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3,433,633

**PHOTOGRAPHIC PRODUCTS AND PROCESSES**  
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15 Claims

## ABSTRACT OF THE DISCLOSURE

The present invention relates to photography, particularly to photographic products specifically adapted for employment in photographic diffusion transfer color processes and, more particularly, to photographic image-receiving elements for diffusion transfer photographic processes which comprises a laminate containing a plurality of essential layers, including, in sequence, a support layer, a polymeric acid layer, a polymeric layer comprising hydroxypropyl cellulose, and a permeable and dyeable polymeric layer.

This application is in part a continuation of my copending U.S. application Ser. No. 447,070, filed Apr. 9, 1965, now abandoned.

The present invention relates to photography and, more particularly, to processes for forming photographic diffusion transfer color images and products particularly adapted for employment in such processes.

It is a primary object of the present invention to provide novel photographic diffusion transfer color processes and novel image-receiving elements particularly adapted for employment in such processes.

Another object of the present invention is to provide photographic diffusion transfer color processes exhibiting increased processing temperature latitude and novel image-receiving elements particularly adapted to accomplish same.

A further object of the present invention is to provide novel photographic diffusion transfer color processes exhibiting constant transfer image color characteristics over an extended temperature range and novel image-receiving elements particularly adapted to accomplish same.

A further object of the present invention is to provide photographic diffusion transfer color processes wherein the hydrogen ion concentration during transfer processing is maintained substantially constant over an extended temperature range and novel image-receiving elements particularly adapted to accomplish same.

A still further object of the present invention is to provide novel photographic diffusion transfer color processes wherein the hydrogen ion concentration during transfer processing is maintained substantially constant for a predetermined time interval, irrespective of the temperature dependent diffusion rate of alkali present, and novel image-receiving elements particularly adapted to accomplish same.

A still further object of the present invention is to provide novel image-receiving elements, particularly adapted for employment in photographic diffusion transfer color processes, which comprise a laminate which includes a specified permeable polymeric material which possesses a temperature inverse permeability to alkali and novel transfer processes employing same.

A still further object of the present invention is to provide novel image-receiving elements, particularly adapted for employment in photographic diffusion transfer color processes, which comprise a flexible laminate which in-

cludes, in sequence, a support layer, a first polymeric acid layer, a second alkali solution permeable polymeric layer having specified permeability characteristics which polymeric layer comprises hydroxypropyl cellulose, and a solution dyeable polymeric layer and novel transfer processes particularly adapted to employ same.

A still further object of the present invention is to provide image-receiving elements, particularly adapted for employment in photographic diffusion transfer color processes, which include a plurality of layers comprising, in sequence, a support layer, a first polymeric alkali metal ion acceptor layer, a second alkali metal ion temperature inversely permeable polymeric layer comprising hydroxypropyl cellulose, and a third polymeric layer adapted to be dyed from an alkaline solution and novel transfer processes particularly adapted to employ same.

Other objects of the present 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 product 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.

U.S. Patents Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; 2,802,735, issued Aug. 13, 1957, disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized which comprise, at least in part, reacting one or more developing agents and one or more color formers to provide a positive color image on a superposed image-receiving layer. U.S. Patent No. 3,019,124, issued Jan. 30, 1962, discloses the manufacture of photographic color screen elements; and U.S. Patents Nos. 2,968,554, issued Jan. 17, 1961 and 2,983,606, issued May 9, 1961 disclose diffusion transfer processes wherein a color screen element is utilized to provide a multicolor positive image to a superposed image-receiving layer. U.S. Patent No. 2,774,668, issued Dec. 18, 1956, the copending U.S. application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956 now U.S. Patent No. 3,345,135 and the previously cited U.S. Patent No. 2,983,606 disclose diffusion transfer processes wherein complete dyes are utilized to provide a positive color image to a superposed image-receiving layer.

