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DIFFUSION TRANSFER PROCESSES UTILIZING PHOTOSENSITIVE ELEMENTS CONTAINING POLYMERIC ACID SPACER LAYERS

Filed May 1, 1963

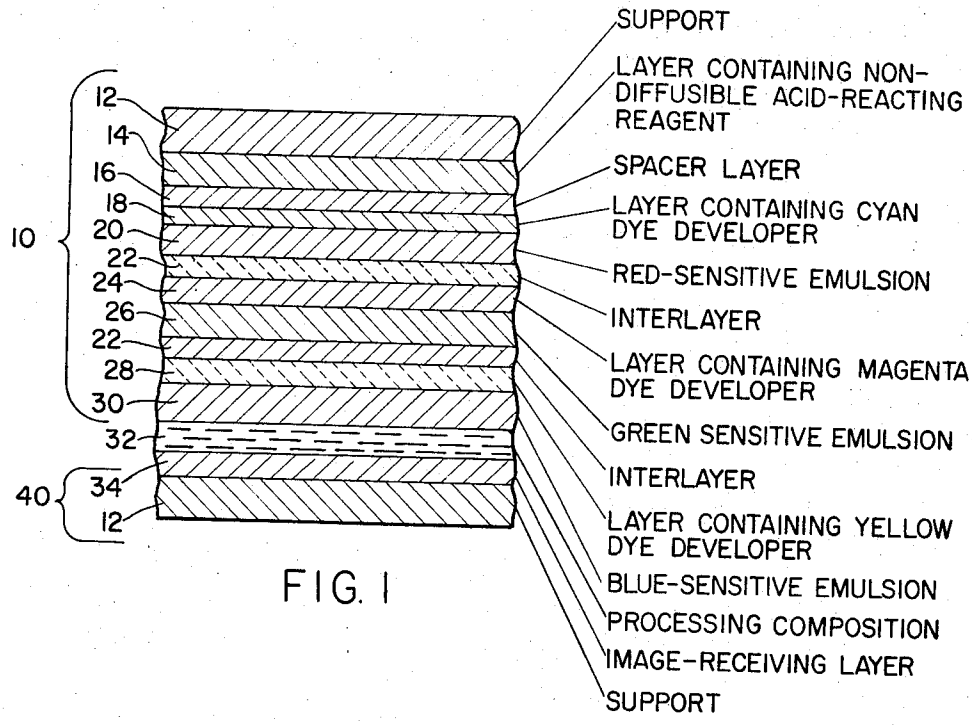


FIG. 1

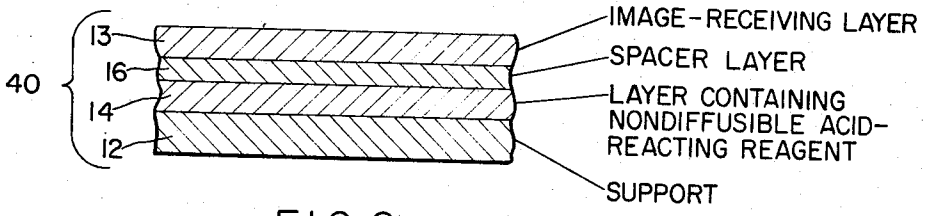


FIG. 2

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DIFFUSION TRANSFER PROCESSES UTILIZING PHOTOSENSITIVE ELEMENTS CONTAINING POLYMERIC ACID SPACER LAYERS

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15 Claims. (Cl. 96—29)

This invention relates to photography and, more particularly, to photographic products and processes for forming photographic images in dyes by diffusion transfer processes.

U.S. Patent No. 2,983,606, issued May 9, 1961, to Howard G. Rogers, discloses processes employing dye developers to form color transfer images and products useful therein. The copending application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956, 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 diffusion transfer processes and, in particular, with the provision of novel diffusion transfer processes and products useful therein whereby images in dye developers are obtained which exhibit unobvious and unexpected properties.

It is a further object of this invention to provide novel photosensitive elements for use in diffusion transfer processes employing dye developers, and processes employing said novel photosensitive elements wherein the color transfer image is only slightly alkaline when it is separated from the exposed and developed photosensitive layers.

Yet another object of this invention is to provide novel photosensitive elements adapted to effect a substantial reduction in the alkalinity of the color transfer image without interfering in the formation of the color transfer image.

A further object of this invention is to provide novel photosensitive elements containing a nondiffusible acid-reacting reagent positioned in a layer adjacent a layer of dye developer present in the photosensitive element.

Still another object of this invention is to provide novel diffusion transfer processes employing a novel photosensitive element and wherein the alkalinity of the transfer image may be controlled and maintained after separation of the transfer image from the image-receiving element.

Another object of this invention is to provide novel diffusion transfer processes employing a photosensitive element which contains a layer of a polymeric acid, transfer being effected to an image-receiving element which also contains a layer of a polymeric acid, whereby the pH of the transfer image is reduced to very low levels prior to exposing the image dyes to air, and processing reagents which are harmful, or potentially harmful, to the image dyes, are removed from effective proximity to such dyes by diffusion to one of said polymeric acid-containing layers.

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 shows a novel photosensitive element containing a layer of a nondiffusible acid-reacting reagent in accordance with this invention, said photosensitive element being shown in superposed relationship with an image-receiving element with a layer of processing liquid therebetween; and

FIG. 2 shows an image-receiving element containing a layer of a nondiffusible acid-reacting reagent, which image-receiving element is particularly useful in combination with the novel photosensitive element shown in FIGURE 1.

