

July 15, 1969

L. C. FARNEY ET AL
 DIFFUSION TRANSFER IMAGE RECEIVING ELEMENT WHOSE ALKALI
 DIFFUSION FLOW RATE VARIES INVERSELY
 WITH THE TEMPERATURE

3,455,686

Filed Aug. 30, 1967

2 Sheets-Sheet 1

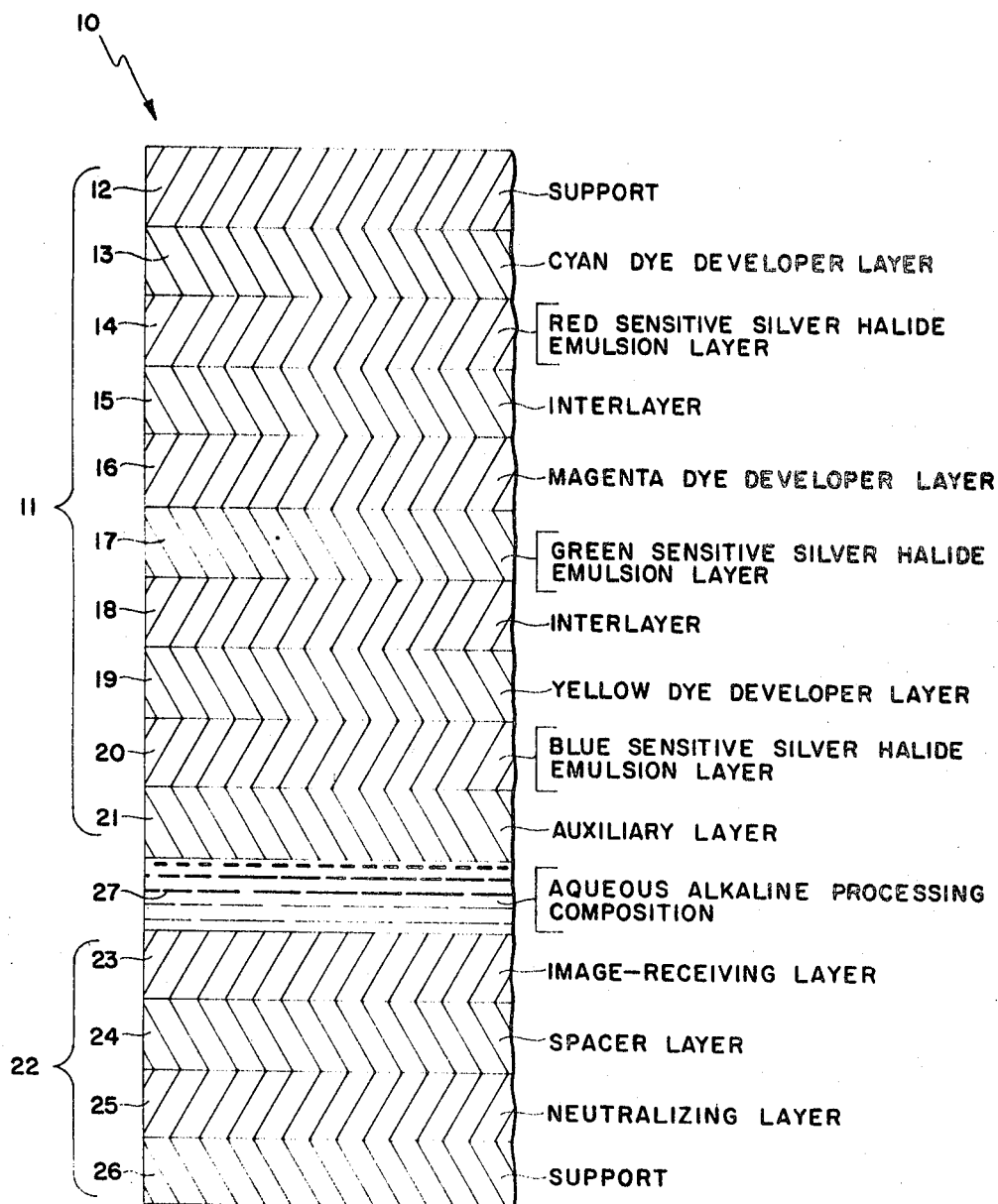


FIG. 1

INVENTORS
Leonard C. Farney
and
Howard S. Rogers
and
Richard W. Young
 BY
Brown and Mikulka
and
Robert M. Ford
 ATTORNEYS