In processes of the type set forth in U.S. Patent No. 2,983,606, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superimposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due 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 de-

veloping agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superimposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the previously noted U.S. Patents Nos. 2,968,554 and 2,983,606. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of said patents, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multi-layer photosensitive element, such as is disclosed in the aforementioned copending U.S. application Ser. No. 565,135, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. How-

ever, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

Copending U.S. application Ser. No. 234,864, filed Nov. 1, 1962 now U.S. Patent No. 3,362,819, discloses image-receiving elements, particularly adapted for employment in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, an inert timing or spacer layer, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned application, the polymeric acid layer comprises 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 disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated 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 and/or potassium salts. One may also 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 set forth in the application, 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 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 methyvinyl ether/maleic anhydride copolymers; etc.

The acid polymer layer is disclosed to contain 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, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

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 is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the quaternary ammonium, sodium or other alkali salt. The diffusion rate of such dye image-forming components 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 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. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be 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 hydroxyl 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 are illustrated, respectively, in the copending application, 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.

It is also disclosed that the layer containing the polymeric acid may 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, mention is made of cellulose acetate, cellulose acetate butyrate, etc. 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 and when necessary or desirable, suitable sub-coats may be employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the aforementioned copending application, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It was stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylons as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Patent No. 3,148,061, issued Sept. 8, 1964.

The objects of the present invention, detailed hereinbefore, are accomplished by employment, in photographic diffusion transfer color processes of the preceding general type, of a novel image-receiving element which comprises a plurality of essential layers including, in sequence, a support layer, a polymeric acid layer, a permeable polymeric spacer layer having an inverse temperature-dependent solution permeability, and a permeable, solution dyeable polymeric layer.

Specifically, the image-receiving element preferably comprises a flexible laminate including a plurality of poly-

meric layers which comprise, in sequence, a support layer, a polymeric alkali ion acceptor layer, for example, an alkali metal or quaternary ammonium ion acceptor layer, a polymeric layer having decreasing permeability to solubilized hydroxyl ion with increasing temperature, and a polymeric layer dyeable from contact with a dye containing alkaline solution.

As disclosed in the aforementioned copending application Ser. No. 234,864, filed Nov. 1, 1962, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, for example, at 95 to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

Copending U.S. application Ser. No. 277,099, filed May 1, 1963, and now abandoned, discloses that preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, as set forth in the last-mentioned application, it was found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was disclosed to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective within the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was found to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates. This barrier resulted in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer image's color definition. In addition, the extended maintenance of the high pH conditions was disclosed to result in deleterious salt formation, on the surface of the transfer image receptive stratum, upon stripping, with the concomitant result that the positive print exhibits an extensive loss in its desired gloss characteristics.

It was further disclosed, in the last-mentioned application, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, and specifically a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned over-extended pH maintenance and/or premature pH reduction were obviated.

As examples of polymers disclosed in the application which exhibit inverse temperature-dependent permeability to alkali, mention was made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl

butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like, and including a mixture of the polymers as, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

Specifically, the spacer layer of the last-described print-receiving element comprises a permeable polymeric layer exhibiting, in a photographic diffusion transfer environment, a photographic processing composition permeability inversely dependent on processing temperature, when compared with, or measured against, polymers disclosed in the art for the identified photographic use. In general, such polymers as are particularly adapted for formulation of the spacer layer exhibit the property of being relatively soluble in cold water, that is, water at a temperature of less than about 40 to 80° C., depending upon the polymer specifically selected for employment, and relatively insoluble in hot water, that is, water at a temperature above the denoted temperature range, according to polymer selected, and irrespective of the fact that a relatively large number of such polymers are substantially insoluble in a caustic photographic processing composition medium, over the range of photographic diffusion transfer processing. Such polymers, however, are permeable to photographic alkaline processing composition as a function of their swelling, which, in turn, is believed to be a function of the free energy of solution decrease caused, at least in part, by the heat evolved as a result of the interaction between the polymer and the processing composition solvent and by an increase of the entropy of the system. This free energy decrease is believed to lessen with increased temperature of the environment and result in a decreased swelling, and thus photographic processing composition permeability, with such temperature increase.

It has now been quite unexpectedly discovered that if the temperature inversely permeable polymeric layer of the last-identified copending application specifically comprises hydroxypropyl cellulose vastly superior cold temperature processing performance, for example, processing at a temperature in the order of less than about 50° F., is achieved.

