April 20, 1971 L. D. TAYLOR 3,575,701

POLYVINYLAMIDE GRAFTS IN SPACER LAYERS FOR COLOR DIFFUSION TRANSFER IMAGE-RECEIVING UNITS

Filed Jan. 13, 1969

5 Sheets-Sheet 1

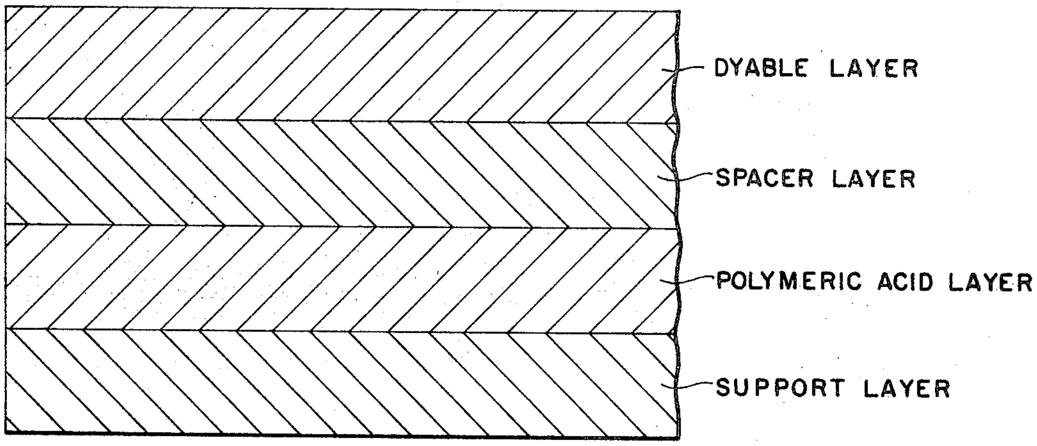

FIG. 1

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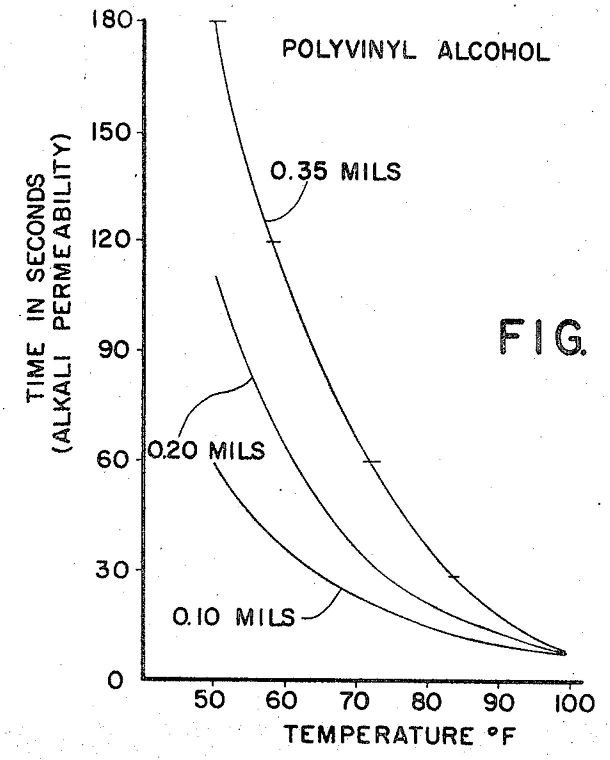

FIG. 2

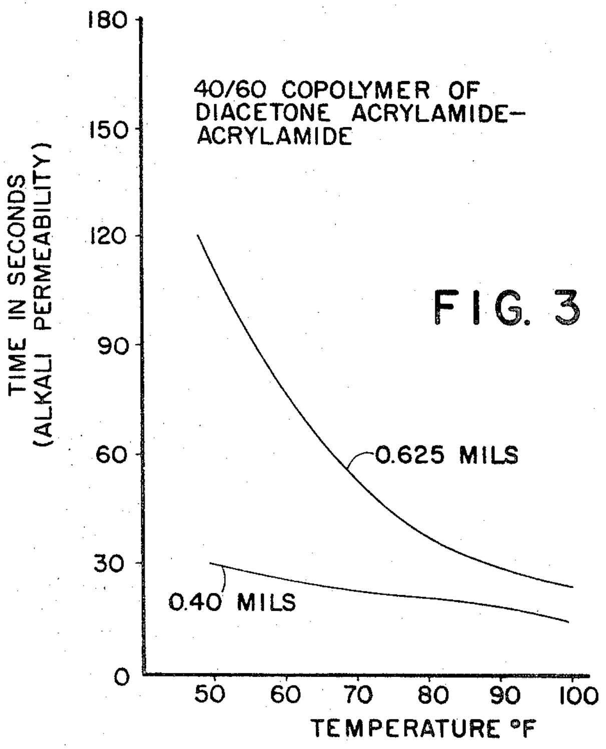

FIG. 3

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DIFFUSION TRANSFER IMAGE-RECEIVING UNITS
Filed Jan. 13, 1969 5 Sheets-Sheet 3