As is now well known in diffusion transfer processes of the type contemplated herein, as set forth in detail for example in the aforementioned U.S. patent, a processing composition is applied to an exposed photosensitive emulsion to effect development thereof and an imagewise distribution of diffusible, unoxidized dye developers is formed as a function of development. At least a portion of such diffusible dye developers is transferred imagewise to an image-receiving layer positioned in superposed relationship with said photosensitive emulsion. At the end of the appropriate imbibition period, the image-receiving layer is separated from its superposed relationship with the developed photosensitive emulsion to permit viewing of the transfer image.

In general, in the processes with which this invention is concerned, a photosensitive element containing a silver halide emulsion is exposed and wetted with a fluid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In one preferred embodiment, the photosensitive element contains a layer of dye developer, and a liquid processing composition is applied to the photosensitive element in a thin, substantially uniform layer as the photosensitive element is brought into superposed position with an image-receiving element.

The processing compositions employed in diffusion transfer processes of the type contemplated herein usually are highly alkaline, having a pH in excess of 12, and frequently have a pH of the order of 14 or even greater hydroxyl ion concentration. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in the developed areas, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solutions. It may also be due, in part, to a tanning effect on the emulsion by oxidized developing agent. At least part of each such imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer which layer receives a depthwise diffusion of the transferred, unoxidized dye developer, without appreciably disturbing the imagewise distribution thereof, to provide a reversed or positive, colored image of the image developed in each silver halide emulsion. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. The transfer image is revealed by separating the image-receiving layer from the photosensitive element at the end of the imbibition period.

In an especially useful embodiment, the dye developers are dissolved in a water-immiscible solvent and the resulting solution is then dispersed in gelatin to provide

the dye developer layers. Numerous examples of suitable dye developers are disclosed in the said U.S. Patent No. 2,983,606 and copending applications noted therein. As set forth therein, 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.

The above-mentioned U.S. Patent No. 2,983,606 discloses and claims a highly useful method of forming color images by diffusion transfer wherein the color-providing substances are dye developers. As set forth therein, 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. It has been proposed that the silver halide developing group be linked to the chromophoric system of the dye developer through a suitable group of atoms which are effective to interrupt any system of conjugation and resonance between the silver halide developing group, e.g., a hydroquinonyl radical, and the chromophoric system or dye portion of the molecule. Such insulating linkages have been found to be quite effective in avoiding or essentially eliminating any significant change in the color characteristics of the dye developer by virtue of the hydroquinonyl group being oxidized to the quinone, e.g., by aerial oxidation of the dye developers in the separated image-receiving layer.

Although such oxidation may not change the characteristic color of the dye developer, such oxidation may have a material and substantial effect upon the stability to light of the resulting dye developer image, as set forth in my copending U.S. application Ser. No. 234,864, filed Nov. 1, 1962. It has been found that if, prior to exposing the surface of the image-receiving layer to air, the alkalinity or pH of the dye developer environment in the image-receiving layer is adjusted to a level at least substantially precluding alkaline oxidation of the developing radical, a tremendous and remarkable improvement in the stability to light of such dye developers is obtained. It has further been found that images of unusual brilliance and luminosity are obtained if the reduction in alkalinity is effected by diffusing the alkaline ions to an adjacent layer where they are captured and retained in place. It is with respect to these discoveries that this invention is concerned and particularly with the provision of products and processes for accomplishing these unobvious results.

The photographic transfer dye image frequently retains substantial amounts of photographic reagents, particularly alkali, with which it has been processed, even though the layer of processing composition is caused to adhere to and remain with the photosensitive layer. The presence of these residual reagents may adversely effect the quality and stability of the image, particularly in the presence of significant quantities of alkali. For example, if the receiving layer is highly alkaline, oxidation by atmospheric oxygen of unreacted developing agent or other components of the processing composition is quite likely to occur, and such reactions or subsequent reactions may impart a stain or otherwise discolor the transfer image, particularly the highlights thereof.

It has been proposed to treat the surface of the separated image-receiving layer with a solution which is effective to remove (as by a washing action), neutralize or otherwise render such residual processing reagents relatively innocuous. It has been found, however, where the transfer image is formed by the dye developer transfer process of the aforementioned Rogers Patent No. 2,983,606 and particularly where development is effected in the presence of a quaternary ammonium compound which is capable of forming an active methylene base in alkali, that the color of some dye developer images nevertheless may change or otherwise become degraded. Although the exact mechanism of this color change is not known, it is believed to be due, at least in part, to a coupling reaction between the active methylene quaternary ammonium compound and an oxidation product of the dye developer or of an auxiliary or accelerating developing agent. This type of color change appears to be due to the formation of a new chromophore which, when superposed on the original chromophore, frequently results in dulling or "greying" of the image, and is particularly noticeable in reproduction of sky and clouds. Such a color-forming reaction has been observed particularly where the dye developer or the auxiliary developing agent contains a hydroquinonyl group, in which event the oxidation product involved may be the quinone or semiquinone. [In test tube experiments, a strong green color appears when N-phenethyl-α-picolinium bromide or N-benzyl-α-picolinium bromide is added to an alkaline solution of tolu-hydroquinone in the presence of air. This initial green color degrades to a yellow-brown with time.] In addition to such undesirable color changes, it also has been found that the oxidation of the transferred dye developers may be an initial step in fading when the images are exposed to light.

Application of an acidic print-coating composition, e.g., a solution containing boric acid (as disclosed and claimed in the copending application of Howard G. Rogers, Ser. No. 93,309, filed Mar. 6, 1961, now U.S. Patent No. 3,239,338, issued Mar. 8, 1966), to the positive image is, of course, effective to reduce the pH thereof. In some instances, and particularly where such a print-coating composition is applied very shortly after separating the positive from the negative, at least part of the color degradation may even be reversed, i.e., it appears that at least some reactions responsible for such color degradation may go through an intermediate stage (or product) which is reversible by the print-coating operation. While such prompt print-coating frequently is effective to prevent a significant amount of permanent color degradation, it is not feasible in practice to print-coat quickly enough to prevent an adverse effect on light stability due to oxidation.