Specifically, employment of hydroxypropyl cellulose, in the manner detailed above, provides, in a cold temperature processing environment, higher transfer image maximum densities, increased photographic speed, increased flexibility of coating layer thickness parameters, and, in multicolor photographic diffusion transfer processes, improved color isolation.

Preferably the hydroxypropyl cellulose employed possesses an M.S. of about 2 to 5 and most preferably of about 2 (average number of moles of reactant combined with the cellulose per anhydroglucose unit during hydroxypropylation, which may be determined by the terminal methyl method reported by Lemieux and Purves beginning at p. 485, vol. 25B, 1947, of the Canadian Journal of Research and/or by the percent carbon method, according to the disclosures of U.S. Patents Nos. 3,278,520 and 3,278,521, both issued Oct. 11, 1966, to Eugene D. Klug) and may be prepared according to the processes set forth in the last-identified patents. As stated in the last-identified patents, hydroxypropyl cellulose having an M.S. of about 2 becomes insoluble in water at a temperature above about 60° C. and that having an M.S. of about 4 becomes insoluble in water at a temperature above about 40° C., recognizing that the respective solubility in water varies inversely with viscosity.

The present invention will be illustrated in greater detail in conjunction with the following specific example which sets out a representative photographic product and process which, however, is intended to be illustrative and not of limiting effect.

## EXAMPLE

An image-receiving element was prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polyethylene/maleic anhydride copolymer which may be prepared by refluxing, for 14 hours, 300 gms. of a DX-840-31 resin (trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity polyethylene/maleic anhydride), 140 gms. of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.3 mil thick. The external surface of the acid layer was coated with a 1% solution of hydroxypropyl cellulose having an M.S. of 2 as defined hereinbefore in water to provide a polymeric spacer layer approximately 0.15 mil thick. The external surface of the spacer layer was then coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mg./ft.<sup>2</sup>, to provide a polymeric image-receiving layer approximately 0.40 mil thick. The thus-prepared image-receiving element was then baked at 180° F. for 30 minutes and then allowed to cool.

A multicolor, multilayer photosensitive element was prepared in a manner similar to that disclosed in the aforementioned copending U.S. application Ser. No. 565,135 and detailed hereinbefore. In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum. In turn, the emulsions had dispersed behind them in water-immiscible organic solvents and contained in separate gelatin polymeric layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A gelatin interlayer was positioned between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements were 1,4-bis-( $\alpha$ -methyl- $\beta$ -hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone (a cyan dye developer); 2-(p-[2',5'-dihydroxyphenethyl]-phenylazo)-4-isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl-carbamyl-4-(p-[hydroquinonyl-ethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Patent No. 3,134,764, issued May 26, 1964, and the cyan dye developer is disclosed in U.S. Patent No. 3,135,606, issued June 2, 1964. This material may also be commercially procured from Polaroid Corporation, Cambridge, Mass., as it comprises the negative component of the photographic film distributed by that corporation under the trade designation of Polacolor film Type 108.

The photosensitive element was then exposed and processed at 50° F. by spreading an aqueous liquid processing composition which may comprise:

Water	-----cc--	100
Potassium hydroxide	-----gms--	11.2
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250]	-----gms--	4.03
Potassium thiosulfate	-----gm--	0.5
Benzotriazole	-----gms--	3.5
N-benzyl- $\alpha$ -picolinium bromide	-----gms--	2.3
Lithium hydroxide	-----gm--	0.3

between said image-receiving element and said exposed multicolor element as they were brought into superposed relationship in a Polaroid Land Camera. After an imbibition period of 1 minute, the picture door of the camera was opened and the image-receiving element separated from the remainder of the film assembly.

For purposes of comparison, an image-receiving element was fabricated in accordance with the last-mentioned procedure with the exception that the spacer layer

comprised a layer of hydroxypropyl methyl cellulose approximately 0.15 mil thick, dry weight and coated from a solution comprising 1% hydroxypropyl methyl cellulose in water.

The last-prepared image-receiving element was then processed, as detailed above, at the temperature designated.