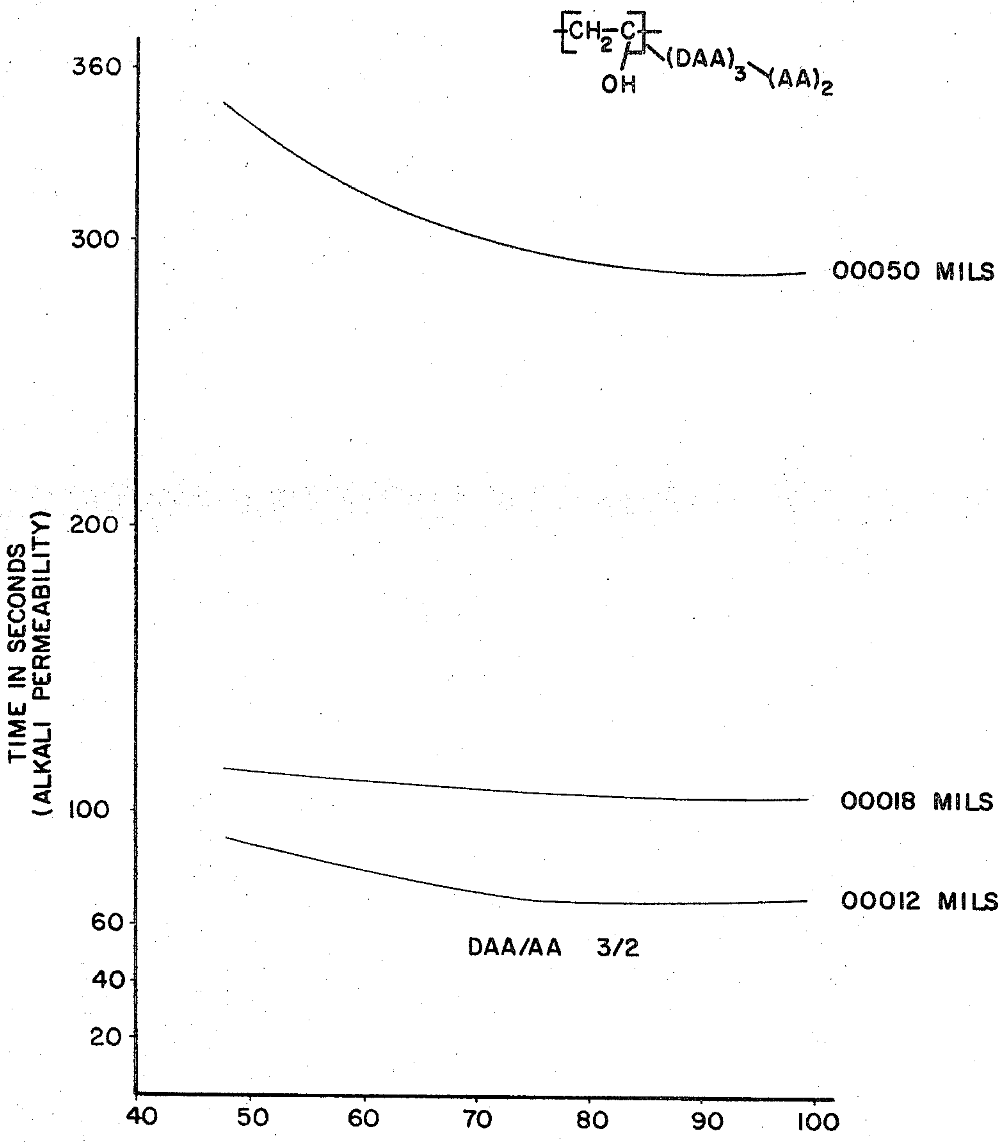

FIG. 4

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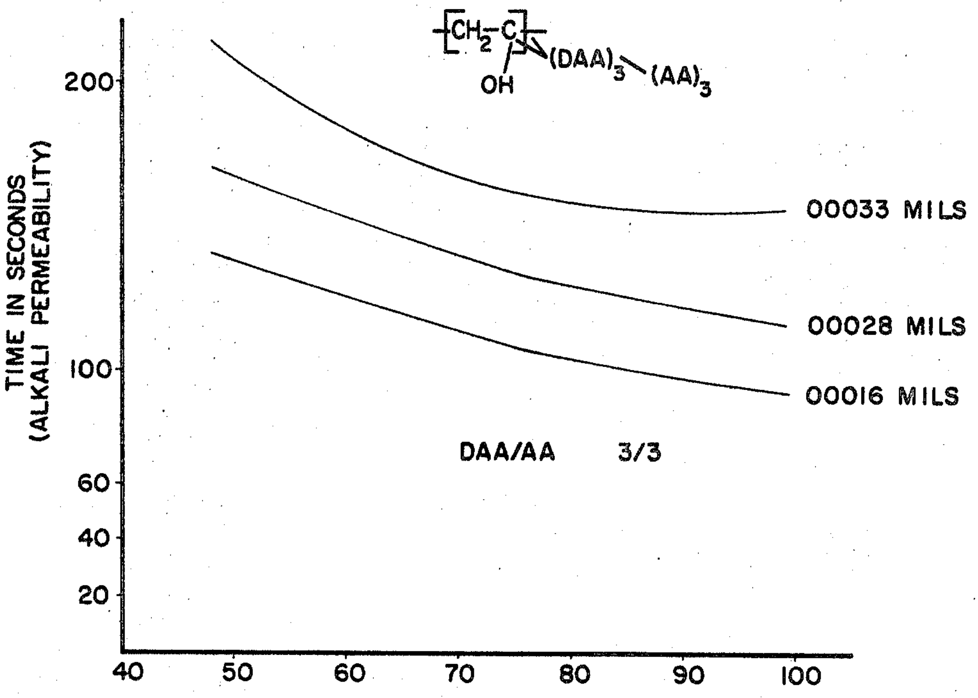

FIG. 5

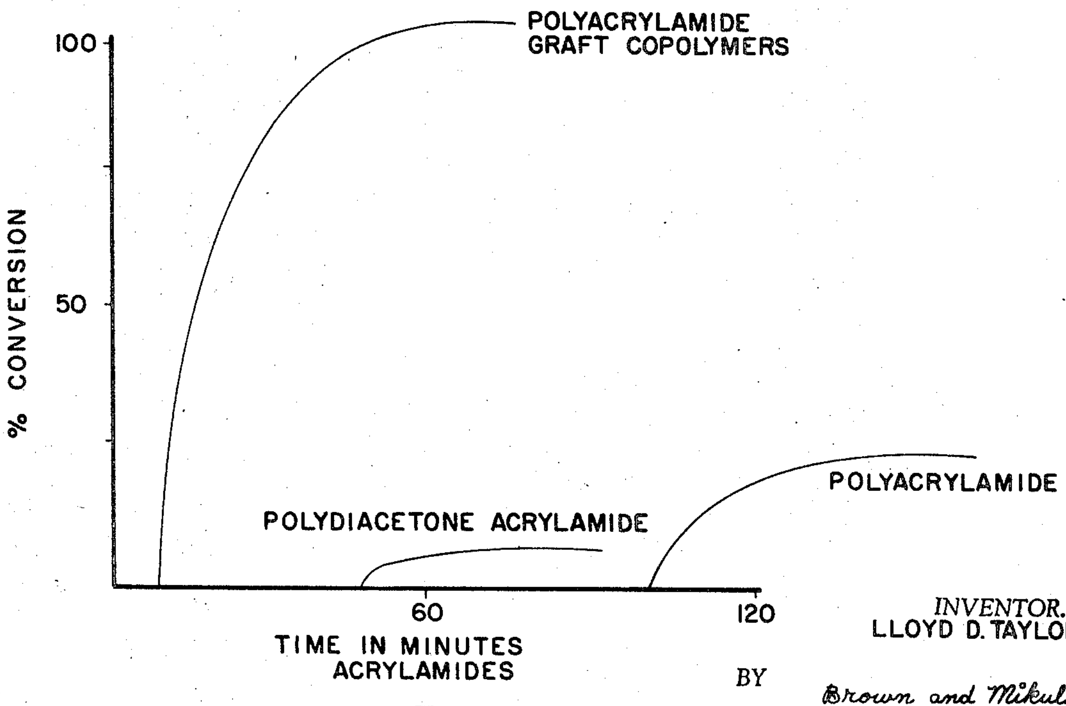

FIG. 7

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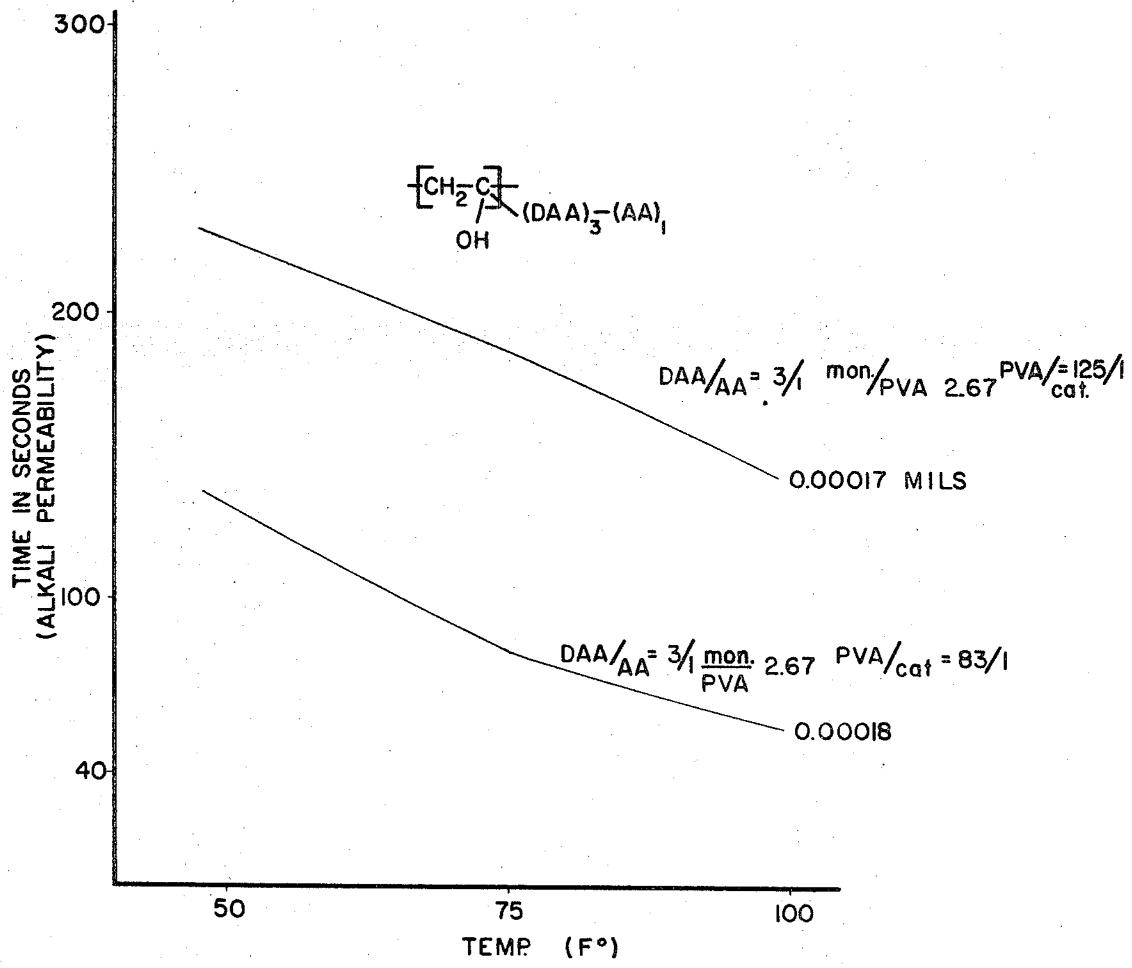

FIG. 6

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United States Patent Office

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POLYVINYLAMIDE GRAFTS IN SPACER LAYERS FOR COLOR DIFFUSION TRANSFER IMAGE-RECEIVING UNITS

Lloyd D. Taylor, Everett, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

Continuation-in-part of application Ser. No. 641,670, May 26, 1967. This application Jan. 13, 1969, Ser. No. 790,747

Int. Cl. G03c *7/00*

U.S. Cl. 96—3 **49 Claims**

ABSTRACT OF THE DISCLOSURE

An image-receiving element for diffusion transfer color processes comprising a polyvinylamide graft copolymer spacer layer.