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2 Sheets-Sheet 2

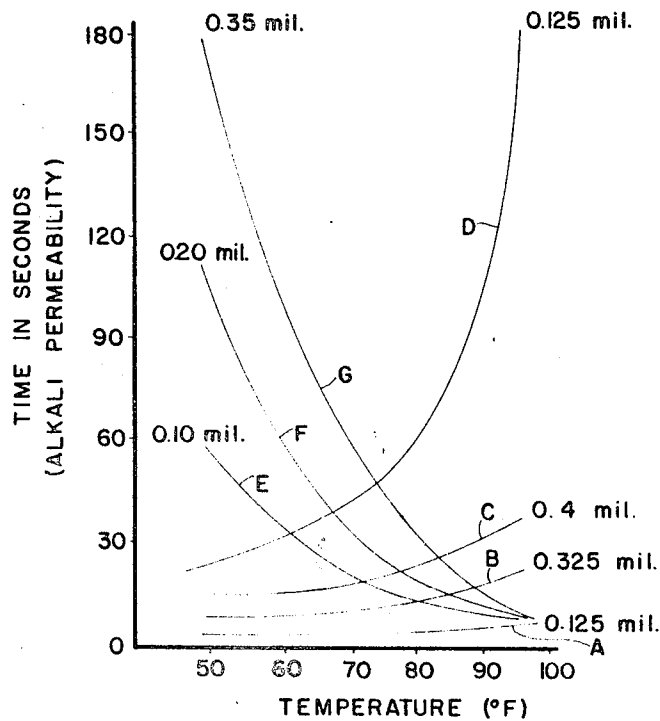


FIG. 2

INVENTORS

Leonard C. Farney
and

Howard G. Rogers
and

Richard W. Young

BY

Brown and Mikulka
and

Robert M. Ford
ATTORNEYS

1

3,455,686

DIFFUSION TRANSFER IMAGE RECEIVING ELEMENT WHOSE ALKALI DIFFUSION FLOW RATE VARIES INVERSELY WITH THE TEMPERATURE

Leonard C. Farney, Melrose, Howard G. Rogers, Weston, and Richard W. Young, Wellesley Hills, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

Continuation-in-part of application Ser. No. 447,100, Apr. 9, 1965, which is a continuation-in-part of application Ser. No. 277,099, May 1, 1963. This application Aug. 30, 1967, Ser. No. 664,503

Int. Cl. G03c 7/00

U.S. Cl. 96—3

20 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 diffusion transfer color process image-receiving elements which comprise a plurality of layers including, in sequence, a support layer, a permeable polymeric acid layer, a polymeric layer possessing decreasing alkaline solution permeability with increasing temperature, and an alkaline solution permeable and dyeable polymeric layer, and to photographic diffusion transfer color processes employing such image-receiving elements.

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.

This application is in part a continuation of our pending application Ser. No. 447,100, filed Apr. 9, 1965, now abandoned which, in turn, is in part a continuation of application Ser. No. 277,099, filed May 1, 1963, now abandoned.

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

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processes, which comprise a laminate which includes a permeable polymeric material which possesses a temperature inverse solubility 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 includes, in sequence, a support layer, a first polymeric acid layer, a second alkali solution permeable polymeric layer having specified permeability characteristics, 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 permeable polymeric layer which comprises a polymer exhibiting temperature inverse solubility, 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 taken in connection with the accompanying drawings wherein:

FIGURE 1 is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process for the production of a multicolor transfer image according to the present invention, the thickness of the various materials being exaggerated; and

FIG. 2 is a graphical representation of the temperature-alkali permeability characteristics of specified 50:50 copolymer of diacetone acrylamide and diethylaminoethylacrylate films and a 90:100 copolymer of N-isopropylacrylamide and dimethylaminoethylacrylamide film of the stated thicknesses, compared with control polyvinyl alcohol films of the stated thicknesses.

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 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 superposed 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 developing 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 superposed 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 orthodihydroxyphenyl 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 multilayer 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. However, 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, 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 methylvinyl 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 12 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 12 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 hydroquinoyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components 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 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 alkali ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments 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 polymeric 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 subcoats 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 nylon 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.

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 which comprises a polymer exhibiting an inverse temperature-dependent permeability, and a permeable, solution dyeable polymeric layer.

Specifically, the image-receiving element preferably comprises a flexible laminate including a plurality of polymeric 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 which comprises a polymer exhibiting decreasing permeability to solubilized alkali 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.

It has now quite unexpectedly been found that preferably the aforementioned rate at which the ions 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, it has now been 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 is 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 provides an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates. This barrier results 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 images' color definition. In addition, the extended maintenance of the high pH

conditions results 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 has now been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a polymer exhibiting permeability inversely dependent on temperature the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction may be obviated.

As employed throughout the instant specification and claims, the phrase "inversely temperature-dependent polymer," and the like, is intended to signify a polymeric material which generally exhibits decreased solubility in aqueous solution with increased temperature and which in the form of a polymeric film exhibits decreasing permeability to solubilized alkali derived ions under conditions of increasing temperature.