Examination of the resultant images shows the following differential maximum densities:

D <sub>max</sub>	Hydroxypropyl cellulose	Hydroxypropyl methyl cellulose
Red.....	1.35	1.13
Green.....	1.71	1.47
Blue.....	1.99	1.60

and the production of the desired glossy image by employment of the designated hydroxypropyl cellulose when compared with the dull image provided by employment of hydroxypropyl methyl cellulose.

A particularly preferred embodiment of the present invention's image-receiving element fabricated in the above example includes a relatively small amount of ethyl cellulose distributed in both the spacer and polymeric acid layers in order to provide maximum adhesion between same. Prior to temperature dependent permeation of the alkali through the inversely permeable spacer layer, the alkali remains close to the negative and close to the image layer. Once alkali has permeated through to the polymeric acid layer, a chemical sink for hydroxyl ion is provided and rapid permeation of hydroxyl ion ensues, whereby to remove alkali ions from the image layer, to swell the spacer polymer, and to provide heat devolved from the neutralization reaction. These factors help to keep the pH high, over an extended ambient temperature range, 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, e.g., 90 seconds, substantially irrespective of the processing temperature. The fact that the pH reduction also acts to create a self-limiting transfer density also permits continued imbibition to proceed without undesired color balance changes.

In the preferred embodiments of this invention, the initial pH of about 14 is reduced to about 9 to 11 after about a 1½ minute imbibition, at which time the positive is separated. 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.

Where desired, the hydroxypropyl cellulose employed may comprise a mixed cellulose ether such as a hydroxypropyl cellulose containing an ionic substituent, for example, having an ionic D.S. (degree of substitution) in the range of about 0.001 to 0.4. Such ionic substituents may comprise an ether substituent such as a carboxyalkyl ether substituent, for example, a carboxymethyl-, a carboxyethyl-, or an  $\alpha$ -methyl-carboxymethyl-substituent; a dialkylaminoalkyl ether substituent, for example, a dimethylaminoethyl-, a diethylaminoethyl- or a dimethylaminoisopropyl-substituent; a sulfoalkyl ether substituent, for example, a sulfomethyl-, a sulfoethyl- or a sulfopropyl-substituent; a sulfate substituent; or a carboxyl substituent. Furthermore, the mixed ether may also comprise hydroxyethyl hydroxypropyl cellulose having a hydroxyethyl M.S. in the range of about 0.05 to 1.0.

Although the preferred image-receiving layer is a mixture of polyvinyl alcohol and poly-4-vinylpyridine, the invention is not limited thereto. Other image-receiving layers are known in the art and may be employed. Similarly, while the preferred embodiment effects de-

velopment in the presence of a quaternary ammonium compound (as disclosed and claimed in 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 represents the logarithm of the reciprocal of the hydrogen ion concentration.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminums; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycolterephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

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 emulsions.

Use of the novel image-receiving elements of this invention makes feasible the use, over an extended range of ambient temperature, of image dyes which are pH sensitive, and particularly the use of the dye developers having less pH insulation since the final pH of the image layer can be more accurately and reproducibly controlled.

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, tolu-hydroquinone, 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 and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

As noted above, this invention contemplates reduction of the positive image pH to a level substantially precluding aerial oxidation of developer moieties. The provision of antioxidants, such as arbutin, prior to exposure of the image to air to provide additional protection against oxidation also is within the scope of this invention. Since 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 would 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 present in a thin overcoat on the image-receiving layer prior to imbibition.

In all preferred embodiments of this invention the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg./ft.<sup>2</sup> coverage. The image-receiving layer is preferably about 0.25 to 0.4 mil thick, the polymeric acid layer is preferably 0.3 to 1.5 mil thick, and the described spacer layer is preferably about 0.07 to 0.8 mil thick.

Although the invention has been illustrated in connec-

tion with dye developers, and the invention is particularly applicable to dye developers because of their susceptibility to aerial oxidation at high pH, the novel image-receiving elements of this invention may be used in other diffusion transfer processes such as those previously described to obtain pH reduction and particularly to obtain transfer images exhibiting great optical clarity and luminosity over an extended range of ambient temperatures.