This application is a continuation-in-part of U.S. application Ser. No. 641,670, filed May 26, 1967 now Pat. No. 3,421,893.

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.

In processes of the type set forth in U.S. Pat. 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 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. One 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 U.S. Pat. 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 U.S. Pat. 3,345,163, issued Oct. 3, 1967, 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 magneta 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.

U.S. Pat. No. 3,362,819, issued Jan. 1, 1968, discloses image-receiving elements particularly adapted for employment in the preceding diffusion transfer processes which elements 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 substances.

As set forth in the last-mentioned patent, 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 carboxy groups, being insoluble in water and 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 patent, 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 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 U.S. Pat. No. 3,362,819, issued Jan. 1, 1968, 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 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 patent, for example, a 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 spacer layer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer into the acid polymer 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 fillers as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials or a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964.

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 characteristics over an extended processing 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 the alkaline processing composition utilized; 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 composite structures which include a permeable polyvinyl amide graft copolymer material; and novel transfer process employing same.

A still further object of the present invention is to provide a novel image-receiving element particularly adapted for employment in photographic diffusion transfer color processes, which comprises a flexible composite structure which includes, in sequence, a support layer; a first polymeric acid layer; a second alkali solution permeable polyvinyl amide graft copolymeric layer having specified permeability characteristics wherein said second polymeric layer comprises a polyvinyl amide graft copolymer, and a third 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 elements 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 a polyvinyl amide graft copolymer; and a third polymeric layer adapted to be dyed from an alkaline solution; and novel transfer processes particularly adapted to employ same.

Yet another object of the present invention is to provide polyvinyl amide graft copolymers obtainable in greater than 99% conversion yields, said graft copolymers capable of forming temperature inverting aqueous emulsions that are catagorized by high solids content, low viscosity and coatability above the inversion temperature of the graft copolymer.

Still another object of the present invention is to provide polyvinyl amide graft copolymers having the same mole ratio of reactants, but having different alkali permeability characteristics.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components 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:

FIG. 1 is a cross-sectional representation of a receiving sheet for use in a diffusion transfer photographic process wherein a polymeric acid layer is superposed upon a support, a spacer layer comprising a polymeric material having predetermined temperature-permeability characteristics is superposed over said polymeric acid layer, and a polymeric, dyeable layer is superposed over said spacer layer;

FIG. 2 is a graphical representation of the relationship of the temperature-alkali permeability characteristics of polyvinyl alcohol films of various thicknesses when contacted with the processing composition of Example 1, below;

FIG. 3 is a graphical representation of the relationship of the temperature-alkali permeability characteristics of films of a 40:60 copolymer of diacetone acrylamide and acrylamide at various thicknesses when contacted with the processing composition of Example 1, below;

FIG. 4 is a graphical representation of the relationship of the temperature-alkali permeability characteristics of films of a diacetone acrylamide (DAA)—acrylamide (AA) graft on a polyvinyl alcohol backbone at various thicknesses when contacted with the processing composition of Example 1, below. The following ratios hold: DAA/AA=3/2; Backbone/monomer=1/3.3; Backbone/catalyst=124/1;

FIG. 5 is a graphical representation of the relationship of the temperature-alkali permeability characteristics of a diacetone acrylamide-acrylamide graft on a polyvinyl alcohol backbone at various thicknesses when contacted with the processing composition of Example 1, below. The following ratios hold: DAA/AA=3/3; Backbone/monomer=1/2.5; Backbone/catalyst=62/1;

FIG. 6 is a graphical representation of the relationship of the temperature-alkali permeability characteristics of diacetone acrylamide-acrylamide grafts on a polyvinyl alcohol backbone when all the ratios are the same, except for the Backbone/catalyst ratio;

FIG. 7 is a graphical representation of the relationship of the percent conversion-time characteristics of polyvinyl alcohol grafts and homopolymers of diacetone acrylamide and acrylamide.

U.S. Pats. 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; and 2,802,735, issued Aug. 13, 1957, disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized, which techniques 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. Pat. No. 3,019,124, issued Jan. 30, 1962, discloses the manufacture of photographic color screen elements; and U.S. Pats. 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. Pat. No. 2,774,668, issued Dec. 18, 1956, U.S. Pat. No. 3,345,163, issued Oct. 3, 1967, and the previously cited U.S. Pat. No. 2,983,606 disclose diffusion transfer processes wherein dyes are utilized to provide a positive color image into a superposed image-receiving layer.

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 preferably acts as a mechanism to compensate for temperature changes in the system; and a permeable, solution dyeable polymeric layer.

Specifically, the image-receiving element preferably comprises a flexible composite structure 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 having predetermined temperature-permeability characteristics; and a polymeric layer dyeable from contact with a dye-containing alkaline solution.

As disclosed in the aforementioned U.S. Pat. No. 3,362,819, issued Jan. 1, 1968, 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 been disclosed in copending U.S. application Ser. No. 664,503, filed on Aug. 30, 1967, now U.S. Pat. No. 3,455,686, that the diffusion rate of an alkali processing composition 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 optimum alkali-permeability characteristics 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.

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 permeable polymeric layer exhibiting permeability inversely dependent upon 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 last-mentioned 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.

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., the precise temperature being dependent upon the polymer specifically selected for employment; and relatively insoluble in hot water, that is, water at a temperature above about 80° C., the precise temperature being dependent upon the polymer selected. A relatively large number of such polymers are substantially insoluble in caustic photographic processing media 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 decrease photographic processing composition permeability with such temperature increase.

It has now been unexpectedly discovered that the use of polyvinyl amide graft copolymers as image-receiving element spacer layers provides for vastly superior cold temperature processing performance, color isolation and temperature independence, at very minute thicknesses, than compounds described in the prior art.

Specifically, temperature inverting polyvinyl amide graft copolymers, when used as image-receiving element spacer layers, produce higher transfer image maximum densities, increased flexibility of coating layer thickness parameters; and, in multicolor photographic diffusion transfer processes, improved color isolation.

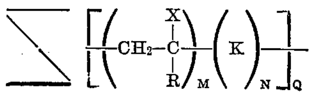
It will be evident from a consideration of the present invention that the polymeric image-receiving element spacer layer utilized herein may fall within an area on a permeation-time vs. temperature graph wherein the average slope of the line varies from slightly positive to slightly negative. A slope of zero would indicate that, at the ordinary processing range of approximately 40° F. to 100° F. the pH lowering mechanism would operate irrespective of the temperature. It must be emphasized that the precise temperature-permeation characteristics of the spacer layer must be tailored to the photographic system selected as a whole and are dependent upon the relative dye diffusion constants and development times of the selected system which are required at various temperatures. In this respect determination of the constituents of suitable polymers for use as a spacer layer in a selected system is substantially empirical.

