacer layer, etc., is effective to prevent edge leakage of light during processing outside of a camera.

Suitable hardening agents may be employed in the image-receiving layer coating solution. Particularly useful hardening agents are acrolein condensates, such as that sold by Shell Development Corporation under the trade name Aldocryl Resin X-12, and disclosed in the copending application of Lloyd D. Taylor, Ser. No. 229,194, filed Oct. 8, 1962.

In a particularly useful embodiment, the processing composition contains a substantial concentration of potassium ions, e.g., at least 50% and more preferably at least 75 to 95% of the alkali metal ions (by weight) present are potassium ions. Use of such potassium containing processing compositions has effected a substantial reduction in imbibition time in processes of the type with which this invention is concerned. When other alkali metal ions also are present, e.g., sodium, lithium, or cesium, particularly useful results are obtained when at least part of such additional alkali metal ions are lithium ions, and the lithium ion concentration preferably is from 1 to 15%, by weight, of the total alkali metal ions present. In general, it may be said that potassium hydroxide is used in a concentration at least equivalent to the normally used sodium hydroxide concentrations, the pH of the processing composition being of the order of at least pH 12 to 14. Useful results may be obtained by the use of potassium hydroxide concentrations within the range of about 2 to 15%, by weight.

Several examples of useful image-receiving elements have been noted above and in the noted patent and copending applications, e.g., polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. The image-receiving element also may contain a development restrainer or arrestor, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Ser. No. 50,849, filed Aug. 22, 1960 (now U.S. Patent No. 3,265,498 issued Aug. 9, 1966).

The symbol pH as used throughout the specification and the attached claims represents the logarithm of the reciprocal of the hydrogen ion concentration. The pH of the transfer image is determined by the use of pH paper wet with distilled water and measured at the surface of the image-receiving layer.

The following examples are given for purposes of illustration and are not intended to be limiting. Unless otherwise indicated, the photosensitive element employed was a commercially available integral multilayer negative of the type commercially available under the designation Polaroid Polacolor Type 108 Land film; the total thickness of the various permeable layers coated on the support was approximately 0.00075". Concentrations of reagents are given as percent by weight.

EXAMPLE 1

A photosensitive element was exposed to a color step wedge. The exposed photosensitive element was then dipped into a container of a nonviscous aqueous alkaline solution containing:

| | Percent |
|--|---------|
| Potassium hydroxide | 10.0 |
| N-benzyl- α -picolinium bromide | 2.0 |
| Benzotriazole | 3.5 |
| Zinc nitrate | 0.5 |

After 8 seconds, the photosensitive element was removed from the container and immediately pressed into face-to-face contact with a dry image-receiving element by passing the two elements between pressure rolls adjusted to firmly press them together without squeezing absorbed processing solution of the photosensitive element. Any excess liquid on the surface of the photosensitive element also was removed by the rolls. The image-receiving element prepared by coating cellulose nitrate subcoated baryta paper with a polymeric acid layer approximately 0.00075" thick comprising the n-butyl half-ester of poly(ethylene/maleic anhydride), followed by a spacer layer approximately 0.0003" thick comprising polyvinyl alcohol, followed by an image-receiving layer approximately 0.0003" thick comprising a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine and also containing a small amount of 1-phenyl-5-mercaptotetrazole.

The photosensitive and image-receiving elements were

held in contact for 60 seconds, after which they were separated.

EXAMPLE 2

The procedure described in Example 1 was repeated except that the processing solution also contained 0.5% potassium thiosulfate. The resulting multicolor transfer image exhibited substantially the same color balance but a higher exposure index or faster film speed than the transfer image obtained in Example 1. The integral blue, green and red H and D curves, taken from the neutral column of the step wedge, of the multicolor transfer image of this example are reproduced in FIG. 3; the following reflection densities were measured in the neutral column:

| | Blue | Green | Red |
|-----------------|------|-------|------|
| D_{max} ----- | 2.10 | 2.06 | 1.59 |
| D_{min} ----- | 0.15 | 0.08 | 0.03 |

Pictures made in accordance with the procedure described in this example exhibit better reds, better flesh tones, and at least twice the resolution as transfer images prepared using the same photosensitive element and image-receiving element and a viscous processing composition.