It has been discovered, as set forth in my aforementioned copending U.S. application Ser. No. 234,864, that if, prior to exposure to atmospheric oxygen, the pH of the image layer is reduced to a level at which aerial oxidation of the developer radical of the dye developers or of auxiliary developing agents, e.g., hydroquinonyl radicals, does not occur, the undesired color degradation does not occur. In addition, the light stability of the dye images is substantially increased.

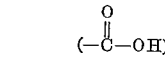
The aforesaid copending U.S. application Ser. No. 234,-864 discloses and claims the use in such diffusion transfer processes of an image-receiving element containing a nondiffusible acid-reacting reagent, or alkali-ion receptor, in a layer adjacent the image-receiving layer. This nondiffusible acid-reacting reagent, which preferably is a polymeric acid, acts to capture alkali ions thereby appreciably reducing the pH or alkalinity of the surface of the image-receiving layer. This reduction in pH is effected after the image dyes have been transferred to the image-receiving element and prior to exposure of the image layer to air. As a result, the alkalinity or pH of the dye developer environment in the image-receiving layer is adjusted to a level at least substantially precluding aerial oxidation of the developing radical of the transferred dye developers. Transfer images obtained employing such image-receiving elements are characterized by unusual brilliance and luminosity, and the image dyes exhibit a remarkable increase in stability to light.

The present invention is concerned with the provision of photosensitive elements containing dye developers wherein a layer of such a nondiffusible acid-reacting reagent is positioned adjacent the support, i.e., between the support and the innermost layer of dye developer. The provision of this layer of nondiffusible acid-reacting reagent in the photosensitive element provides a number of

advantages, particularly in multicolor transfer processes, which advantages will be discussed in detail hereinafter.

As indicated above, it has been discovered that the pH of the image-receiving element may be controlled very effectively by providing an acid-reacting layer adjacent the support of a photosensitive element containing dye developers as the image-forming reagents, whereby alkali ions are caused to diffuse to said acid-reacting layer and are there trapped or precipitated. The image-receiving element used with photosensitive elements containing such an acid-reacting layer also may contain such an acid-reacting layer, and the respective acid-reacting layers may be the same or different. The acid-reacting layer contains nondiffusible acid groups, e.g., acid groups attached to a polymer so as to be nondiffusible. This method of pH reduction in effect "washes" the image layer by internally diffusing the alkali ions and salt-forming reagents out of the image layer and into said acid-reacting layer or layers where they are precipitated. The acid-reacting layer thus may be considered to be a mordant for alkali, and is sometimes referred to as an "alkali ion receptor."

In accordance with the preferred embodiment of the invention, a layer containing an acid-reacting polymer, and particularly a polymer containing free carboxyl



groups, is provided in the photosensitive element and is positioned adjacent the support, i.e., between the innermost layer of dye developer and the support. For simplicity, this layer is sometimes referred to herein as the "polymeric acid layer" or as "acid polymer layer." A similar polymeric acid layer may be present in the image-receiving element and, if present, is positioned between the image-receiving layer [i.e., the layer in which the dye image is formed, and frequently referred to herein as the image layer] and the support.

The pH of the alkaline processing composition 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 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period; where the image-receiving element also contains an acid polymer layer. The pH of the positive image layer preferably is further reduced 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 about 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 9 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 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, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. This processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor processes using multilayer negatives.

It will be noted that this invention positions a polymeric acid layer in the negative on the opposite side of the silver halide emulsion(s) from the image-receiving layer. It also will be noted that the transfer image is formed by diffusion to the image-receiving layer of unoxidized dye developers in the form of an alkali salt. It ordinarily would be expected that the provision of a polymeric acid layer so positioned and capable of trapping alkali ions would unduly interfere with diffusion of the dye developers in the opposite direction by removing alkali ions needed to effect the dye developer transfer. It therefore was unobvious that not only would the thus-positioned polymeric acid layer not prevent transfer, but also that the pH of the image-receiving layer would be reduced even more than if the polymeric acid layer were positioned in the image-receiving element, as will be illustrated by examples given below.

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, so that the acid groups do not become available to any significant extent until after the desired transfer has been effected. 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. Plasticizers may be added, if desired, to the polymeric acid layer and/or other layers, to provide increased flexibility.

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, nondiffusible 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 and/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 orthosulfobenzoic anhydride; 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 further been discovered 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 as 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.

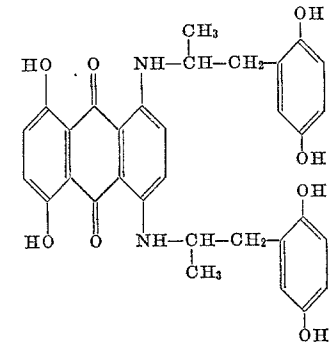
In a particularly useful embodiment, the spacer layer referred to above comprises a polymer which exhibits a permeability to alkali ions which is inversely temperature dependent, i.e., it exhibits decreasing permeability to solubilized alkali ions, such as alkali metal and quaternary ammonium ions, under 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, as a continuation-in-part of Ser. No. 277,099 filed May 1, 1963 (now abandoned). As examples of such polymers, mention may be made of hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxpropyl 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 8% 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 methyl cellulose 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.