As indicated in the above-cited applications, inverse temperature dependence of a polymeric film with regard to alkali permeability is not an unknown phenomenon, the use of this property having been disclosed for utilization in diffusion transfer photographic receiving sheets. Benefits are derived from using a temperature-inverting material in a process which depends upon permeation of liquids, at a variety of temperatures, since, as the ambient temperature decreases, the polymer tends to form hydrates and swells, thus facilitating permeation as a function of the degree of swell of the polymer—deswelling being inherent with an increase in temperature. It is well known that the diffusion rate of a liquid, for example, an alkali will increase as the temperature increases. Since, in a typical diffusion transfer photographic process this rate is directly proportional to the progress of the transfer image formation per unit time, the benefit of devising a mechanism for controlling the diffusion rate inversely with temperature is recognized. The desired result is to have the temperature inverting material approximately counteract changes in temperature. Temperature inversion is, therefore, relative, since the precise properties desired would be dependent upon the response of the whole system to changes in temperature.

Extreme inverse temperature characteristics are generally not particularly desirable 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 image-receiving element 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, as a function of development, in order to form a positive image in the receiving sheet within a predetermined time, irrespective of the processing temperature employed.

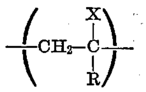
The temperature inverting characteristic of members of the class of polyvinyl amide graft copolymers useful in the instant invention is probably attributable to the presence of a predetermined balance of hydrophobic groups to hydrophilic groups in the polymer molecule. The probable mechanism through 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 the preferred polymers useful in the practice of the present invention are those which contain hydrophilic groups which cause swelling as a function of the solvatability 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 are forces such as hydrogen-bonding and hydrophobic bonding forces.

It has unexpectedly been found that a class of polyvinyl amide graft copolymers represented by the formula:



$$Z\left[\left(-CH_2-\overset{X}{\underset{R}{C}}-\right)_M\left(K\right)_N\right]_Q$$

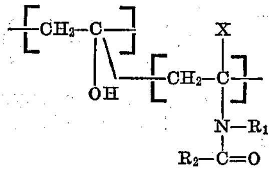
wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state; said catalyst having an oxidation potential, in acidic solution, of at least about 1 volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; X is selected from the group consisting of carboxamido, carbamyl, sulphonamido and sulfamyl; R is hydrogen or lower alkyl; K is a monomer copolymerizable with

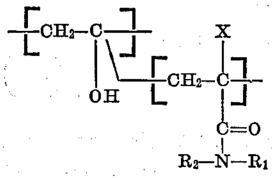


$$\left(-CH_2-\overset{X}{\underset{R}{C}}-\right)$$

M is equal to or greater than one, N is equal to or greater than zero, and Q is greater than one, provide far better results when considering the above-mentioned criteria, and those to be discussed below, than other groups of polymers heretofore employed for the instant purposes.

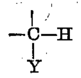
Preferred graft polymers within the scope of the present invention comprise polyvinyl amides grafted onto polyvinyl alcohol backbones, said preferred graft polymers being represented by the formulae:





and most preferably polyacrylamides of the last identified formula, wherein R_1 and R_2 may be hydrogen, alkyl, and aryl, groups. It should be understood that within the scope of the instant invention as claimed, both R_1 and R_2 are intended to encompass equivalents thereof and accordingly may comprise substituted or unsubstituted alkyl and aryl groups, etc. to conform to the desires of the operator, and X is hydrogen or lower alkyl, as outlined above. In general, then, R_1 and R_2 may be any group which functionally contributes the desired hydrophilicity or hydrophobicity to the polymer.

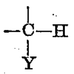
With regards to the backbone polymer of the graft copolymer, in general, any organic polymer comprising repeating units comprising structural units containing the



$$-\overset{|}{\underset{Y}{C}}-H$$

grouping; wherein Y is selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl, are capable of being oxidized by a transition metal ion catalyst as stated above, and are therefore useful in the present invention. The terms hydroxyl, acyl and aroyl as used above are intended to encompass partial acetals of these particular functional group terms. Preferred backbones are substituted or unsubstituted cellulosic or polyvinyl polymers, and most preferably, a backbone selected from the group consisting of polymeric polyols, polyvinyl alcohol, gelatin, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, poyaldehydes, etc.

It is believed that upon oxidation of the



$$-\overset{|}{\underset{Y}{C}}-H$$

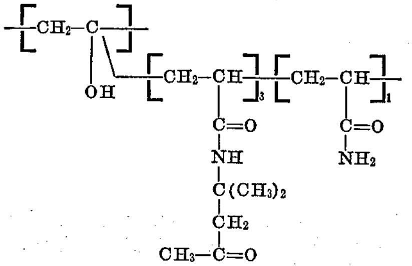
grouping, the free radical is formed, which attacks the double bond of the vinyl amide monomer, thus initiating polymerization.

As examples of K class compounds, mention may be made of acrylonitrile, vinyl acetate, methyl methacrylate, ethylacrylate, etc.

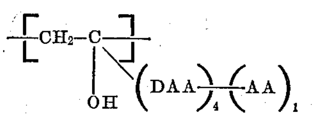
Monomers of interest which are useful in making graft copolymers with the necessary hydrophilic-hydrophobic balance include: acrylamide; N-methyl acrylamide, methacrylamide; N-methyl methacrylamide; ethyl acrylate; N-ethyl acrylamide; N-methylolacrylamide; N,N-dimethyl methacrylamide; N-(n-propyl)-acrylamide; N-isopropyl acrylamide; N-(β-hydroxyl ethyl) acrylamide; N-[β-(dimethylamino)ethyl] acrylamide; N-t-butyl acrylamide; β-(acrylamido)ethyl trimethyl ammonium p-toluene sulfonate; N-[β-(dimethylamino)ethyl]methacrylamide; 2-[2'-(acrylamido)ethoxy]ethanol; N-[3'-methoxy propyl]acrylamide; 2-hydroxy-3-methacryloxy propyl trimethyl ammonium chloride; 2-acrylamido-3-methyl butyramide; acrylamido acetamide; methacrylamido acetamide; 2-[2'-methacrylamido-3'-methyl butyramido]acetamide; N-vinyl pyrrolidone; diacetone acrylamide; dimethylamino ethyl methacrylate; dimethylamino ethyl acrylate; vinyl acetate, p-styrene sulfonamide, N-isopropyl ethylene sulfonamide, etc.

Graft polymers which are found to be useful in the instant invention are:

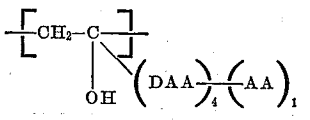
(1) Acrylamide-diacetone acrylamide graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.67/1.



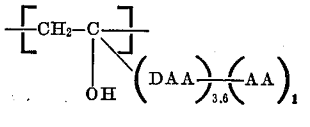
(2) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol. DAA/AA=4/1; monomer/PVA=2.67/1.



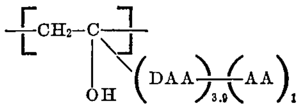
(3) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=4/1; monomer/PVA=3.33/1.



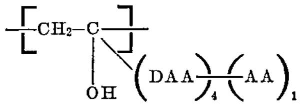
(4) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.6/1; monomer/PVA=3.00/1.



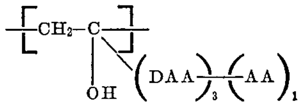
(5) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.9/1; monomer/PVA=3.30/1.



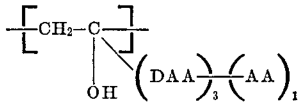
(6) Acrylamide (AA)-diacetone acylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=4/1; monomer/PVA=3.56/1.



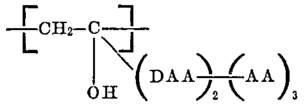
(7) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.0/1.



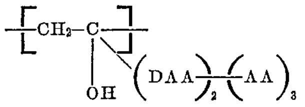
(8) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.2/1.



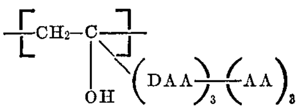
(9) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PV). DAA/AA=2/3; monomer/PVA=5.3/1.



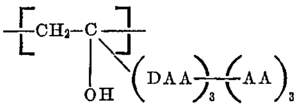
(10) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/3; monomer/PVA=2.67/1.



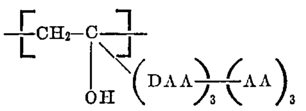
(11) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3; monomer/PVA=1.75/1.