EXAMPLE 3

The procedure described in Example 2 was repeated, the image-receiving element being essentially identical to that employed in Example 2 except that it did not contain the polymeric acid layer or the spacer layer. The integral blue, green and red H and D curves, taken from the neutral column of the step wedge, of the resulting multicolor transfer image are reproduced in FIG. 4; the following reflection densities were measured in the neutral column:

| | Blue | Green | Red |
|-----------------|------|-------|------|
| D_{max} ----- | 1.43 | 1.45 | 1.38 |
| D_{min} ----- | 0.17 | 0.09 | 0.02 |

A comparison of the multicolor transfer images obtained in Examples 3 and 4 showed that the film speeds were substantially the same, but that the transfer image of Example 3 had much better color balance, and greater densities, particularly the magenta and yellow densities, without increased highlight densities.

EXAMPLE 4

The procedure described in Example 2 was repeated, except that the benzotriazole concentration was reduced to 1.5%. The resulting multicolor transfer image exhibited a lower D_{min} and better greens than the image obtained in Example 2.

EXAMPLE 5

The procedure described in Example 2 was repeated using a nonviscous aqueous alkaline processing solution containing:

| | Percent |
|--|---------|
| Potassium hydroxide ----- | 10.0 |
| N-benzyl- α -picolinium bromide ----- | 1.0 |
| Benzotriazole ----- | 1.75 |
| Zinc nitrate ----- | 0.25 |
| Potassium thiosulfate ----- | 0.25 |

The resulting multicolor transfer image exhibited greater cyan density.

EXAMPLE 6

The procedure described in Example 2 was repeated, adding 0.5% lithium nitrate to the processing solution. This resulted in improved color balance in room temperature processing, and substantially increased cyan transfer. Very good quality multicolor transfer images were made even when the time the photosensitive and image-receiving elements were in face-to-face contact was reduced to 20 seconds.

EXAMPLE 7

The procedures described in Examples 4 and 5 were repeated at 45° F., the solution being heated to 72° F. Good transfer images were obtained when the photosensitive element and image-receiving element were in contact for 60 seconds; if this contact time were increased to 120 seconds, the resulting multicolor step wedge transfer images were substantially similar to those obtained when the transfer was effected at 72° F. These experiments show that excellent transfer images may be effected at low temperatures if the initial permeation and development are effected at a relatively higher temperature, e.g., room temperature.

EXAMPLE 8

The procedure described in Example 2 was repeated at a temperature of 95° F. by conditioning all the components for 2 hours at 95° F. Very good transfer images were obtained with the photosensitive element dipped into the processing solution for 6 seconds, employing an imbibition or transfer time of 60 seconds.

EXAMPLE 9

When the procedure described in Example 8 was repeated at 50° F., good transfer images were obtained by dipping the photosensitive element into the solution for 15 seconds, and allowing the photosensitive and image-receiving elements to imbibe for 120 seconds. Addition of 0.5% lithium nitrate to the processing solution permitted shortening the time the photosensitive element was in the solution to 12 seconds.

EXAMPLE 10

The procedure described in Example 2 was repeated with all components conditioned at 72° F., but the superposed photosensitive element and image-receiving element were immediately subjected to a temperature of 43° F. The transfer image obtained in 60 seconds in this manner exhibited only very slightly less density, primarily cyan density, than the transfer image obtained when imbibition was effected at 72° F. This example, like Example 7, shows the importance of the temperature at which development is initiated.

Experiments using the commercially available photosensitive element of Polaroid Polacolor Type 108 Land film and the image-receiving element of Example 1 show that good results can be obtained if the photosensitive element is allowed to contact the processing solution for a period of about 4 to 15 seconds, and the thus-impregnated photosensitive element is held in face-to-face contact with the image-receiving element for a period of about 15 to 120 seconds; longer imbibition times do not significantly change transfer density or color balance. Longer contact times of the photosensitive element with the processing solution may result in reduced transfer image density, particularly yellow density, while if this time is shorter, the transfer image density, primarily cyan, is reduced, and this reduced density is not brought back by longer imbibition.