Referring to the drawing, there is shown in FIGURE 1 an integral multilayer, multicolor photosensitive element **10** embodying a polymeric acid layer in accordance with the preferred embodiment of this invention, the photosensitive element **10** being positioned in superposed relationship with an image-receiving element **40** with a layer **32** of processing composition therebetween. The multicolor photosensitive element **10** comprises a support **12** bearing, in turn, a layer **14** containing, as a nondiffusible acid-reacting reagent, a polymeric carboxylic acid, an interlayer **16**, a layer **18** containing a cyan dye developer, a layer **20** of a red-sensitive silver halide emulsion, an interlayer **22**, a layer **24** containing a magenta dye developer, a layer **26** of a green-sensitive silver halide emulsion, an interlayer **22**, a layer **28** of a yellow dye developer, and a layer **30** of a blue-sensitive silver halide emulsion. The image-receiving element **40** comprises a support **12** carrying an image-receiving layer **34**.

As noted above, the image-receiving element also may contain a layer containing a nondiffusible acid-reacting reagent. A preferred embodiment of such an image-receiving element is shown in FIG. 2, wherein an image-receiving element **40***a* comprises a support **12** carrying, in turn, a layer **14** containing, as a nondiffusible acid-reacting reagent, a polymeric carboxylic acid, a spacer layer **16**, and an image-receiving layer **34**.

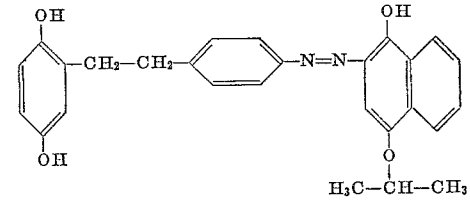
In the following examples, the multilayer photosensitive elements or negatives, unless otherwise indicated, have a structure like that shown in FIGURE 1, and contain layers of gelatin as the interlayers **22**, the dye developer layers are provided by dissolving the developers in water-immiscible solvents and dispersing the resulting dye developer solutions in gelatin, and the dye developers used were:

cyan:



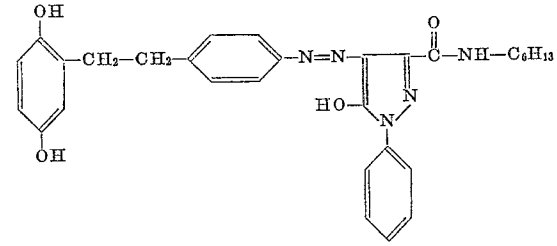
1,4-bis-[α-methyl-β-hydroquinonyl-ethylamino]-5,8-dihydroxy-anthraquinone

magenta:



2-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-napthol

yellow:



1-phenyl-3-N-n-hexylcarbamyl-4-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

The following examples are given for purposes of illustration and are not intended to be limiting:

Example 1

A multilayer photosensitive element was prepared as follows: a solution of 5 g. cellulose acetate and 5 g. cellulose acetate hydrogen phthalate (commercially available from Eastman Kodak Co., Rochester, N.Y., and having approximately 35% phthalyl and 18% acetyl content) dissolved in 100 g. of acetone was coated on a subcoated cellulose acetate film base to a thickness of approximately 1 mil. Over this polymeric acid layer there then were ap-

plied the layers of cyan, magenta and yellow dye developers, gelatin interlayers, and red, green and blue-sensitive silver halide emulsions described above.

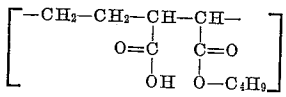
An image-receiving element was prepared by coating a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine on a cellulose acetate-subcoated baryta paper to provide an image-receiving layer approximately 0.40 mil thick. This multicolor negative then was exposed and a layer approximately 0.0050" thick of processing composition comprising:

Water	cc.	100
Sodium hydroxide	g.	5.17
Potassium hydroxide	g.	3.75
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Del., under the trade name Natrasol 250]	g.	4.03
Sodium thiosulfate	g.	0.5
Cesium hydroxide	g.	0.5
Benzotriazole	g.	2.3
N-benzyl-α-picolinium bromide	g.	2.3

was spread between said image-receiving element and said exposed multi-color negative as they were brought into superposed relationship. After an imbibition period of approximately 5 minutes, the image-receiving element was separated and contained a multicolor image. The surface of the image-receiving layer had a pH of 10 immediately after separation of said elements. In a control experiment in which the same conditions were employed except that the polymeric acid layer of cellulose acetate hydrogen phthalate and cellulose acetate was omitted, the surface of the image-receiving layer exhibited a pH in excess of 11 immediately after separation of the superposed elements.

Example 2

300 g. of high viscosity poly(ethylene/maleic anhydride) [commercially available from Monsanto Chemical Co., St. Louis, Mo., under the trade name DX-840-31 Resin] was dissolved in 1500 cc. of acetone. 150 g. of n-butyl alcohol and 1 cc. of 85% phosphoric acid were added and the mixture was refluxed for 14 hours. The resulting solution of a polymer containing recurring segments of the formula:



was allowed to cool and then coated on a cellulose nitrate subcoated baryta paper to give a polymeric acid layer about 0.8 mil thick. A thin layer of cellulose acetate was then coated using a solution containing 3% cellulose acetate dissolved in a mixture of methanol and ethyl acetate to provide a spacer layer. Cyan, magenta and yellow dye developer layers, gelatin interlayers, acid red, green and blue-sensitive silver halide emulsions were then applied to form a photosensitive element of the type shown in FIGURE 1. This photosensitive element was exposed and then processed by spreading a layer approximately 0.0068" thick of a processing composition comprising:

Water	cc.	100
NaOH	g.	5.17
Hydroxyethyl cellulose (high viscosity [commercially available from Hercules Powder Co., Wilmington 99, Del., under the trade name Natrasol 250]	g.	4.03
Sodium thiosulfate	g.	1.15
Benzotriazole	g.	2.3
N-benzyl-α-picolinium bromide	g.	2.3
4'-methylphenyl-hydroquinone	g.	0.4

between the exposed negative and an image-receiving element of the type described in Example 1. After an imbibition period of approximately 2 minutes, the image-receiving element was separated and contained a multicolor transfer image. The surface of the image-receiving layer had a pH of 11 immediately after separation from the developed negative.