As indicated above, in accordance with the instant discovery the spacer layer of the 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 photographic use detailed and, specifically, polyvinyl alcohol. In general, polymers 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 in the form of a film, 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 contact 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 will be evident from a consideration of the present invention that the polymer employed in the practice of the present invention will possess in film form a negative alkaline processing composition permeation time-temperature relationship, which may be readily defined and individually delineated by plotting permeation time vs. temperature wherein the slope of the resultant plotted curve is negative, that is, exhibits an increase in the time required for permeation with increasing temperature, with relation to a plotted curve possessing a slope of zero; the latter slope exhibiting a substantially constant permeation time irrespective of processing temperature at the ordinary ambient temperature processing range, that is, approximately 40° F. to 100° F. It should be emphasized, however, that the precise negative temperature-permeation characteristics of the spacer layer selected, as an entirety, should be tailored to the photographic system selected as a whole and will be, at least in part, dependent upon the relative dye diffusion constants and development times of the selected photographic system at various temperatures. In this respect and to this extent selection of specific polymers for optimal employment as a spacer layer in a selected system is empirical.

Benefits are thus derived from employing a temperature-

inverting polymer, as stated, in a photographic process which depends upon permeation of components in liquid, at a variety of temperatures through a variety of media, since, as the ambient temperature decreases, such polymer tends to form hydrates and swell, thus facilitating permeation as a function of the degree of swell of the polymer—deswelling being inherent with an increase in temperature. As is well known, the diffusion rate of a liquid, for example, an alkaline fluid will increase as the temperature increases. Since, in a typical diffusion transfer photographic process this rate may be disproportionate with respect to optimum transfer image formation, the benefit of devising a mechanism for controlling the diffusion rate inversely with temperature, for the reasons previously stated, is recognized. The desired result is thus to employ a temperature inverting polymer approximately counteracting changes in diffusion rate of the permeating material with changes in temperature which deleteriously affect transfer image formation. The question of temperature inversion is, therefore, relative, since the precise properties desired, in an individual instance, are dependent upon the response of the specific system selected to changes in temperature.

Extreme inverse temperature characteristics, therefore, may not be particularly desirable, in a particular instance, since the development of the photosensitive part of the system and the dye transfer are temperature dependent processes and should be functionally compatible with the temperature-permeation properties of the receiving sheet. An ideal spacer layer, therefore, should provide the system which it comprises with the proper dye permeation-temperature properties so that dye may diffuse from the photosensitive part of the system to the receiving sheet, directly as a function of development, in order to form a transfer image in the receiving sheet within a predetermined time, irrespective of the processing temperature employed.

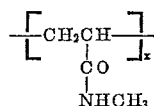
The temperature inverting characteristic of various polymers useful in the instant invention is probably attributable to the presence of a balance of hydrophobic groups to hydrophilic groups in the polymer molecule. The probable mechanism through which temperature inversion occurs is by the formation of hydrogen bonds between the hydrophilic portion of the polymer and the hydrogen of the solvent at low temperatures; the hydrogen bonding being discouraged as the temperature of the material is raised due to thermal destruction.

The system thereupon takes the form of a less-hydrated, less-swollen, therefore less-permeable polymer as a function of the increase in temperature. It may then be said that certain preferred polymers useful in the practice of the present invention are those which contain hydrophilic groups which cause swelling as a function of the solvability of that group in a given solvent, and hydrophobic groups which modulate the swelling so that at some definite ratio of hydrophilic to hydrophobic groups, the resultant compound will have temperature-inverting properties. It may further be concluded, that the interactions responsible for temperature inversion may be forces such as hydrogen-bonding and hydrophobic-hydrophobic bonding forces.

In general, the polymers thus advocated for employment in the practice of the present invention possess a negative solubility coefficient, that is, their solubility decreases with increase in temperature of the medium.

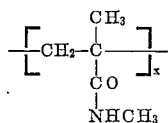
Preferred polymers comprise cellulosic and vinyl polymers which exhibit inverse temperature-dependent permeability to alkali. As examples of specific polymers which exhibit such inverse temperature-dependent permeability, mention may be made of:

Poly N-methylacrylamide:

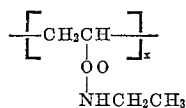


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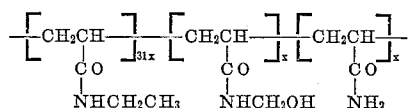
Poly N-methylmethacrylamide:



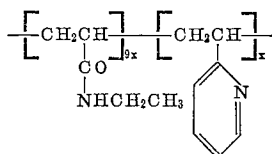
Poly N-ethylacrylamide:



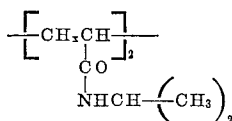
31:1:1 terpolymer of N-ethylacrylamide:N-methylol-acrylamide:acrylamide



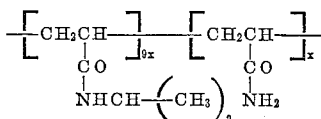
9:1 copolymer of N-ethylacrylamide:2-vinylpyridine



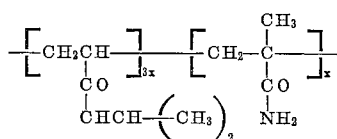
Poly N-isopropylacrylamide:



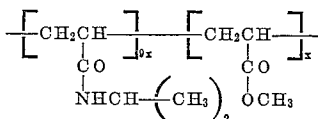
9:1 copolymer of N-isopropylacrylamide:acrylamide:



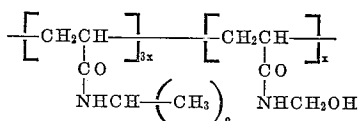
3:1 copolymer of N-isopropylacrylamide:methacrylamide:



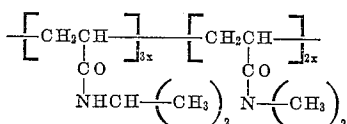
9:1 copolymer of N-isopropylacrylamide:acrylamide:



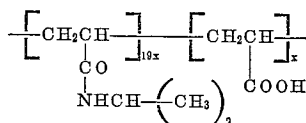
3:1 copolymer of N-isopropylacrylamide:N-methylol-acrylamide:



3:2 copolymer of N-isopropylacrylamide:N,N-dimethyl-acrylamide

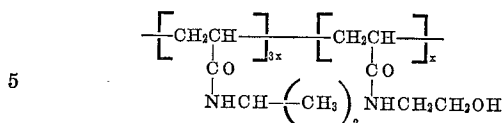


19:1 copolymer of N-isopropylacrylamide:acrylic acid

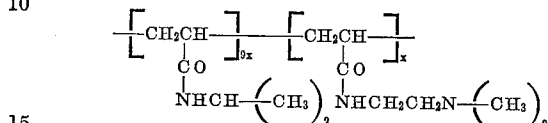


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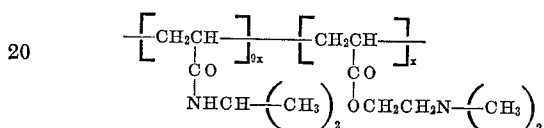
3:1 copolymer of N-isopropylacrylamide:N-(β-hydroxy-ethyl)acrylamide



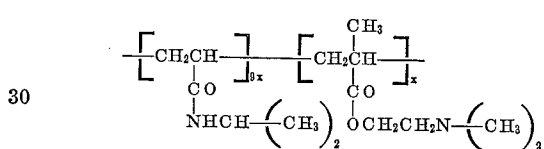
9:1 copolymer of N-isopropylacrylamide:N-[β-(dimethyl-amino)ethyl]acrylamide



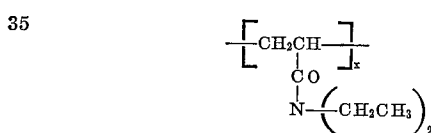
9:1 copolymer of N-isopropylacrylamide:dimethylamino ethyl acrylate



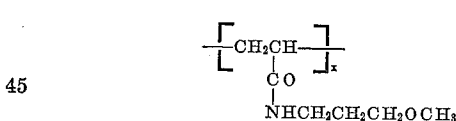
9:1 copolymer of N-isopropylacrylamide:dimethylamino ethyl methacrylate



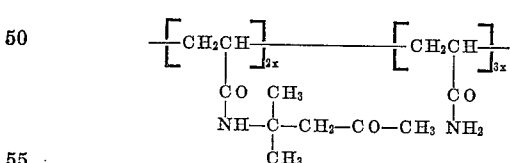
Poly N,N-diethylacrylamide



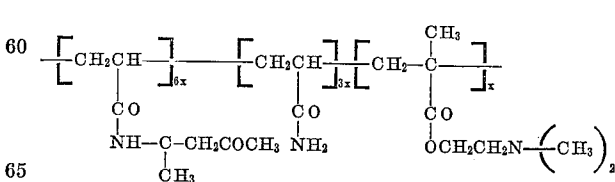
Poly N-[3'-methoxypropyl]acrylamide



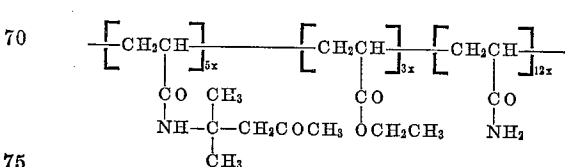
2:3 copolymer of diacetone acrylamide and acrylamide



