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COLOR DIFFUSION TRANSFER IMAGE-RECEIVING LAYER COMPRISING A GRAFT COPOLYMER WHEREIN THE GRAFTED MOIETY HAS MORDANT CAPABILITY

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ABSTRACT OF THE DISCLOSURE

A diffusion transfer photographic product including an image-receiving element comprising an alkaline solution permeable and dyeable layer for receiving a dye image; said layer comprises a graft copolymer wherein the grafted moiety provides a mordant capability.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of U.S. application Ser. No. 58,685 filed July 27, 1970, now abandoned.

The present invention relates to photography and, more particularly, to processes for forming photographic diffusion transfer color images and to novel graft copolymers 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 image wise 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.

In accordance with aforementioned U.S. Pat. No. 2,983,606, the image-receiving layer need not be separated

from its superposed contact with the photosensitive element, subsequent to transfer image formation, if the image-receiving element is transparent and a processing composition containing a substance rendering the dried processing composition layer opaque is spread between the image-receiving layer and the silver halide emulsion layer.

The dye developer, 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. Pats. 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 magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

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 carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the 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 the processing composition preferably is of the order 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. Where the image-receiving element is maintained in contact with the photosensitive element, subsequent to dye developer transfer image formation, and includes the presence of an alkaline processing composition, necessarily having a pH at which dye developer, for example, in reduced form, diffuses to form the dye transfer image, intermediate the elements, the transfer image thus formed is unstable over an extended period of time. The dye image instability is due, at least in part to the presence of what is, in general, a relatively high pH alkaline composition in intimate contact with the dye or dyes forming the image. This contact itself provides instability to the molecular structure of dye by, for example, catalyzing degradation and undesirable structural shifts effecting the spectral absorption characteristics of the image dye. In addition, the presence of an alkaline composition, possessing a pH at which the dye, for example, in reduced form, diffuses also provides an integral dynamic system wherein oxidized dye, immobolized in areas of the photosensitive element, as a function of its development, with the pasage of time attempts to generate, in such areas, an equilibrium between oxidized and reduced dye. In that the pH of the dynamic system is such that diffusion of the reduced form of the dye will occur, such reduced dye will, at least in part, transfer to the image-receiving layer and the resultant diffusion will imbalance the equilibrium, in such areas of the photosensitive element, in favor of additional formation of reduced dye. As a function of the efficiency of the image-receiving layer, as a dye sink, such nonimagewise dyeing of the image-carrying layer still further imbalances the equilibrium in favor of the additional formation of dye in reduced, diffusible form. Under such circumstances, the transfer image definition, originally carried by the image-receiving layer, will suffer a continuous decrease in the delta between the image's maximum and minimum densities and may, ultimately, result in the image-receiving element's loss of all semblance of image definition; merely becoming a polymeric stratum carrying a relatively uniform overall dyeing.

Any attempt to decrease the dye sink capacity of the image-carrying layer, for example, by reduction of its mordant capacity, in order to alleviate, at least to an extent, the action of the image-receiving layer as a dye sink, however, will enhance diffusion of the dye, comprising the transfer image, from the image-carrying layer, to the remainder of the element due, at least in part, to the continued presence of the alkaline composition having a pH at which the reduced form of the dye, forming the transfer image, is diffusible. The ultimate result is substantially the same overall image distortion as occurs when the image-receiving layer acts as a dye sink, with the exception that the dye is more extensively distributed throughout the film unit and the ultimate overall dyeing of the image-receiving layer itself is of lower saturation.

The problems inherent in fabricating a film unit of the type wherein the image-receiving element, the alkaline processing composition and the photosensitive element are maintained in contiguous contact subsequent to dye transfer image formation, for example, a film unit of the type described hereinbefore with reference to aforementioned U.S. Pat. No. 2,983,606, may be effectively obviated by fabrication of a film unit in accordance with the physical parameters specifically set forth in U.S. Pats. Nos. 3,415,644; 3,415,645; and 3,415,646 as well as those described in U.S. Pats. Nos. 3,573,044 and 3,672,890 all in the name of Edwin H. Land; and Ser. No. 39,646, now U.S. Pats. Nos. 3,594,165 and 39,666, now U.S. Pat. No. 3,594,164 of Howard G. Rogers, filed May 22, 1970.