In addition to the described essential layers, it will be recognized that the image-receiving elements may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, or improving adhesion, etc.

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

What is claimed is:

1. A photographic image-receiving element for diffusion transfer photographic processes which comprises a flexible laminate containing a plurality of essential layers including in sequence, a support layer, a polymeric acid layer, a polymeric layer comprising hydroxypropyl cellulose and a permeable and dyeable polymeric layer.

2. A photographic image-receiving element for diffusion transfer photographic processes which comprises a flexible laminate containing a plurality of layers including, in sequence, a support layer, a polymeric alkali acceptor layer, a polymeric layer comprising hydroxypropyl cellulose and a permeable solution dyeable polymeric layer.

3. A flexible laminate as defined in claim 2, wherein said polymeric alkali acceptor layer comprises cellulose acetate hydrogen phthalate.

4. A flexible laminate as defined in claim 2, wherein said polymeric alkali acceptor layer is cellulose acetate hydrogen succinate.

5. A flexible laminate as defined in claim 2, wherein said polymeric alkali acceptor layer comprises a partial ester of poly(methylvinyl ether/maleic anhydride) copolymer.

6. A flexible laminate as defined in claim 5, wherein said partial ester comprises the butyl ester.

7. A flexible laminate as defined in claim 2, wherein said polymeric alkali acceptor layer comprises a partial ester of poly(ethylene/maleic anhydride) copolymer.

8. A flexible laminate as defined in claim 2, wherein said solution dyeable polymeric layer comprises poly-4-vinyl pyridine and polyvinyl alcohol.

9. A flexible laminate as defined in claim 2, wherein said solution dyeable polymeric layer comprises poly-4-vinyl pyridine and gelatin.

10. In a process of forming diffusion transfer images in color which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent, by contacting said element with an aqueous alkaline solution, immobilizing said dye in the exposed areas of said element, as a result of development, forming thereby an imagewise distribution of mobile dye, as a function of the point-to-point degree of exposure of said element, transferring, by imbibition, at least a portion of said imagewise distribution of mobile dye to a superposed image-receiving element which com-

prises a plurality of layers including, in sequence, a support layer, a polymeric acid layer, a polymeric layer comprising hydroxypropyl cellulose, and a solution dyeable and permeable polymeric layer, to provide to said dyeable polymeric layer a positive dye image, transferring, by imbibition, subsequent to substantial positive image formation, at least a portion of the ions of said alkaline solution through each of said permeable polymeric layers to said polymeric acid layer to thereby reduce the alkalinity of said solution.

11. In a multicolor diffusion transfer process which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers having positioned contiguous, respectively, yellow, magenta and cyan dyes, each of said yellow, magenta and cyan dyes being silver halide developing agents, by permeating said photosensitive element with an aqueous alkaline processing composition having an initial pH of not less than about 12, immobilizing said yellow, magenta and cyan dyes, in exposed areas, as a result of development, thereby forming an imagewise distribution of mobile yellow, magenta and cyan dye, as a function of the point-to-point degree of exposure of said element, transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element comprising a plurality of essential layers including, in sequence, a support layer, a polymeric alkali acceptor layer, a polymeric layer comprising hydroxypropyl cellulose, and an alkaline solution dyeable and permeable polymeric layer, to provide to said dyeable polymeric layer a multicolor positive transfer dye image, transferring, by imbibition, subsequent to substantial positive transfer image formation, at least a sufficient portion of the alkali of said processing composition through each of said permeable polymeric layers to said polymeric alkali acceptor layer to provide thereby a reduction of the pH of said composition to a pH of not greater than about 10, and then separating said image-receiving element from said superposed relationship.

12. A process as defined in claim 11, wherein said aqueous alkaline composition comprises alkali metal ions.

13. A process as defined in claim 11, wherein said aqueous alkaline composition comprises quaternary ammonium ions.

14. A process as defined in claim 11, wherein said hydroxypropyl cellulose has an M.S. within the range of about 2 to 5.

15. A process as defined in claim 14, wherein said hydroxypropyl cellulose has an M.S. of 2.

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