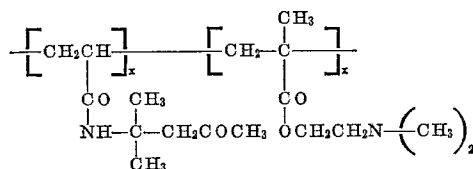
6:3:1 terpolymer of diacetone acrylamide:acrylamide:dimethylamino ethyl methacrylate



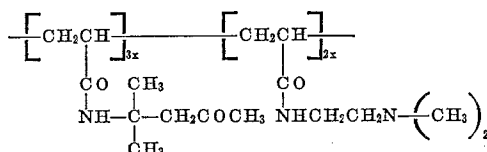
5:3:12 terpolymer of diacetone acrylamide:ethylacrylate:acrylamide



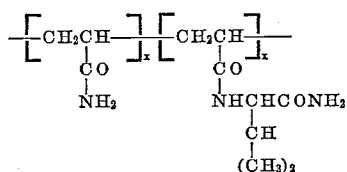
1:1 copolymer of diacetone acrylamide and dimethylamino ethyl methacrylate



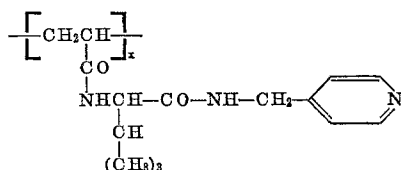
3:2 copolymer of diacetone acrylamide and N-[β -(dimethylamino)ethyl]acrylamide



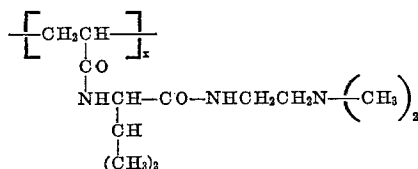
1:1 copolymer of acrylamide and 2-acrylamido-3-methylbutyramide



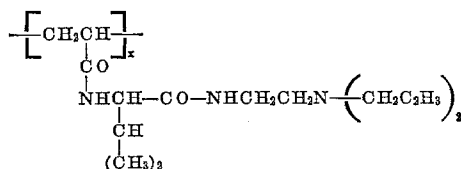
Poly N-(pyrid-4-ylmethyl)-2-acrylamido-3-methyl butyramide



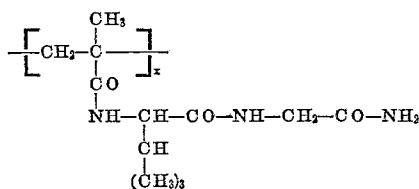
Poly 2-acrylamido-3-methyl-N-[β -(dimethylamino)ethyl] butyramide



Poly 2-acrylamido-3-methyl-N-[β -(diethylamino)ethyl] butyramide



Poly 2 - [2' - methacrylamido - 3' - methylbutyramido] acetamide



hydroxypropyl polyvinyl alcohol; cyanoethyl polyvinyl alcohol; polyvinyl methyl ether; polyvinyl oxazolidinone; polyethylene oxide; hydroxypropyl methyl cellulose; hydroxypropyl cellulose; partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal,

partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1000, preferably of about 1000 to 50,000, possessing a degree of acetalation within about 10 to 30%, 10 to 30%, 20 to 80%, and 10 to 40%, of the polyvinyl alcohol's theoretical polymeric hydroxyl groups, respectively. It will be recognized that mixed acetals also may be employed where desired and that the specified acetals comprise the condensation product of polyvinyl alcohol and butyraldehyde, formaldehyde, acetaldehyde and propionaldehyde, respectively. The aldehyde employed may also be a substituted aldehyde such as β -methoxypropionaldehyde, β -ethoxypropionaldehyde, etc. A specifically preferred acetal comprises a relatively high molecular weight acetaldehyde acetal of polyvinyl alcohol possessing acetalation of about 50% of the polyvinyl alcohol's theoretical hydroxyl groups.

Employment of polyvinyl amides, including those detailed above, for the fabrication of the spacer layer of a print-receiving element is disclosed and claimed in copending U.S. application Ser. No. 641,670, filed May 26, 1967, and employment of cyanoethylated polyvinyl alcohol is disclosed and claimed in copending U.S. application Ser. No. 641,657, filed May 26, 1967.

It will be recognized that, where desired, a mixture of polymers may be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

A polymer of the class type detailed which is specifically preferred for employment in the fabrication of print-receiving elements' spacer layer comprises hydroxypropyl cellulose and, specifically, hydroxypropyl cellulose possessing an M.S. of about 2 to 5 and most preferably of about 2, as disclosed and claimed in copending U.S. application Ser. No. 623,243, filed Mar. 15, 1967.