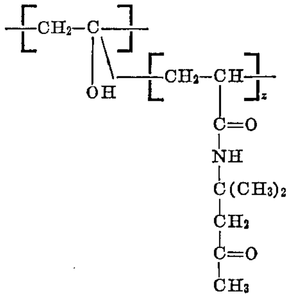
(12) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3; monomer/PVA=5.3/1.



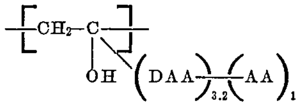
(13) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3; monomer/PVA=3.33/1.



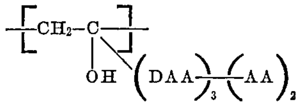
(14) Diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA); monomer/PVA=2.0/1.



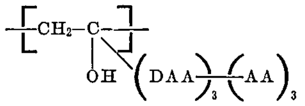
(15) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.2/1; monomer/PV=2.8/1.



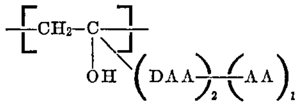
(16) Acrylamide (AA)—diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/2; monomer/PV=3.3/1.



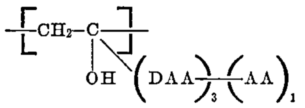
(17) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DDAA/AA=3/3; monomer/PVA=0.4/1.



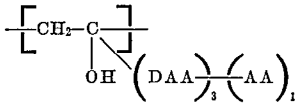
(18) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/1; monomer/PV=3.0/1.



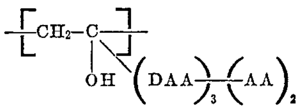
(19) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA/1.4/1.



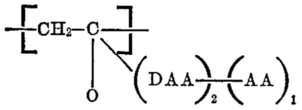
(20) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=4.0/1.



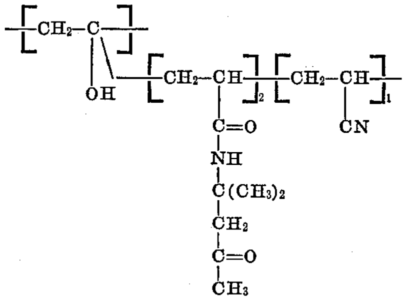
(21) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/2; monomer/PVA=2.67/1.



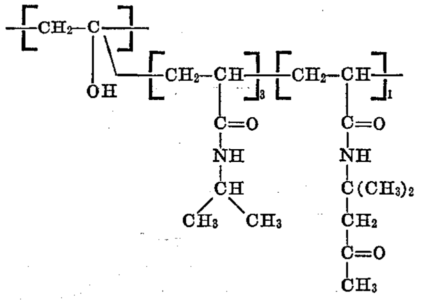
(22) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/1; monomer/PVA=4.1/1.



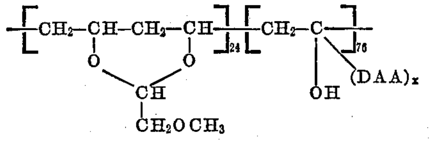
(23) Diacetone acrylamide (DAA) acrylonitrile graft on polyvinyl alcohol (PVA). DAA/acrylonitrile=2/1; monomer/PVA=3.5/1.



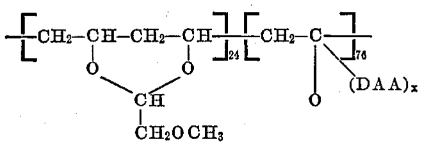
(24) Acrylamide (AA)-isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA). IspAA/AA=3/1; monomer/PVA=1/1.1.



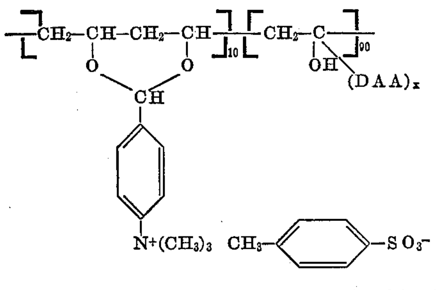
(25) Diacetone acrylamide (DAA) graft on the partial acetal of polyvinyl alcohol-methoxy acetaldehyde; monomer/PVA acetal=3/1.



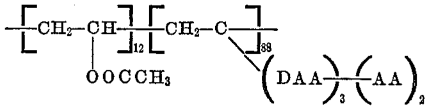
(26) Diacetone acrylamide (DAA) graft on the partial acetal of polyvinyl alcohol-methoxy acetaldehyde; monomer/PVA acetal=1/1.



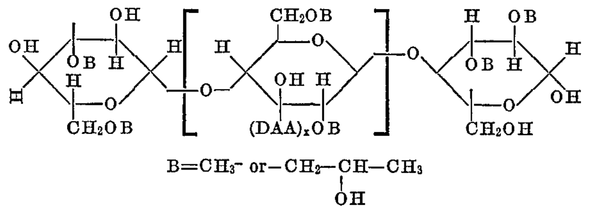
(27) Diacetone acrylamide (DAA) graft on the copolymer of a benzal mordant and polyvinyl alcohol (PVA); monomer/PVA copolymer=0.5/1.



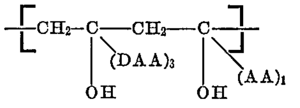
(28) Acrylamide (AA)-diacetone acrylamide (DAA) graft on partially hydrolyzed polyvinyl acetate. DAA/AA=3/2; monomer/partially hydrolyzed polyvinyl acetate=1/1.



(29) Diacetone acrylamide (DAA) graft on methyl hydroxy propyl cellulose.

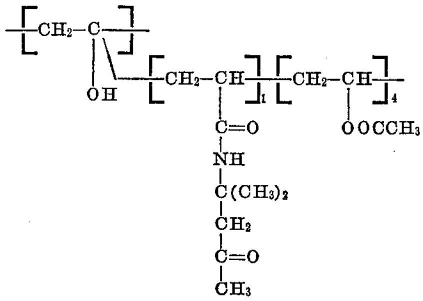


(30) Acrylamide (AA) and diacetone acrylamide (DAA) sequentially grafted on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.66/1.

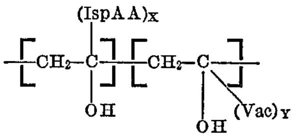


(31) Diacetone acrylamide (DAA)-vinyl acetate (Vac) graft on polyvinyl alcohol (PVA).

DVV/Vac=1/4; monomer/PVA=5.1/1.

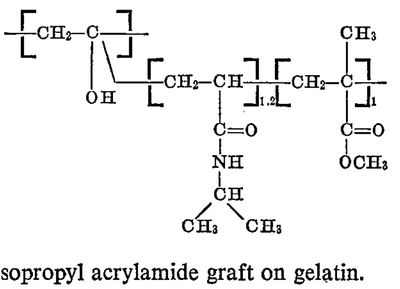


(32) Vinyl acetate graft (Vac) on isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA).

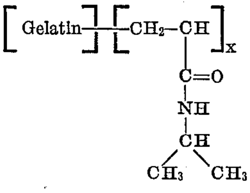


(33) Isopropyl acrylamide (IspAA)-methyl methacrylate (MM) graft on polyvinyl alcohol (PVA).

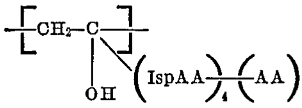
IspAA/MM=1.2/1; monomer/PVA=1.3/1



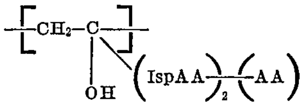
(34) Isopropyl acrylamide graft on gelatin.



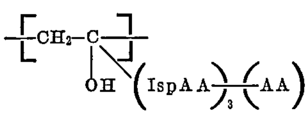
(35) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=4/1; monomer/PVA=3/1.



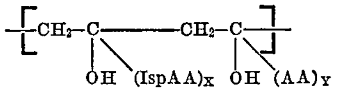
(36) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=2/1; monomer/PVA=3.5/1.



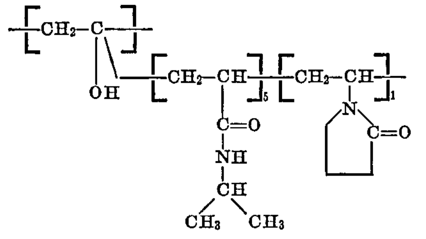
(37) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=3/1; monomer/polymer=3/1.