Example 3

An image-receiving element was prepared by applying a 1:1 mixture, by weight, of cellulose acetate and cellulose acetate hydrogen phthalate (35% phthalyl, 18% acetyl) on subcoated baryta paper to provide a polymeric acid layer approximately 1 mil thick. An image-receiving layer approximately 0.25–0.35 mil thick and comprising a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine was then applied. When the procedure described in Example 2 was repeated using the just-described image-receiving element, the surface of the image-receiving layer had a pH of 10 immediately after separation of the superposed elements.

Example 4

A multilayer multicolor negative was prepared as described in Example 1, except that the photosensitive element support was paper. After exposure, a layer approximately 0.0060" thick of the processing composition described in Example 1 was spread between the exposed negative and an image-receiving element prepared as described in Example 3. After an imbibition period of approximately 3 minutes, the image-receiving element was separated and the surface of the image-receiving layer exhibited a pH of 9.5.

Example 5

A photosensitive element of the type shown in FIGURE 1 was prepared by coating a subcoated paper base with a layer approximately 0.55 mil thick of a partial butyl half-ester of poly(ethylene/maleic anhydride), prepared as described in Example 2, over which was applied a layer of polyvinyl alcohol approximately 0.6 mil thick. The usual cyan, magenta and yellow dye developer layers, gelatin interlayers, and red, green and blue sensitive emulsion layers were then applied. This multi-color negative was then exposed, and a layer approximately 0.0050" thick of processing composition comprising:

Water	cc.	100
Sodium hydroxide	g.	5.17
Potassium hydroxide	g.	3.75
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Del., under the trade name Natrasol 250]		4.03
Sodium thiosulfate	g.	0.5
Cesium hydroxide	g.	0.5
Benzotriazole	g.	2.3
N-benzyl-α-picolinium bromide	g.	2.3
4'-methylphenyl-hydroquinone	g.	0.2

was spread between the exposed multicolor photosensitive element and an image-receiving element (prepared as described in Example 1) as said elements were brought into superposed relationship. After an imbibition period of approximately 2 minutes, the superposed elements were separated. The surface of the image-receiving layer showed a pH of 8.5 immediately after separation, and this pH had not changed when measured again 3 minutes after separation.

Example 6

The procedure described in Example 5 was repeated using an image-receiving element of the type shown in FIG. 2, the polymeric acid layer comprising a layer approximately 0.0008" (0.8 mil) thick and composed of partial butyl half-ester of poly(ethylene/maleic anhydride), a spacer layer approximately 0.00035" (0.35 mil) thick and composed of polyvinyl alcohol, and an image-receiving layer approximately 0.0003" (0.3 mil) thick and composed of a 2:1 mixture, by weight, of poly-

vinyl alcohol and poly-4-vinyl pyridine. The pH of the surface of the image-receiving layer immediately after separation was 8. The following table shows the pH of the surface of the positive image as recorded at the stated times after the positive was separated.

Time:	pH
30"	7.5
1'	7
1½'	5.5
2'	5.5

It will be noted that the pH of the positive obtained in Example 5, as measured at the surface, did not drop with time after the negative and positive were separated. It thus will be seen that incorporation of the polymeric acid layer in the photosensitive element permits a type of control of the pH of the positive image not obtainable when the polymeric acid layer is present only in the image-receiving element. In the latter instance, the pH can continue to drop because internal diffusion of alkali to the polymeric acid layer is possible and does, in fact, occur. In the embodiment of Example 5, however, the polymeric acid layer is physically removed from further contact with the image-receiving layer, and a further pH drop from alkali extraction (diffusion) is not possible. This embodiment is partciularly useful where it is desired to maintain the final pH of the positive at an alkaline level, and particularly at a pH within a fairly narrow range, as, for example, where the desired color or stability characteristics of an image dye manifest themselves at such intermediate pH levels.

Use of the polymeric acid layer in the photosensitive element also is particularly advantageous where the transfer image is formed on a transparent support and is intended to be viewed as a transparency. This permits the pH of the positive image to be controlled without adding an additional layer in the positive or image-receiving element.

In the above examples, the polymeric acid layer has been exemplified by the partial butyl half-ester of poly(ethylene/maleic anhydride) and by cellulose acetate hydrogen phthalate mixed with cellulose acetate. As previously noted, many other acid polymers may be used. Thus, one may use the partial esters of poly(ethylene/maleic anhydride) with 2-ethylhexyl alcohol, hexyl alcohol, propyl alcohol, amyl alcohol, etc., and the degree of substitution of the maleic anhydride groups may vary over a wide range but preferably is within the range of about 25 to 75%. As an example of a cellulose half-ester which may be used without mixture with cellulose acetate, mention may be made of cellulose acetate hydrogen phthalate having a phthalyl content of approximately 16%.

The diffusion transfer images obtained in accordance with this invention by employing photosensitive elements containing a polymeric acid layer adjacent the support, and particularly those obtained using such a photosensitive element in combination with an image-receiving element containing a polymeric acid layer, are characterized by being unusually luminous and this luminosity is retained with the passage of time. This luminosity is believed to be a direct result of the extraction of the alkali ions from the image layer and trapping them in the polymeric acid layer or layers. In addition to the fact that subsequent print-coating operations, such as previously proposed for improving light stability and image quality, may be completely avoided by use of such photosensitive elements, the image obtained have a luminosity and quality which could not be obtained by such print-coating procedures, even if a polymer were included in the coating solution to increase the image gloss. Salts present are extracted into the polymeric acid layer, where they appear to be substantially permanently retained. Removal of the alkali ions from the image-receiving layers helps to decrease their permeability to oxygen and to increase the rigidity of the polymer; this is especially true where the image-receiving layer contains polyvinyl alcohol as in the above examples.