In a preferred embodiment of the present invention, the photosensitive element is employed which is specifically soluble in the reduced form only at the first pH, color dye transfer image and comprises a dimensionally stable support layer carrying at least two selectively sensitized silver halide emulsion strata each having a dye developer material of predetermined color associated therewith is soluble and diffusible in alkali at a first pH. The preferred photoinsensitive image-receiving element comprises an alkaline solution permeable polymeric layer dyeable by the dye developer; a polymeric spacer layer comprising a polymer possessing decreasing alkaline solution permeability with increasing temperature; an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial multicolor transfer dye image formation, of the image-receiving element from the first pH to a second pH, at which the dye image-providing material is insoluble and nondiffusible; and the dimensionally stable transparent layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

In the preferred embodiment, each of the emulsion strata, and its associated dye, is separated from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers and the dyeable polymeric layer is separated from the polymeric acid layer by an alkaline solution permeable polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

In such preferred embodiment of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil. in thickness; the polymeric spacer layer intermediate the dyeable polymeric layer and the polymeric acid layer is transparent and about 0.1 to 0.7 mil. in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mils. in thickness; and each of the dimensionally stable support layers are alkaline solution impermeable and about 2 to 6 mils. in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

In the preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable support layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the support layer and the magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing that the relative order of such units may be varied in accordance with the desires of the operator.

Reference is now made to FIGURE 1 of the drawings wherein there is illustrated a preferred film unit of the present invention.

As illustrated in FIGURE 1, film unit 10 comprises a photosensitive laminate 11 including, in order, dimensionally stable support layer 12, preferably a flexible sheet material; cyan dye developer layer 13; red-sensitive silver halide emulsion layer 14; interlayer 15; magenta dye developer layer 16; green-sensitive silver halide emulsion layer 17; interlayer 18; yellow dye developer layer 19; blue-sensitive silver halide emulsion layer 20; auxiliary layer 21, which may contain an auxiliary silver halide developing agent; and an image-receiving element 22 including image-receiving layer 23; spacer layer 24; neutralizing layer 25; and dimensionally stable support layer 26, preferably a flexible sheet material.

As shown in the drawing, the multilayer exposed photosensitive element 11 is shown in processing relationship with an image-receiving element 22 and a layer 27 of processing solution distributed intermediate elements 11 and 22.

In the performance of a diffusion transfer multicolor process employing film unit 10, the unit is exposed to radiation, actinic to photosensitive laminate 11.

Subsequent to exposure, film unit 10 may be processed by being passed through opposed suitably gapped rolls in order to apply compressive pressure to a frangible container in order and to effect rupture of the container and distribution of alkaline processing composition 27, having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer 23 and auxiliary layer 21.

Alkaline processing solution 27 permeates emulsion layers 14, 17 and 20 to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers 14, 17 and 20, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and non-diffusible oxidized form, thereby providing imagewise

distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer 23 to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline solution 27 transfers, by diffusion, through permeable polymeric layer 23, permeable spacer layer 24 and to permeable polymeric acid layer 25 whereby alkaline solution 27 decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image.

Subsequent to substantial transfer image formation, print-receiving element 22 may be manually dissociated from the remainder of the film unit, for example, by stripping.

The present invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative photographic products and processes which, however, are also intended to be illustrative and not of limiting effect.

Example 1

An image-receiving element was prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of poly-ethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 grams of DX-840-31 Resin [trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity poly-(ethylene/maleic anhydride)], 140 grams 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 4% solution of partial acetaldehyde acetal of polyvinyl alcohol in water-methanol-isopropanol 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 mgs./ft.², 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-(α -methyl- β -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 and the cyan dye developer is disclosed in U.S. Patent No. 3,135,606.

The photosensitive element was then exposed and

processed at 35 to 40° F. by spreading an aqueous liquid processing composition comprising:

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
Potassium thiosulfate	g	0.5
Benzotriazole	g	3.5
N-benzyl- α -picolinum bromide	g	2.3
Lithium hydroxide	g	0.3

between said image-receiving element and said exposed multicolor element as they are brought into superposed relationship in a Polaroid Land Camera. After an imbibition period of 3 minutes, the picture door of the camera was opened and the image-receiving element separated from the remainder of the film assembly.

The last-mentioned procedure was then repeated at room temperature and at 90 to 95° F. employing an imbibition period of 1 minute.

For purposes of comparison, an image-receiving element was fabricated in accordance with the last-mentioned procedure with the exception that the inert spacer comprised a layer of polyvinyl alcohol approximately 0.5 mil. thick and coated from a solution comprising 7 parts of polyvinyl alcohol/100 parts of water, by weight.