Specifically, an integral photographic film unit particularly adapted for the production of a dye transfer image of unexpectedly improved stability and other properties, by a color diffusion transfer process will be constructed, for example, in accordance with aforementioned U.S. Pat. No. 3,415,644, to include a photosensitive element comprising a laminate having, in sequence, as essential layers, a dimensionally stable opaque layer; a photosensitive silver halide emulsion layer having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH; an alkaline solution permeable polymeric layer dyeable by the dye image-providing material; a polymeric acid layer such as those disclosed in aforementioned U.S. Pat. No. 3,362,819 containing sufficient acidifying groups to effect reduction, subsequent to substantial transfer dye image formation, of a selected processing solution having the first pH to a second pH at which said dye image-providing material is insoluble and nondiffusible; and a dimensionally stable transparent layer. In combination with the laminate, a rupturable container retaining an aqueous alkaline processing composition having the first pH and containing an opacifying agent, in a quantity sufficient to mask the dye image-providing material, is fixedly positioned and extends transverse a leading edge of the laminate whereby to effect unidirectional discharge of the container's contents between the alkaline solution permeable and dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto, upon application of compressive force to the container.

It will also be recognized that the dimensionally stable polymeric support layer next adjacent the photosensitive silver halide emulsion layer or layers may be transparent, as disclosed in aforementioned U.S. Pat. No. 3,415,646, and that in such instance, the opacifying agent may be initially dispersed in the composite film unit intermediate the dyeable polymeric layer and the silver halide emulsion layer next adjacent, as disclosed in aforementioned U.S. Pat. No. 3,415,645.

Employment of the last-mentioned film units, according to the described color diffusion transfer photographic process, specifically provides for the production of a highly stable color transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by in process adjustment of the environmental pH of the film unit from a pH at which transfer processing is operative to a pH at which dye transfer is inoperative subsequent to substantial transfer image formation by means of the stated polymeric acid layer. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during exposure, processing, viewing, and storage of the unit, which transfer image exhibits the required maximum and minimum dye transfer image densities, dye saturation, hues and definition.

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 of the stated polymeric acid component are disclosed to be so distributed in the acid polymer layer that the rate of their availability to the alkaline 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 aforementioned U.S. Pat. No. 3,362,819, 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 and 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, 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.

It has been disclosed in U.S. Pat. No. 3,455,686, issued July 15, 1969, 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 temperature, 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 patent, 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 patent 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.

Additional polymers which may be particularly advantageously employed are temperature-inverting polyvinylamide graft copolymers, as disclosed in U.S. Pat. 3,575,701 of Lloyd D. Taylor.

U.S. Pat. 3,573,044 to Edwin H. Land, discloses an alternative means for effectively obviating the problems inherent in fabricating a film unit of the type where the image-receiving element, the alkali processing composition and the photosensitive element are maintained in contiguous contact during processing and subsequent to dye transfer image formation, for example, a film unit of the type described, with reference to aforementioned U.S. Pat. No. 2,983,606. Specifically, it is disclosed in U.S. Pat. 3,573,044 that an integral photographic film unit of simplified construction and particularly adapted for the production of dye transfer images of improved stability and other desirable properties by a color diffusion transfer process can be constructed to include a photosensitive element comprising a composite structure possessing, in sequence, as essential layers, a first dimensionally stable layer, a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is soluble and diffusible at a first processing composition solvent concentration, a polymeric layer dyeable by the dye image-forming material, and a second dimensionally stable layer transparent to incident actinic radiation, wherein the dimensionally stable layers taken together, possess a processing composition solvent vapor permeability sufficient to effect, subsequent to substantial dye transfer image formation and preceding substantial dye transfer image degradation, osmotic transpiration of processing composition solvent in a quantity effective to decrease the first solvent concentration, at which the dye image-forming material is soluble and diffusible, to a second solvent concentration, at which the dye image-forming material is substantially nondiffusible. In combination with the composite structure, a rupturable container retaining a processing composition comprising the solvent is fixedly positioned and extends transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent, in a quantity sufficient to provide the first solvent concentration.