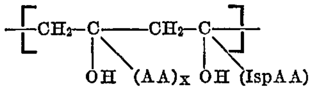
(38) Acrylamide (AA) graft on isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA).



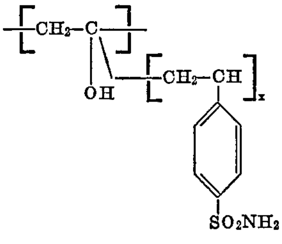
(39) Isopropyl acrylamide (IspAA)-N-vinyl pyrrolidone on polyvinyl alcohol (PVA). IspAA/N-vinyl pyrrolidone=5/1; monomer/PVA=2.6/1.



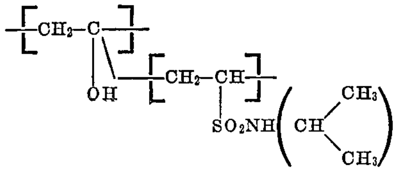
(40) Isopropyl acrylamide (IspAA) graft on acrylamide (AA) graft on polyvinyl alcohol (PVA).



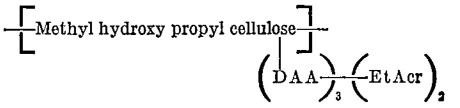
(41) P-styrene sulfonamide graft on polyvinyl alcohol (PVA).



(41) N-isopropyl ethylene sulfonamide graft on polyvinyl alcohol (PVA).



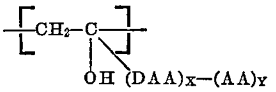
(43) Diacetone acrylamide (DAA)-ethyl acrylate (EtAcr) copolymer graft on methyl hydroxy propyl cellulose. DAA/EtAcr=3/2.

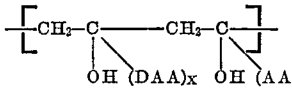


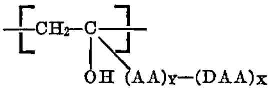
Throughout the above listing of graft polymers, certain ratios have been used. These are molar ratios, with 44 grams of polyvinyl alcohol being equal to one mole. In light of the numerous examples cited, it is apparent that the R groups on a backbone can be different or the same, the only requirement being that they satisfy the criteria set out above.

It is to be understood that the various polymers listed above have differing temperature-alkali permeability characteristics.

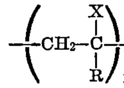
From the hereinbefore set out list of graft polymers, one sees that R can either change or be the same throughout the backbone. Also, any two or more monomers can be grafted onto a particular backbone in a number of ways. For example, an acrylamide-diacetone acrylamide graft on polyvinyl alcohol could, depending upon the mode of the monomers, take the following structural forms:





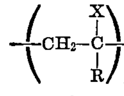


The same type of reasoning holds true when one has a K type of compound incorporated into the graft copolymer. This is borne out by reference to hereinbefore set out graft copolymers 31 and 32. In copolymer 31, vinyl acetate is directly attached to the



$$\left(-CH_2-\overset{X}{\underset{R}{C}}-\right)_M$$

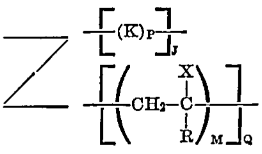
group, whereas in copolymer 32 the vinyl acetate is grafted directly onto the backbone. In this latter type of compound, (K) is directly attached to the backbone Z, and not to the



$$\left(-CH_2-\overset{X}{\underset{R}{C}}-\right)_M$$

group as depicted in Formula I.

Graft copolymers of this class are represented by the formula:



wherein Z, K, R, M, and Q are the same as in Formula I, J is greater than one, and P is greater than one. Surprisingly, it has been discovered, that in any given polymer, the temperature-alkali permeability characteristics can be manipulated by the judicious choice of backbone/catalyst ratio. In general, any two polymers, having the same backbone, comprised of the same monomers, and having the same monomer to monomer and monomer to polymer ratios, will have different diffusion (alkali) characteristics if they are prepared in the presence of different backbone/catalyst ratios. Reference is made to FIG. 6, which shows the effect of varying the backbone to catalyst ratio, all other ratios being equal. In general, decreasing the amount of catalyst, which has the effect of increasing the backbone/catalyst ratio, results in increased impermeability and flatter temperature response.

As was stated hereinbefore, any transition metal ion catalyst of a first oxidation state having an oxidation potential, in acidic solution of at least about 1 volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state, is operable in the present invention. As preferred catalysts, mention may be made of transition metal ion catalysts comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

In general, a backbone/catalyst ratio of from about 30 to about 130 is the most useful range, irrespective of the monomers used.

In general, it may be said that a completely hydrophilic material will not be temperature inverting. As the hydrophobic content is increased the solubility— which is directly associated with the swellability of the polymer—will decrease until the polymer is soluble, or swellable, as the case may be, only in cold water. As the hydrophobic content is further increased the polymer becomes insoluble but even coatings of such materials when applied from a solvent other than water may exhibit temperature inverse permeability to water.

The thickness of the temperature inverting layer will be somewhat critical since the hydration mechanism of the layer may form tunnels in the film through which processing composition may preferentially diffuse. In the case of graft copolymers, diffusion takes place not only through the film, but can also take place at the interface of the polymer balls, when the polymer is cast in film form of the selected thickness.

In order to maintain uniformity in processing time, the thicknesses of the individual polymer layers utilized should be predetermined to achieve uniform permeation time throughout the operative temperature range. As a rule, thicknesses from 0.05 to 0.5 mil is the range in which desired processing times for permeation of the processing solution found in, for example, Polaroid type 108 film packs, is achieved.

Many of the compounds useful in the instant invention are insoluble in neutral or basic environments and must, therefore, be coated from an acid system. The polymer layer when coated from acid solution is actually present in the form of an acid salt. When contacted with the highly basic processing composition utilized in processes of the instant type, the polymer insolubilizes and results in a thin alkali-permeable layer.

As stated above, the acid polymer layer utilized in a diffusion transfer receiving sheet is designed to decrease the hydrogen ion concentration of the processing composition and is at the same time a sink for salt residues which may form in the top layer of the receiving sheet during the development process. If the processing temperature is too hot and no temperature inverting layer is used as a "timing valve," poor dye densities and "gappiness" may be evident in the photograph. These phenomena are probably due to premature neutralization of the processing composition. When the temperature is cold and no temperature inverting timing layer is used, the neutralization of the developing composition is too slow, and may result in the maintenance of undesirable salts in the top layer of the photographic picture. This manifests itself by way of dull, muddy colors and causes, in any instances, developing reagents to adhere to the top of the print rather than being selectively stripped away with the photosensitive sheet.

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

EXAMPLE I

Three image-receiving elements were prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polethylene/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 0.7 mil thick. The external surface of said acid layer was coated with an emulsion of an acrylamide-diacetone acrylamide graft on polyvinyl alcohol, in thicknesses of 0.12 mil, 0.19 mil, and 0.5 mil, respectively. The external surface of each spacer layer was then coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinyl pyridine, at a coverage of approximately 600 mg./ft.^{2}. The thus prepared image-receiving element was then baked at 180° F. for 30 minutes and then allowed to cool.

The acrylamide-diacetone acrylamide graft on polyvinyl alcohol was prepared as follows: to a solution of 33 g. of polyvinyl alcohol (0.75 m.) in 1500 cc. of H_2O under nitrogen was added 271.5 g. diacetone acrylamide (1.5 m.) and 71 g. acrylamide (1.0 m.). The pH was adjusted to 1.5 with concentrated HNO_3 and 3.3 g.

$$Ce(NH_4)_2(NO_3)_6$$

in 20 cc. H_2O was added and stirring continued for 3 hours. The resulting emulsion was then coated as described above.

A multicolor, multilayer photosensitive element may be prepared in a manner similar to that disclosed in U.S. Pat. No. 3,345,163, issued Oct. 7, 1967.

In general, the photosensitive elements will comprise 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 may have 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 may be positioned between the yellow dye developer layer and the green-sensitive emulsion stratuum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements may comprise, for example, 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-[hydroquinonylethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Pat. No. 3,134,764, issued May 26, 1964, and the cyan dye developer is disclosed in U.S. Pat. No. 3,135,606, issued June 2, 1964. Multicolor photosensitive material of the tripack type employing dye developers may also be commercially procured from Polaroid Corporation, Cambridge, Mass., as the negative component of the photographic film distributed by that corporation under the trade designation of Polacolor film Type 108.