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

Examination of the resultant transfer prints revealed that the pH drop, dye densities and apparent film speeds were substantially equal, at each temperature range tested, employing the image-receiving element of the present application, whereas the control transfer prints exhibited characteristic faults such as speed loss and slow pH drop, when processed at the low temperature range, and premature pH drop and reduced cyan density, when processed at the high temperature range.

Example 2

The procedure of Example 1 was repeated with the exception that the spacer comprised a layer of hydroxypropyl methyl cellulose approximately 0.4 mil. thick and coated from a solution comprising 2 parts hydroxypropyl methyl cellulose in 100 parts water, by weight.

Examination of the resultant transfer prints revealed repetition of favorable results detailed in Example 1.

Further repetition of the preceding samples, employing the remaining illustrative polymeric materials, detailed hereinbefore for illustrative purposes, also provides for the production of transfer prints exhibiting the advantageous results detailed with respect to Example 1.

Specifically, there is shown graphically in FIG. 2 the temperature-alkaline processing composition permeability characteristics of a 0.150 mil. spacer layer comprising a 50:50 copolymer of diacetone acrylamide and diethylamino-ethylacrylate as Curve A; a 0.325 mil. spacer layer of the same polymer as Curve B; a 0.4 mil. spacer layer of the same polymer as Curve C; a 0.125 mil. spacer layer comprising a 90:10 copolymer of N-isopropylacrylamide and dimethylaminoethylacrylamide as Curve D; compared with 0.10, 0.20 and 0.35 mil. spacer layers comprising polyvinyl alcohol as Curves E, F and G, respectively.

Examination of FIG. 2 clearly illustrates the negative alkaline solution permeation time vs. temperature relationship of specified materials according to the present invention compared with the positive alkaline solution permeation time vs. temperature relationship achieved employing polyvinyl alcohol material of the prior art.

One important feature in the operation of this invention appears to be 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 temperature

dependent permeation of the alkali through the inversely permeable spacer layer, the equilibria favor the alkali remaining close to the negative and close to the image layer. Once alkali has permeated through to the polymeric acid layer, the equilibria are shifted by the trapping of that alkali. In addition, the water formed by reaction of the acid polymer with the alkali helps to remove alkali ions from the image layer and helps swell the spacer polymer, thereby increasing the rate at which the alkali diffuses through the spacer layer to the polymeric acid layer. 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 release of this water of reaction also 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.

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.

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 development 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 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, tolhydroquinone, 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.

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 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, of 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 or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic diffusion transfer color process image-receiving element which comprises a plurality of substantially discrete layers including, in sequence, a support layer, a permeable polymeric acid layer adapted to neutralize alkali contacted therewith, a polymeric layer possessing decreasing alkaline solution permeability with increasing temperature, and an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed.

2. A photographic diffusion transfer process image-receiving element as defined in claim 1, wherein said polymeric layer possessing decreasing alkaline solution permeability with increasing temperature comprises a polymeric layer selected from the group consisting of cellulosic and vinyl polymeric layers possessing decreasing alkaline solution permeability with increasing temperature.

3. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric acid layer comprises cellulose acetate hydrogen phthalate.

4. A photographic diffusion transfer process image-re-

ceiving element as defined in claim 2, wherein said polymeric acid layer is cellulose acetate hydrogen succinate.

5. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric acid layer comprises a partial ester of poly(methylvinyl ether/maleic anhydride) copolymer.

6. A photographic diffusion transfer process image-receiving element as defined in claim 5, wherein said partial ester comprises the butyl ester.

7. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric acid layer comprises a partial ester of poly(ethylene/maleic anhydride) copolymer.

8. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric layer possessing decreasing permeability with increasing temperature comprises hydroxypropyl methyl cellulose.

9. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric layer possessing decreasing permeability with increasing temperature comprises partial polyvinyl formal.

10. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric layer possessing decreasing permeability with increasing temperature comprises partial polyvinyl acetal.

11. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric layer possessing decreasing permeability with increasing temperature comprises partial polyvinyl propanal.

12. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said polymeric layer possessing decreasing permeability with increasing temperature comprises partial polyvinyl butyral.

13. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said solution dyeable polymeric layer comprises poly-4-vinyl pyridine and polyvinyl alcohol.

14. A photographic diffusion transfer process image-receiving element as defined in claim 2, wherein said solution dyeable polymeric layer comprises poly-4-vinyl pyridine and gelatin.