Twenty-four (24) photosensitive elements, each 2½" x 2½", of the type used in Example 2 were dipped in the processing solution of Example 2 for 8 seconds each. The wet negatives were weighed after being removed and passed through the rollers (without the image-receiving element). The solution left in the container after all 24 negatives had been treated also was weighed. It was found that each 2½" x 2½" negative absorbed an average of approximately 0.268 g. or 0.25 cc. of the processing solution. This is substantially less than the amount of solution available in the commercially practised viscous solution embodiment, wherein 0.95 g. of viscous reagent is used to process an image area of 2½" x 3½", approximately 60-75% of this reagent being retained between the image areas of the negative and positive sheets.

It will be understood that this invention may be utilized to process individual sheets of film, or it may be employed

in continuous processing of long strips of film, e.g., movie film. The sheet materials employed may be substantially plain sheets or webs, requiring none of the masks, traps, containers or other arrangements for providing the processing liquid, controlling the distribution of the processing composition, or the trapping and retaining of the processing composition, as are utilized with viscous processing solutions. If desired, a white border on the transfer image may be provided by a white light exposure of a marginal strip of each frame prior to photoexposure, or by other techniques obvious to one skilled in the art.

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

What is claimed is:

1. A diffusion transfer process for forming a transfer image in color, comprising the steps of: (a) exposing a photosensitive element containing at least one silver halide emulsion, each said silver halide emulsion having associated therewith a dye developer; (b) contacting said exposed photosensitive element with a nonviscous aqueous alkaline processing solution for a short period whereby a relatively small quantity of said processing solution is absorbed by said exposed photosensitive element and development of said exposed photosensitive element is thereby initiated; (c) bringing said exposed photosensitive element containing said absorbed processing solution into face-to-face contact with a dry image-receiving element, said image-receiving element including an image-receiving layer and a non-diffusible, acid-reacting reagent positioned in a layer adjacent to said image-receiving layer; (d) forming, as a function of said development, an image-wise distribution of diffusible dye developer in undeveloped areas of each said silver halide emulsion, and transferring at least a portion of each said imagewise distribution of diffusible dye developer, by diffusion, to said image-receiving layer to form said transfer image in color, said absorbed small quantity of processing composition being sufficient to effect said development and said transfer, said exposed photosensitive element containing said absorbed processing solution being pressed into face-to-face contact with said dry image-receiving element before any significant quantity of dye developer has diffused out of said photosensitive element.

2. A diffusion transfer process as defined in claim 1, wherein said period during which said exposed photosensitive element is in contact with said processing solution is substantially less than the period during which said exposed photosensitive element is in contact with said image-receiving element.

3. A diffusion transfer process as defined in claim 1, wherein said photosensitive element contains a layer of a blue-sensitive silver halide emulsion, a layer of a green-sensitive silver halide emulsion, and a layer of a red-sensitive silver halide emulsion, said silver halide emulsions being superposed on the same support and having associated therewith, respectively, a yellow dye developer, a magenta dye developer, and a cyan dye developer, each of said dye developers containing a hydroquinonyl radical.

4. A diffusion transfer process as defined in claim 1, wherein an inert, alkali-permeable layer is positioned between said image-receiving layer and said layer containing a non-diffusible, acid-reacting reagent.

5. A diffusion transfer process as defined in claim 1, wherein said non-diffusible, acid-reacting reagent is a polymeric acid.

6. A diffusion transfer process as defined in claim 1, wherein the reaction of said non-diffusible, acid-reacting reagent with alkali releases water.