The photosensitive element may then be exposed and processed at various temperatures by spreading an aqueous liquid processing composition at a pH of not less than about 12 which may comprise:

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

between an image-receiving element and the exposed multicolor element as they are brought into superposed relationship in a Polaroid Land Pack Camera. After an imbibition of 60 seconds or 135 seconds, for tests carried out over a range of 40°–100° F., the image-receiving elements may be separated from the remainder of the film assembly.

For purposes of comparison, 5 image-receiving elements were fabricated in accordance with the above-described procedure with the exception that three spacer layers comprised polyvinyl alcohol in optimized thicknesses of 0.10, 0.20 and 0.35 mil, and the other two comprised a 40:60 copolymer of diacetone acrylamide-acrylamide at optimized thicknesses of 0.4 and 0.625 mil. These last-prepared image-receiving elements were then processed, as generally detailed above.

Reference is now made to FIGS. 2, 3, and 4, which show temperature-alkali permeability characteristics of the image-receiving elements comprised of polyvinyl alcohol, the 40:60 copolymer of diacetone acrylamide-acrylamide, and the diacetone acrylamide-acrylamide graft on polyvinyl alcohol, respectively.

From a comparison of these figures, it is evident that the graft polymer gives somewhat the same temperature-alkali permeability characteristics with layers, orders of magnitude thinner than the other materials tested.

EXAMPLE II

The general procedure of Example I was carried out using a receiving sheet which comprised a spacer layer comprising an acrylamide-diacetone acrylamide graft on polyvinyl alcohol. This graft polymer differed from the one used in Example I in that the DAA/AA ration was 3/3 instead of 3/2, the monomer/PVA ratio was 0.4/1 instead of 3.3/1, and the PVA/catalyst ratio was 62/1 instead of 124/1. The graft polymer was coated to thicknesses of 0.16, 0.28, and 0.33 mil, being prepared in the following manner: To a solution of 16.5 g. of polyvinyl alcohol (0.375 m.) in 1500 cc. of H_2O under nitrogen was added 135.75 g. diacetone acrylamide (0.75 m.) and 53.25 g. acrylamide (0.7 m.). The pH was adjusted to 1.5 with concentrated HNO_3 and 3.3 g. of $Ce(NH_4)_2(NO_3)_6$ were added in 10 cc. of H_2O. Stirring was continued for 2.5 hours, and the resulting emulsion was cast in the thicknesses set out above. The temperature-alkali permeability characteristics of these films are set out in FIG. 5.

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 Pat. No. 3,173,786, issued on Mar. 3, 1965) and particularly a quarternary 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 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 glycol terephthalic 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 inhibition 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 temperatures, 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, toluhydroquinone, tertiary-butylhydroquinone, and 2,5-triptycene diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative. Particularly useful results are obtained when 4'-methylphenylhydroquinone is dispersed in one or more of the gelatin interlayers and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

As noted above, this invention comtemplates reduction of the positive image pH to a level substantially precluding aerial oxidation of developer moieties. The provisions 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.

In a preferred embodiment, the polyvinyl amide graft copolymers of the present invention are used as spacer layers in photographic products as disclosed in U.S. Pats. Nos. 3,415,644, 3,415,645, and 3,415,646, issued Dec. 10, 1968, and, more particularly in the photographic products of U.S. Pat. No. 3,415,644, which comprise a composite photosensitive structure which contains a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers each having associated dye image-providing materials which are soluble and diffusible, in alkali, at a first pH; a polymeric image-receiving layer; a polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing composition from a first pH to a second pH at which the dye image-providing materials are insoluble and nondiffusible; and a dimensionally stable transparent layer.

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.

A wide variety of temperature inverting polymers can not be coated from water alone and dried above their inversion temperature to give clear films. Many of the graft polymers of the present invention not only give clear films when coated above their inversion temperatures, but can also be coated at high solids content and fast coating machine speeds. The grafts of the present invention give stable aqueous emulsions having low viscosity in addition to high solids content as mentioned above. The preferred range is 18–25% solids, with the resulting emulsion having a viscosity of 200–400 centipoises. Depending upon the use, the solids content can vary ±10%.

The method of preparation of the graft polymers is generally the same as that outlined in the hereinbefore stated examples, although pH's up to about 7 have been successfully used in some instances.

Although the transition metal ion catalysts hereinbefore described will initiate the homopolymerization of monomers such as diacetone acrylamide, acrylamide, etc., the induction periods are so long and the rates so slow, that under grafting conditions, little or no such polymerization can occur. The results of such a study are graphically shown in FIG. 7, which sets out the percent conversion-time characteristics of a typical acrylamide-diacetone acrylamide graft on polyvinyl alcohol, and the homopolymers of the respective monomers.

As a rule, the graft polymers of the present invention are usually obtained in greater than 99% conversion, and most often in the order of 99.9% conversion. Batches of acrylamide-diacetone acrylamide grafts on polyvinyl alcohol were prepared, with the original charges of monomer being 181 g./l. of DDA and 23.6 g./l. of AA. At the end of each batch run, the residual monomer concentration was determined by vapor phase chromatographic analysis, the results of which are set out below in Table I.

TABLE I

Batch No.	Residual monomer, AA/DAA	Surface tension, dynes/cm.
1	.21/.31	47.4
2	.19/.30	49.4
3	.07/.09	50.2
4	.42/.96	48.2
5	.13/.10	49.9
6	.06/.09	49.8

In each batch, the charge of polyvinyl alcohol was 22 g./l.

In preferred embodiments of this invention the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg. per foot^2 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 image-receiving element spacer layer is preferably about 0.05 to 0.5 mil thick.

Throughout the specification and claims, the expression "superposed" has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in separated condition and including between them at least a layer of fluid processing composition.

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

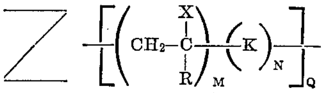
What is claimed is:

1. An image-receiving element for use in a photographic diffusion transfer process comprising a plurality of substantially discrete layers including, in sequence, a support layer, a permeable polymeric acid layer adapted to neutralize alkali contacted therewith, an alkaline solution permeable polymeric layer comprising a polyvinyl amide graft copolymer, and an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed.

2. The invention of claim **1** wherein said polyvinyl amide graft copolymer comprises a polyacrylamide graft copolymer.

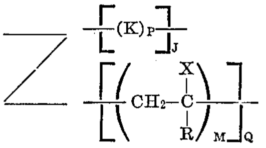
3. The invention of claim **2** wherein said polyacrylamide graft copolymer layer comprises an acrylamide grafted onto a polyvinyl alcohol backbone.

4. The invention of claim **1** wherein said polyvinyl amide graft copolymer is represented by the formulae:



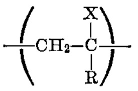
$$Z\left[\left(\mathrm{CH_2}-\overset{\displaystyle X}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}\right)_M(K)_N\right]_Q$$

and



$$Z\begin{matrix}\left[(K)_P\right]_J\\ \left[\left(\mathrm{CH_2}-\overset{\displaystyle X}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}\right)_M\right]_Q\end{matrix}$$

wherein Z is an organic polymeric backbone comprising repeating units which comprise structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state, said catalyst having an oxidation potential, in acidic solution, of at least about one volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; X is selected from the group consisting of carboxamido, carbamyl, sulphonamido and sulfamyl groups; R is selected from the group consisting of hydrogen and lower alkyl groups; K is a monomer copolymerizable with



$$\left(\mathrm{CH_2}-\overset{\displaystyle X}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}\right)$$

M is equal to or greater than one; N is equal to or greater than zero; and each of Q, J and P is greater than one.

5. The invention of claim **4** wherein said polyvinyl amide graft copolymer layer is a polyacrylamide graft copolymer layer.

6. The invention of claim **4** wherein said organic polymeric backbone is selected from the group consisting of cellulosic and vinyl polymers.

7. The invention of claim **4** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl.

8. The invention of claim **4** wherein said organic polymeric backbone is selected from the group consisting of polymeric polyols, gelatin, polyvinyl alcohol, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, and polyaldehydes.