15. 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 image-providing material, by contacting said element with an aqueous alkaline solution, immobilizing said dye image-providing material, as a result of development, forming thereby an imagewise distribution of mobile dye image-providing material, 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 image-providing material to a superposed image-receiving element which comprises a plurality of substantially discrete layers including, in sequence, a support layer, a polymeric acid layer adapted to neutralize alkali contacted therewith, a polymeric layer possessing decreasing alkaline solution permeability with increasing temperature, and a solution dyeable and permeable polymeric layer, within which a color image is adapted to be formed, to provide to said dyeable polymeric layer a dye image, and transferring, by imbibition, subsequent to substantial dye 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 image-receiving element.

16. A process of forming transfer images in color as defined in claim 15, which comprises, in combination, the steps of exposing a photosensitive element which includes a support layer carrying on one surface at least two selectively sensitized silver halide emulsion layers each having

a dye, which dye is a silver halide developing agent, of predetermined color associated therewith, each of said dyes being soluble and diffusible, in alkali; contacting said exposed photosensitive element with an aqueous alkaline processing composition; effecting thereby development of the latent images contained in each of said silver halide emulsions; immobilizing the dye associated with each of said emulsions as a result of said development; forming thereby an imagewise distribution of mobile dye, as a function of the point-to-point degree of exposure thereof; transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element which comprises a plurality of substantially discrete layers including, in sequence, a support layer, a permeable polymeric acid layer adapted to neutralize alkali contacted therewith, a polymeric layer having decreasing alkaline solution permeability with increasing temperature, and an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed, to provide thereto a multicolor dye image; and transferring, by imbibition, subsequent to substantial transfer image formation, at least a portion of the alkali ions of said processing composition through each of said permeable polymeric layers of said image-receiving element to said polymeric acid layer to thereby provide a reduction in the pH of said image-receiving element.

17. A process as defined in claim 16, wherein each of said selectively sensitized photosensitive silver halide emulsion layers has predominant spectral sensitivity to separate regions of the spectrum and the dye associated with each of said silver halide emulsion layers possesses a spectral absorption range substantially complementary to the predominant sensitivity range of its associated silver halide emulsion layer.

18. A process of forming a transfer image in color as defined in claim 16, which comprises, in combination, the steps of exposing a photosensitive element comprising at least two selectively sensitized silver halide emulsion strata, each of said silver halide emulsions having associated therewith a dye, which dye is a silver halide developing agent, of predetermined color, soluble and diffusible in alkali, at a first pH; applying an aqueous alkaline processing composition having said first pH to said photosensitive element; effecting thereby development of the latent image contained in each of said silver halide emulsions; immobilizing the dye associated with each of said emulsions as a result of said development; forming thereby an image-wise distribution of mobile dye, as a function of the point-to-point degree of exposure thereof; transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element which comprises, as essentially discrete layers, in sequence, an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed, a polymeric layer selected from the group consisting of a cellulosic and vinyl polymeric layer exhibiting decreasing alkaline solution permeability with increasing temperature, an alkaline solution permeable polymeric acid layer adapted to neutralize alkali contacted therewith, and a support layer, to provide to said alkaline solu-

tion permeable and dyeable polymeric layer a dye image; and transferring, by imbibition, subsequent to substantial transfer dye image formation, a sufficient portion of the ions of said aqueous alkaline composition to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said image-receiving element to a second pH at which said dyes are substantially insoluble and non-diffusible.

19. A process of forming a transfer image in color as defined in claim 17, which comprises, in combination, the steps of exposing a photosensitive element including blue-sensitive, green-sensitive and red-sensitive gelatino silver halide emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers having associated therewith, respectively, yellow, magenta and cyan dyes, each of said dyes being a silver halide developing agent soluble and diffusible in alkali, at a first pH; contacting said exposed photosensitive element with an aqueous alkaline processing composition having said first pH; effecting thereby development of the latent image contained in each of said silver halide emulsions; immobilizing said yellow, magenta and cyan dye, as a function of development of their respective associated silver halide emulsion; forming thereby an imagewise distribution of mobile yellow, magenta and cyan dye, as a function of the point-to-point degree of their respective associated silver halide emulsion; transferring, by diffusion, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element which comprises a plurality of substantially discrete layers including an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed, a polymeric layer selected from the group consisting of a cellulosic and a vinyl polymeric layer exhibiting decreasing alkaline solution permeability with increasing temperature, and an alkaline solution permeable polymeric acid layer adapted to neutralize alkali contacted therewith mounted on a common support to provide to said alkaline solution permeable and dyeable polymeric layer a multicolor dye image; and transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline composition to said alkaline solution permeable polymeric layer to thereby reduce the alkalinity of said image-receiving element to a second pH at which said dyes are substantially insoluble and nondiffusible.

20. A process as defined in claim 19, wherein said first pH is not less than 12 and said second pH is not greater than 11.

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NORMAN G. TORCHIN, Primary Examiner

ALFONSO T. SUROPICO, Assistant Examiner

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