Employment of the detailed film unit of the invention of the last-mentioned copending application in color diffusion transfer processes specifically provides for the production of a highly stable transfer image accomplished, at least in part, by in process adjustment of the environmental processing composition solvent concentration from a solvent concentration at which dye diffusion or transfer is operative to a solvent concentration at which dye transfer is inoperative subsequent to substantial transfer image formation.

U.S. Pat. 3,597,197 and copending application Ser. No. 867,583, filed Oct. 20, 1969, now abandoned, in the names of Sheldon A. Buckler, Terry W. Milligan, and Howard G. Rogers, disclose still other means for effectively obviating the problems inherent in fabricating a film unit of the type where the image-receiving element, the alkali processing composition and the photosensitive element are maintained in contiguous contact during processing and subsequent to dye transfer image formation.

Specifically, it is disclosed in U.S. Pat. 3,597,197 and application Ser. No. 867,583 that an integral photographic film unit particularly adapted for the production of dye transfer images of improved stability and other desirable properties by a color diffusion transfer process can be constructed to include a photosensitive element comprising a composite structure possessing, in sequence as essential layers, a first dimensionally stable layer, a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material which is soluble and diffusible as a function of the point-to-point degree of emulsion photoexposure, a polymeric layer dyeable by the dye image-forming material, and a second dimensionally stable layer transparent to incident actinic radiation. In combination with the composite structure, a rupturable container retaining a processing composition is fixedly positioned and extends transverse a leading edge of the composite structure whereby to effect, upon application of compressive pressure, discharge of the processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion and associated dye image-forming material next adjacent thereto. In addition, the aforementioned integral photographic film unit possesses means for interposing between said dyeable polymeric layer and the photosensitive silver emulsion next adjacent thereto, a continuous dye image-forming material impermeable polymeric layer after substantial image formation has been accomplished in said dyeable polymeric layer in order to obviate further dye migration. Means for the formation of such a continuous polymeric layer include, for example, incorporating in the processing composition a particulate dispersion of a processing composition insoluble polymer as a discontinuous phase, said polymer being adapted, upon decrease in processing composition solvent, to coalesce at ambient temperature. As examples of processing composition insoluble polymers suitable for such an application, mention may be made of the various polymeric solid and liquid materials which provide a latex when dispersed in a solvent in which they are insoluble and stable and, particularly when dispersed in water possessing a preselected pH, known in the art to coalesce at ambient temperatures and at relatively rapid rates upon loss of dispersant solvent to provide relatively impermeable substantially continuous films or polymeric layers including butadiene/styrene copolymers; polyacrylamides; polymethylmethacrylates; polyvinyl chlorides and copolymers thereof; polyvinyl acetates and copolymers thereof; acrylonitrile/ethyl acrylate copolymers; acrylonitrile/styrene/butadiene terpolymers; and the like.

Other techniques for the formation of a continuous dye image-forming material impermeable polymeric stratum, as disclosed in the last-mentioned copending applications, include the coating of a polymeric material intermediate the polymeric dye image-receiving layer and the photosensitive silver halide emulsion layer next adjacent thereto with a polymeric material whose dye image-forming material permeability is a direct function of the pH of the system; i.e., as the pH of the system is increased the permeability of the polymeric layer increases whereby dye image-forming material freely passes therethrough. However, as the pH of the system is decreased, e.g., by the use of a polymeric acid component of the type set forth in U.S. Pat. No. 3,362,819, the permeability of such a material decreases to an ultimate point at which dye image-forming material is incapable of passing therethrough. Such a system may be visualized as a pH valve. As examples of polymeric materials which may be used to provide a substantially continuous dye image-forming material impermeable stratum between the image-receiving layer and the photosensitive silver halide emulsion layer next adjacent thereto, mention may be made of the various polymeric materials which are known to act as a "pH valve" as aforenoted, such as, for example, polyphenolic polymers such as the acetal of hydroxybenzaldehyde and polyvinyl alcohol; sulfonamides, such as, for example, the acetal of a primary formyl benzene sulfonamide and polyvinyl alcohol; polymers comprising α-trifluoromethylvinyl alcohol segments; the benzene sulfonamide of deacetylated chitin; polyhydroxymethylene; the acetal of 3-hydroxybenzaldehyde and a vinyl alcohol-α-trifluoromethylvinyl alcohol copolymer; novolactic phenol formaldehyde polymers; Santolite MHP (trade name of Monsanto Chemical Company for a formaldehyde benzene-sulfonamide condensation polymer); poly-α,α-bis(hydroxyethyl) methylene; etc. Generally speaking, such materials comprise weakly ionized polymeric acids, for example, those having an ionization constant between about 10^{-4} and 10^{-12}.