7. A diffusion transfer process for forming a transfer image in color, comprising the steps of: (a) exposing a photosensitive element containing at least one silver ha-

lide emulsion, each said silver halide emulsion having associated therewith a dye developer; (b) absorbing a relatively small quantity of a non-viscous processing solution into said exposed photosensitive element, thereby initiating development of said exposed photosensitive element; (c) bringing said exposed photosensitive element containing said absorbed processing solution into face-to-face contact with a dry image-receiving element, said image-receiving element including an image-receiving layer and a non-diffusible, acid-reacting reagent positioned in a layer adjacent to said image-receiving layer; (d) forming, as a function of said development, an image-wise distribution of diffusible dye developer in undeveloped areas of each said silver halide emulsion, and transferring at least a portion of each said imagewise distribution of diffusible dye developer, by diffusion, to said image-receiving layer to form said transfer image in color, said absorbed small quantity of processing composition being sufficient to effect said development and said transfer.

8. A diffusion transfer process for forming a multi-color transfer image, comprising the steps of: (a) exposing a photosensitive element comprising a layer of a blue-sensitive silver halide emulsion, a layer of a green-sensitive silver halide emulsion, and a layer of a red-sensitive silver halide emulsion, said silver halide emulsions being superposed on the same support and having associated therewith, respectively, a yellow dye developer, a magenta dye developer, and a cyan dye developer; (b) passing said exposed photosensitive element through a nonviscous aqueous alkaline processing solution at a rate such that a relatively small quantity of said processing solution is absorbed by said exposed photosensitive element and development of said exposed photosensitive element is thereby initiated; (c) bringing said exposed photosensitive element containing said absorbed processing solution into face-to-face contact with a dry image-receiving element, said image-receiving element including an image-receiving layer and a layer containing a polymeric acid positioned between the support and said image-receiving layer; (d) forming, as a function of said development, an imagewise distribution of diffusible dye developer in undeveloped areas of each said silver halide emulsion, and transferring at least a portion of each said imagewise distribution of diffusible dye developer, by diffusion, to said image-receiving layer to form said multi-color transfer image, said absorbed small quantity of processing composition being sufficient to effect said development and said transfer.

9. A diffusion transfer process as defined in claim 8, wherein said exposed photosensitive element is in said processing solution for a period of about 4 to 15 seconds, after which it is immediately brought into said face-to-face contact with said dry image-receiving element.

10. A diffusion transfer process as defined in claim 9, wherein said photosensitive element and said image-receiving element are maintained in said face-to-face contact for a period of about 15 to 120 seconds.

11. A diffusion transfer process as defined in claim 8, wherein said aqueous alkaline processing composition has a pH of at least 12, and said polymeric acid is present in a quantity sufficient to reduce the pH of the image-receiving layer to less than 8.

12. A diffusion transfer process for forming a transfer image in color, comprising the steps of: (a) exposing a photosensitive element containing at least one silver halide emulsion, each said silver halide emulsion having associated therewith a dye developer; (b) absorbing a relatively small quantity of a processing solution into said exposed photosensitive element, thereby initiating development of said exposed photosensitive element; (c) bringing said exposed photosensitive element containing said absorbed processing solution into face-to-face contact with a dry image-receiving element, said image-re-

15

ceiving element including an image-receiving layer and a non-diffusible, acid reacting reagent positioned in a layer adjacent to said image-receiving layer; (d) forming, as a function of said development, an imagewise distribution of diffusible dye developer in undeveloped areas of each said silver halide emulsion, and transferring at least a portion of each said imagewise distribution of diffusible dye developer, by diffusion, to said image-receiving layer to form said transfer image in color, said absorbed small quantity of processing composition being sufficient to effect said development and said transfer, said diffusion transfer being performed at a temperature which is lower than the temperature of said processing solution when said processing solution is absorbed into said photosensitive element.

5
10
15

16

References Cited

UNITED STATES PATENTS

| | | | |
|-----------|---------|-------|-------|
| 1,907,252 | 5/1933 | Debie | 96—48 |
| 2,500,421 | 3/1950 | Land | 96—29 |
| 3,345,172 | 10/1967 | Land | 96—48 |
| 3,362,819 | 1/1968 | Land | 96—3 |
| 3,362,821 | 1/1968 | Land | 96—29 |

NORMAN G. TORCHIN, Primary Examiner
A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—3