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 equilibra 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 inert 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.

Examination of cross-sections of processed image-receiving elements containing inert spacer layers, e.g., a polyvinyl alcohol interlayer, showed that essentially all of the image dyes were contained in the image-receiving layer, the polyvinyl alcohol spacer layer being clear and essentially free of dye developer. Removal of the ions from the image layer permits the molecules around the dyes to come closer tagether for a tougher bond which imbeds the image dyes in a clear, brilliant, neutral or near neutral layer that permits usually luminous colors.

In the preferred embodiments of this invention, the initial pH of about 14 is reduced to about 9 to 11 after about an imbibition period of about 45 to 90 seconds at 75° F., at which time the positive is separated. Where the image-receiving element also contains a polymeric acid layer, the pH of the positive continues to drop, e.g., to about 7 to 8 within a minute after stripping the negative and positive apart. In some instances, the pH has dropped to values as low as 6 or even lower within several minutes after imbibition was terminated.

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 the copending application of Howard C. Haas, Ser. No. 50,848, filed Aug. 22, 1960, now U.S. Patent No. 3,148,-061 issued 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 Mar. 8, 1966], are known in the art and may be employed. Similarly, while the preferred embodiment effects development in the presence of a quaternary ammonium compound (as disclosed and claimed in the copending application of Milton Green and Howard G. Rogers, Ser. No. 50,851, filed Aug. 22, 1960, now U.S. Patent No. 3,173,786, issued 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 symbol pH as used throughout the specification and the attached claims represent the logarithm of the reciprocal of the hydrogen ion concentration. The pH was determined by the use of pH paper wet with distilled water and measured at the surface of the image-receiving layer.

Use of the novel photosensitive elements of this invention makes feasible the use of image dyes which are pH sensitive, and particularly the use of dye developers having less pH insulation than otherwise would be desirable since the final pH of the image layer can be more accurately and reproducibly controlled. In addition, this invention facilitates the use of image dyes which are pH sensitive, and which are incorporated in the negative at a pH such that they are light-transmittant, and which shift to a desired light-absorbent state by appropriate pH adjustment.

It is recognized that it has been previously proposed to incorporate a dye developer in a layer of cellulose acetate hydrogen phthalate to provide a dye developer layer, e.g., as noted in the aforementioned U.S. Patent No. 2,983,606, issued to Howard G. Rogers on May 9, 1961. The present invention may be distinguished from such prior practices by virtue of the fact that the polymeric acid layer herein contemplated is positioned between such a dye developer-containing layer and the support. Furthermore, the quantity of nondiffusible acid-reacting groups herein contemplated is substantially greater than would be provided by prior use of cellulose acetate hydrogen phthalate as a dye carrier. Thus, the pH of the surface of the image-receiving layer is appreciably in excess of 12, where the only source of polymeric acid groups is the cellulose acetate hydrogen phthalate previously employed as the dye carrier. In addition, the acid groups present in a dye layer containing cellulose acetate hydrogen phthalate are available for reaction simultaneously with the permeation of alkali into the dye layer to effect the necessary solubilization of the dye developer; this results in a consumption of alkali prior to dye transfer in direct contrast to the delayed consumption of alkali effected in the present invention.

It has previously been proposed, in U.S. Patent No. 2,635,048, issued Apr. 14, 1953, to Edwin H. Land, to neutralize at least part of any residual alkali by incorporating an acidic reacting reagent, e.g., a derivature of an organic acid, in a layer behind the image-receiving lyer, which derivative is effective to release an organic acid during imbibition and thereby reduce the alkalinity of the image-receiving layer. While this approach is useful in some instances, it requires careful control lest the diffusing acid interfere with the transfer process, e.g., by diffusing into the developing silver halide emulsion stratum and prematurely stopping development. In addition, such a procedure results in the introduction of additional ions into the image layer with attendant disadvantages, and the alkali salt is retained in the image layer instead of being formed in a layer separate thereform. Although the resulting image layer may be "neutralized," it cannot be considered as having been "washed."

U.S. Patent No. 2,584,030, issued Jan. 29, 1954, to Edwin H. Land, also proposes to effect a neutralization of at least part of the residual alkali by employing a soluble substance of acid reaction. Insofar as this patent contemplates the use of metal salts, e.g., lead nitrate, the above comments regarding U.S. Patent No. 2,635,048 also are applicable. There is a disclosure, however, in U.S. Patent No. 2,584,030, of the use of a polymeric acid such as cellulose acetate hydrogen phthalate, as a component of image-receiving elements effective to obtain pH reduction in silver transfer processes. The instant invention may be distinguished therefrom, among other ways, by the use of dye developers, the use of dyeable polymers as the image layer, and by the relatively thicker polymeric acid layers as compared with the image layer.

In all embodiments of this invention involving a polymeric acid layer, the polymeric acid layer is relatively thick as compared, e.g., with the dye layers. 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 mils thick. If an inert spacer layer is present, that layer is preferably about 0.1 to 0.7 mil thick. If the image-receiving element also contains a polymeric acid layer, said layer may be of substantially the same thickness as the corresponding layer in the photosensitive element, but advantageously may be thinner; the ability to balance, i.e., vary, the respective polymeric acid layers provides a novel and highly useful technique for closely controlling the final pH of the transfer image. 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.

As noted above, the preferred embodiment of this invention contemplates reduction of the positive image pH to a level substantially precluding aerial oxidation of developer moieties. The provision of anti-oxidants, such as arbutin, e.g., in a layer of the image-receiving element or as a component of the processing compositions, so that it is associated with the dye image prior to exposure of the image to air to provide additional protection against oxidation also is within the scope of this invention. In embodiments in which the reduction in pH continues for at least a short time after the positive image is separated from the negative, provision of such an antioxidant permits the positive to be separated at a slightly higher pH than might be otherwise desirable.