9. The invention of claim **4** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

10. The invention of claim **4** wherein said polyvinyl amide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymeric layer with predetermined temperature-alkali permeability characteristics.

11. The invention of claim **5** wherein said polyacrylamide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymeric layer with predetermined temperature-alkali permeability characteristics.

12. The invention of claim **11** wherein said polyacrylamide graft copolymer is selected from the group consisting of polyacrylamide graft copolymers having the same backbone to monomer and monomer to monomer ratios, but having different backbone to catalyst ratios.

13. The invention of claim **11** wherein said polyacrylamide graft copolymer is a diacetone acrylamide-acrylamide graft on polyvinyl alcohol.

14. The invention of claim **11** wherein said polyacrylamide graft copolymer is a diacetone acrylamide graft on polyvinyl alcohol.

15. The invention of claim **11** wherein said polyacrylamide graft copolymer is a diacetone acrylamide graft on the partial acetal of polyvinyl alcohol methoxy acetaldehyde.

16. The invention of claim **11** wherein said polyacrylamide graft copolymer is a diacetone acrylamide graft on methyl hydroxy propyl cellulose.

17. The invention of claim **4** wherein said polyvinyl amide graft copolymer is present in the form of an acid salt.

18. The invention of claim **15** wherein said polyacrylamide graft copolymer is present in the form of an acid salt.

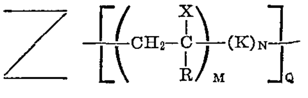
19. A process for forming diffusion transfer images in color which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye image-providing material, by contacting said element 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 comprising a polyvinyl amide graft copolymer, and a solution dyeable and permeable polymeric layer within which a dye 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.

20. A process for forming diffusion transfer images in color as defined in claim **19**, 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 comprising a polyvinyl amide graft copolymer, 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.

21. The invention of claim **20** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

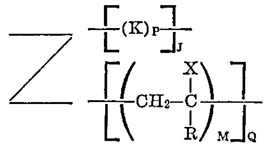
22. The invention of claim **20** wherein said polyacrylamide graft copolymer comprises an acrylamide grafted onto a polyvinyl alcohol backbone.

23. The invention of claim **20** wherein said polyvinyl amide graft copolymer is represented by the formulae:



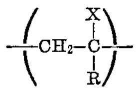
$$Z\left[\left(CH_2-\underset{R}{\overset{X}{C}}\right)_M-(K)_N\right]_Q$$

and



$$Z\begin{matrix}\left[(K)_P\right]_J\\ \left[\left(CH_2-\underset{R}{\overset{X}{C}}\right)_M\right]_Q\end{matrix}$$

wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state, said catalyst having an oxidation potential, in acidic solution of at least about one volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; X is selected from the group consisting of carboxamido, carbamyl, sulphonamido and sulfamyl groups; R is selected from the group consisting of hydrogen and lower alkyl groups; K is a monomer copolymerizable with



$$\left(CH_2-\underset{R}{\overset{X}{C}}\right)$$

M is equal to or greater than one; N is equal to or greater than zero; and each of Q, J and P is greater than one.

24. The invention of claim **23** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer layer.

25. The invention of claim **23** wherein said organic polymeric backbone is selected from the group consisting of cellulosic and vinyl polymers.

26. The invention of claim **23** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl.

27. The invention of claim **23** wherein said organic polymeric backbone is selected from the group consisting of polymeric polyols, gelatin, polyvinyl alcohol, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, and polyaldehydes.

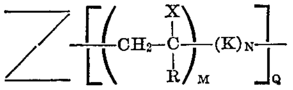
28. The invention of claim **23** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

29. A process for forming diffusion transfer images in color as defined in claim **20**, which comprises, in combination, the steps of exposing a photosensitive element including blue-sensitive, green-sensitive and red-sensitive 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; contacting said exposed photosensitive element with an aqueous alkaline processing composition; 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 comprising a polyvinyl amide graft copolymer, and an alkaline solution permeable polymeric acid layer adapted to neutralize alkali contacted therewith, mounted on a common support, to provide 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.

30. The invention of claim **29** wherein said polyvinyl amide graft copolymer comprises a polyacrylamide graft copolymer.

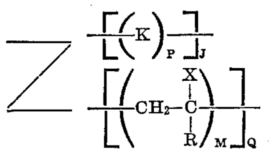
31. The invention of claim **30** wherein said polyacrylamide graft copolymer comprises acrylamides grafted onto a polyvinyl alcohol backbone.

32. The invention of claim **29** wherein said polyvinyl amide graft copolymer is represented by the formulae: and



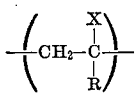
$$Z\left[\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M-(K)_N\right]_Q$$

and



$$Z\begin{matrix}\left[\left(K\right)_P\right]_J\\ \left[\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M\right]_Q\end{matrix}$$

wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state, said catalyst having an oxidation potential, in acidic solution, of at least about one volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; X is selected from the group consisting of carboxamido, carbamyl, sulphonamido and sulfamyl groups; R is selected from the group consisting of hydrogen and lower alkyl groups; K is selected from the group consisting of monomers copolymerizable with



$$\left(CH_2-\overset{X}{\underset{R}{C}}\right)$$

M is equal to or greater than one; N is equal to or greater than zero; and each of Q, J and P is greater than one.

33. The invention of claim **32** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer layer.

34. The invention of claim **32** wherein said organic polymeric backbone is selected from the group consisting of cellulosic and vinyl polymers.

35. The invention of claim **32** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl.

36. The invention of claim **32** wherein said organic polymeric backbone is selected from the group consisting of polymeric polyols, gelatin, polyvinyl alcohol, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, and polyaldehydes.

37. The invention of claim **32** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

38. The invention of claim **33** wherein said polyacrylamide graft copolymer is a diacetone acrylamide-acrylamide graft on polyvinyl alcohol.

39. The invention of claim **33** wherein said polyacrylamide graft copolymer is a diacetone acrylamide-graft on polyvinyl alcohol.

40. The invention of claim **33** wherein said polyacrylamide graft copolymer is a diacetone acrylamide graft on the partial acetal of polyvinyl alcohol-methoxy acetaldehyde.

41. The invention of claim **33** wherein said polyacrylamide graft copolymer is a diacetone acrylamide graft on methyl hydroxy propyl cellulose.

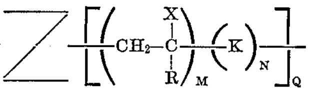
42. A photographic film unit which comprises, in combination:

a photosensitive element having a diffusion transfer image-receiving element affixed in a superposed position thereto, said photosensitive element comprising a plurality of layers including at least one silver halide emulsion layer, at least one of said plurality of layers containing a dye-image-providing material; said image-receiving element comprising 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 comprising a polyvinyl amide graft copolymer, and an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed.

43. The invention of claim **42** wherein said polyvinyl amide graft copolymer comprises a polyacrylamide graft copolymer.

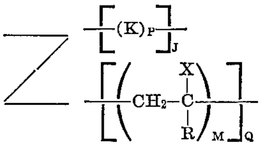
44. The invention of claim **43** wherein said polyacrylamide graft copolymer comprises an acrylamide grafted onto a polyvinyl alcohol backbone.

45. The invention of claim **42** wherein said polyvinyl amide graft copolymer is represented by the formulae:



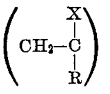
$$Z\left[\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M\left(K\right)_N\right]_Q$$

and



$$Z\begin{matrix}\left[(K)_P\right]_J\\ \left[\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M\right]_Q\end{matrix}$$

wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state, said catalyst having an oxidation potential, in acidic solution, of at least about one volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state; X is selected from the group consisting of carboxamido, carbamyl, sulphonamido and sulfamyl; R is selected from the group consisting of hydrogen and lower alkyl; K is a monomer copolymerizable with



$$\left(CH_2-\overset{X}{\underset{R}{C}}\right)$$

M is equal to or greater than one; N is equal to or greater than zero; and each of Q, J and P is greater than one.

46. The invention of claim 45 wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

47. The invention of claim 46 wherein said organic polymeric backbone is selected from the group consisting of cellulosic and vinyl polymers.

48. The invention of claim 46 wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl.

49. The invention of claim 46 wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

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96—29; 260—8