The above-denoted polymeric compositions whose permeability is directly related to the environmental pH may be utilized by being dissolved in the alkaline processing composition and being spread between the image-receiving layer and the next adjacent photosensitive layer to provide a substantially continuous stratum; or such materials may be coated intermediate the photosensitive silver halide emulsion next adjacent the image-receiving layer, and the image-receiving layer, as a continuous film to be rendered permeable at such time as the processing composition container is ruptured to thereby release the alkaline processing composition whereby the pH valve is rendered permeable to image-producing material until such time as the pH of the system is dropped below a dataum level.

In another system which is disclosed in copending application Ser. No. 867,583 referred to supra, the viscosity-increasing ingredients utilized in the processing composition are cross-linked subsequent to substantial image formation in the image-receiving layer to the extent required to provide an image-forming material impermeable layer between the image-receiving layer and the next adjacent silver halide emulsion layer. Such a system may be carried out by incorporating a diffusible cross-linking agent or suitable precursors thereof in the composite photosensitive structure, which, following rupture of the processing composition container, diffuse into distributed processing composition to thereby cross-link a thickening substance or other polymeric material incorporated in said processing composition. As was discussed above, hydroxyethyl cellulose is commonly utilized as a viscosity-increasing agent in conventional diffusion transfer processes, as more fully disclosed and discussed in numerous of the aforementioned patents and particularly in U.S. Pat. No. 2,983,606; suitable cross-linking agents for this and similar materials include divinyl sulfone and precursors thereof, e.g., bis-pyridinium ethyl sulfone chloride, and β-ketoethyl onium salts as disclosed in U.S. Pat. No. 3,345,177.

A still further technique for accomplishing the above-denoted barrier formation as disclosed in aforementioned copending application Ser. No. 867,583 is to provide a coating intermediate the dye image-forming layer and the photosensitive silver halide emulsion next adjacent thereto wherein a cross-linking agent for the material comprising said coating is incorporated in an element of the photographic film unit whereby after substantial image formation in the polymeric dye image-receiving layer sufficient cross-linking agent contacts said coating to render it substantially impermeable to dye image-forming materials. Thus, for example, a polyvinyl alcohol overcoat may be utilized either over the image-receiving layer or over the next adjacent photosensitive silver halide layer, and a cross-linking agent therefor which will not have a substantial deleterious effect on gelatin may be incorporated within one of the layers comprising the film unit, as, for example, in the denoted interlayer between the red-sensitive silver halide emulsion layer and the magenta dye developer layer. Within such an embodiment, for example, a boric acid cross-linking agent for polyvinyl alcohol may be incorporated in the above-denoted interlayer. Upon rupture of the processing composition container, processing composition is distributed between the image-receiving element and the negative element, rendering the boric acid material diffusible within the system. As this material comes into contact with the polyvinyl alcohol overcoat between the image-receiving layer and the next adjacent photosensitive emulsion layer, the polyvinyl alcohol is cross-linked and becomes impermeable to image-forming materials.