It is also contemplated to provide other adjuvants, e.g., ultraviolet absorbers, effective to improve the light stability or other properties of the positive image. Thus, an ultraviolet absorber may be included in the processing composition and deposited on the image-receiving layer during imbibition, or it may be resent in a thin overoat on the image-receiving layer prior to imbibition.

When the dye mordant in the image-receiving layer is acid soluble, e.g., poly-4-vinylpyridine, and the image dye is alkali-soluble, e.g., a dye developer, the greatest increases in stability to light are found where the dye layer is rendered substantially neutral, and a stratum of an inert, substantially neutral polymeric material separates the image layer from the polymeric acid layer.

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'-methylphenylhydroquinone, toluhydroquinone, tertiary-butylhydroquinone, 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, now abandoned.

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 about 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.

The following example of such a potassium-containing processing composition is given for purposes of illustration only:

Example 7

Water	cc.	100
Potassium hydroxide	g.	11.2
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Del., under the trade name Natrasol 250]	g.	4.03
Benzotriazole	g.	3.5
Potassium thiosulfate	g.	0.5
Lithium nitrate	g.	0.5
Zinc nitrate	g.	0.5
N-benzyl-α-picolinium bromide	g.	2.3

It is also to be understood that this 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 a processing technique wherein the photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, is 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. The processing composition, either viscous or nonviscous, may be applied to the exposed photosensitive element and/or the image-receiving element, by imbibition or other techniques, before said elements are brought into superposed relation or contact for carrying out the transfer of non-immobilized color-providing substances.

Incorporation of the polymeric acid layer in the photosensitive element, in accordance with this invention, is particularly useful in embodiments in which an image-receiving element is prewet with a processing composition, and the prewet image-receiving element is brought into superposed relationship with a dry, exposed photosensitive element. In such an embodiment, a polymeric acid layer located in the image-receiving element might be activated prematurely. Nonviscous processing compositions suitable for use in such embodiments may be prepared, for example, by omitting the hydroxyethyl cellulose from the processing compositions set forth in the above specific examples.

As noted above, the provision of an inert spacer layer between the image layer and the polymeric acid layer, has been found to be beneficial in improving the control of the rate of pH reduction. In such embodiments, the layer in which the image dyes are deposited is relatively thin, e.g., on the order of about 0.25–0.35 mil in thickness It also has been found that, in lieu of such an inert spacer or interlayer, one may employ a relatively thick image-receiving layer, the rearward portion of such a thick image-receiving layer acting as an inert interlayer. In one such embodiment, an image-receiving element was prepared with a 0.7 mil thick layer of the butyl half-ester of poly(ethylene/maleic anhydride) over which was coated a 0.75 mil thick layer of a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine. When this image-receiving element was used with a photosensitive element which did not contain a polymeric acid layer, i.e., in the process disclosed and claimed in my aforementioned copending U.S. application Ser. No. 234,864, it was found that very good multicolor images could be obtained at a processing temperature of 30° F. Examination of a photomicrograph of a cross-section of the processed image-receiving element showed that the dyes forming the blacks or neutral $D_{max.}$ portion of the dye transfer image were located in approximately the upper one-third of the image-receiving layer. At least the lower or rear one-third portion of the image-receiving layer was clear and free of dye and hence effectively acted as an interlayer to insulate the dye image from the polymeric acid layer. Thus, an image-receiving element analogous to that shown in FIG. 2 is obtained, the image-receiving layer **34** and the spacer layer **16** being provided by a single layer of the same composition and having a thickness on the order of the sum of the thicknesses of the two separating layers.

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, 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 3,265,498.

This invention is especially useful in composite film units intended for use in a Polaroid Land camera, made by Polaroid Corporation, Cambridge 39, Mass., or a similar camer structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on Feb. 10, 1948. In general, such composite film units comprise a photosensitive element, an image-receiving element and a rupturable pod containing an aqueous alkaline processing solution, and may take the form of roll film, sheet film, or film packs. The elements and pod are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pod may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of such pods is well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, isued to Edwin H. Land.

Although the invention has been illustrated in connection with dye developers, and the invention is particularly

applicable to dye developers because of their susceptibility to aerial oxidation, the herein disclosed inventive concepts may be used in other diffusion transfer processes to obtain pH reduction and particularly to obtain transfer images exhibiting great optical clarity and luminosity.

It has also been found that diffusion transfer color images having unique properties and utility, may be obtained if a specularly light-reflecting layer is positioned between the image-carrying layer and the support. The specularly light-reflecting layer preferably is highly polished and has a mirrorlike surface so that the maximum amount of light incident upon the image-carrying layer and passing therethrough to the specularly light-reflecting layer will be reflected back through the image-carrying layer and out through the surface of the image-receiving element. The image-receiving element may or may not contain a layer of a non-diffusible acid-reacting reagent positioned between the image-receiving layer and the reflecting layer.

Suitable specularly light-reflecting layers may be provided by laminating a suitable aluminum foil to the support, by evaporating a layer of aluminum upon the support, or by other procedures well known in the art for providing a thin layer of aluminum or other metal which is or can be polished to provide the desired specularly light-reflecting surface. Color transfer images formed upon an image-receiving element containing such a specularly light-reflecting layer, even though the support be nontransparent, are uniquely adapted for projection viewing, i.e., by directing a source of light upon the surface of the image-receiving element and projecting the reflected light through a suitable lens system to a screen for viewing.

The provision of the specularly light-reflecting image-receiving layer permits the formation of projectable color transfer images having many of the desirable features of color transparency images, while requiring no more dye density than is customarily employed in forming reflection prints. This is in sharp contrast to the much greater (at least two times) dye density usually required for color transparencies. Because of this, one may obtain either reflection prints or projectable images by depositing substantially the same dye density upon the appropriate image-receiving element.

In lieu of employing a specularly light-reflecting layer within the image-receiving element, one may form the transfer image upon a transparent base and thereafter optically bond the image to a suitable reflecting surface, e.g., aluminum, by a suitable material, e.g., a thin layer of mercury, coated on the surface of the reflector. In either case, the reflecting surface is so arranged that it is intersected by the optical axes of the condenser lens and the projector lens at equal angles. The specular light is projected to the screen only after being transmitted twice through the image. Very high contrast projected images thus may be obtained. Undesired specular reflection from the surface of the image may be controlled by use of polarizers in combination with a birefringement transparent base in the positive.

While this invention has been illustrated in connection with multilayer multicolor negatives, it will be understood that the inventive concepts also are applicable to monochrome negatives, e.g., for forming black dye transfer images, and to screen-type negatives, such as those prepared by the procedures disclosed in the U.S. Patent No. 3,032,008, issued to Edwin H, Land et al. on May 1, 1962.

It also is within the scope of this invention to coat the various layers of the photosensitive element over the image-receiving layer. Thus, the layers comprising image-receiving element **40***a* may be coated on a transparent support **12**, and the appropriate silver halide emulsion layers, spacer layers and dye developer layers coated thereover, with the blue-sensitive silver halide emulsion layer **30** being closest to the image-receiving layer **34**. In this embodiment, the polymeric acid layer **14** is positioned adjacent the transparent support **12**. Exposure is effected through the transparent support **12** and the processing composition is applied to the back of the cyan dye developer layer **18**, using a spreading sheet if desired to aid in application of said composition. After the desired imbibition period, the layers comprising image-receiving element **40***a* are separated from the remaining layers. A stripping layer may be positioned between the image-receiving layer **34** and the blue-sensitive silver halide emulsion layer **30** to facilitate such separation.

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 of forming color transfer images wherein a photosensitive element is exposed, an alkaline processing composition is applied to said photosensitive element to effect development thereof and imagewise diffusion transfer of a dye image-forming substance from said photosensitive element to an image-receiving layer in superposed relationship therewith to form a positive dye image, the improvement wherein said photosensitive element contains a layer of a nondiffusible polymeric acid positioned between the support and the innermost layer containing said dye image-forming substance, said layer containing said polymeric acid containing sufficient acid groups to effect a reduction in the pH of the surface of said image-receiving layer of at least 2 pH units, as compared with the initial pH of said alkaline processing composition, prior to completion of the imbibition period.

2. A process as defined in claim **1** wherein said image-receiving layer is carried on a separate support, and a second layer containing a nondiffusible polymeric acid is positioned between said image-receiving layer and said support therefor.

3. A process as defined in claim **1**, wherein said polymeric acid is cellulose acetate hydrogen phthalate.

4. A process as defined in claim **1**, wherein said polymeric acid is a butyl half-ester of poly(ethylene/maleic anhydride).

5. A process as defined in claim **1**, wherein said transferred dye image-forming substance is an unoxidized dye developer.

6. A process of forming multicolor diffusion transfer images comprising exposing a photosensitive element containing 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, said photosensitive element also containing a layer of a polymeric acid positioned between said support and the dye developer-containing layer positioned nearest said support; applying to said exposed photosensitive element an alkaline processing composition containing a quaternary ammonium salt; developing said exposed photosensitive element and forming, as a function of said development an imagewise distribution of unoxidized dye developer of each of said yellow, magenta and cyan dye developers; and transferring, by diffusion, at least a portion of each said imagewise distribution of unoxidized dye developer to an image-receiving layer positioned in superposed relationship with said silver halide emulsions to form a multicolor transfer image, said polymeric acid being present in a concentration effective to reduce the pH of said transfer image, after said transfer image has been formed and prior to separation of said image-receiving layer from said photosensitive element, to a pH level at least about 2 pH units lower than the initial pH of said alkaline processing composition, there-

by substantially precluding aerial oxidation of said hydroquinonyl radicals upon exposure of said transfer image to air.

7. A process as defined in claim 6, wherein said image-receiving layer is carried on a separate support, and a second layer of a polymeric acid is positioned between said support and said image-receiving layer.

8. A process as defined in claim 6, wherein at least one of said dye developers is pH sensitive, and said pH reduction is effective, prior to separating said image-receiving layer from said superposed relationship, to provide a pH at which said pH-sensitive dye developer exhibits a color substantially complementary to the sensitivity of its respective silver halide emulsion.

9. A process as defined in claim 6, wherein said quaternary ammonium compound is capable of forming an active methylene base when dissolved in alkali.

10. A process as defined in claim 6, wherein a layer of an inert, alkali-permeable polymer is positioned between said layer of polymeric acid and said dye developer-containing layer positioned nearest said support.

11. A process as defined in claim 6, wherein said development is effected in the presence of a substantially colorless hydroquinone.

12. A process as defined in claim 6, wherein the reaction of said polymeric acid with said alkali releases water.

13. A process as defined in claim 6, wherein said alkaline processing composition has a pH of at least 13, and said reduced pH is below about 11, and said reduction is effected within 45 to 90 seconds at 75° F.

14. A process as defined in claim 7, wherein a specularly light-reflecting layer of aluminum is positioned between said support carrying said image-receiving layer and said layer of polymeric acid.

15. A process as defined in claim 6, wherein each of said dye developers is contained in a layer behind its respective silver halide emulsion, and said layer of polymeric acid is about 0.5 to 1.5 mil thick and is positioned between said support and said dye developer-containing layer positioned nearest said support.

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