In addition to techniques as described above, alternative diffusion transfer color processes known to the photographic art may be employed. Thus, for example, U.S. Pat. No. 3,019,124, issued Jan. 30, 1962, discloses the manufacture of photographic color screen elements; and U.S. Patents Nos. 2,968,554, issued Jan. 17, 1961 and 2,983,606, issued May 9, 1961 disclose diffusion transfer processes wherein a color screen element is utilized to provide a multicolor positive image to a superposed image-receiving layer. Also in place of the aforementioned dye developers, there may be employed dye image-forming materials such as those described in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,445,228; 3,443,940; 3,443,941; 3,443,043; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pats. Nos. 2,774,668; 2,983,606; 3,087,817; and 3,345,163 wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

As examples of materials which heretofore have been found to be useful as image-receiving layers in diffusion transfer color photographic processes, 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 of a similar nature. Particularly useful materials have comprised polyvinyl alcohol or gelatin, having admixed therewith a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964. However, while image-receiving layers comprising the aforementioned materials have provided excellent photographic images, they have nonetheless had certain inherent drawbacks. Thus, for example, where the image-receiving layer comprises poly-4-vinylpyridine as disclosed in aforementioned U.S. Pat. No. 3,148,061, it is generally necessary to coat the polymer with a small amount of acid, which is preferably volatile but which is then also diffusable; any unevaporated acid residue has an adverse effect on the stability of the photographic unit when the image-receiving element and the photosensitive element are stored in face-to-face contact prior to exposure and development of the unit. Also, particularly in embodiments where the image-receiving element is not stripped away but is maintained in contact with the photosensitive element subsequent to dye developer transfer image formation, the resulting images have a tendency to show mottle, and to darken somewhat with the passage of time.

The image-receiving elements to which the present invention is directed comprise at least a dyeable stratum or image-receiving layer to be described with particularity hereinafter and may optionally include other strata performing specific desired functions, e.g., the polymeric acid and/or spaced layers described previously. They may be separate from the photosensitive element or they may be present in unitary film units including the photosensitive strata, e.g., one or more silver halide layers and associated color-providing material.

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

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

Another object of the present invention is to provide novel image-receiving elements for diffusion transfer color photographic processes particularly adapted to result in images exhibiting excellent dye saturation over an extended processing temperature range.

A further object of the present invention is to provide novel image-receiving elements for diffusion transfer color photographic processes particularly adapted to result in mottle-free images of excellent stability.

A still further object of the present invention is to provide novel-image-receiving materials for diffusion transfer color photographic processes which are coatable at neutral pH and/or at high alkaline pH, e.g., 8–11 and at high solids content of coating solution.

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 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 polymeric layer having specified permeability characteristics; and a third solution dyeable polymeric layer comprising a permeable graft copolymer; 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 permeable polymeric layer; and a third polymeric layer adapted to be dyed from an alkaline solution comprising a permeable graft copolymer; and novel transfer processes particularly adapted to employ same.

A still further object is to provide novel procedures for forming color transfer images wherein a photosensitive element or film unit including at least one light-sensitive silver halide layer and associated color-providing material is exposed to form a developable image and then developed by contacting it with a processing composition to provide an imagewise distribution of diffusible color-providing material which is then transferred, by diffusion, to a dyeable stratum of the foregoing description to impart thereto a color transfer image.

Yet another object of the present invention is to provide novel graft copolymers particularly adapted for employment in diffusion transfer photographic products and processes.

Still another object is to provide novel graft copolymers having temperature-inverting permeability characteristics such that said graft copolymer thereby imparts a built-in mechanism for achieving some degree of temperature independence in the processing function of a diffusion transfer photographic process.

Still another object of the present invention is to provide novel graft copolymers obtainable in greater than 99% conversion yields, said graft copolymers capable of forming aqueous emulsions that are categorized by high solids content, low viscosity, and coatability at neutral and/or high alkaline pH.

Still another object of the present invention is to provide novel 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 and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In accordance with the practice of the present invention, the dyeable stratum of the diffusion transfer products described above comprise a polymeric, film forming material wherein a moiety which can provide a mordant capability is grafted to, e.g., pendant from the backbone of the polymer substrate. Accordingly, the essence of the present invention resides in the unexpected discovery that the use of a polymeric material wherein a moiety providing a mordant capability is grafted to the polymeric chain or backbone as the dyeable stratum of diffusion transfer color image-receiving elements provide images exhibiting excellent dye densities over a wide temperature range, with faster dye saturation, as compared with compounds described in the prior art. Moreover, such images are characterized by superior light stability, and reduced degree of darkening. It has further been discovered that the novel graft polymers or copolymers employed in the present invention can be coated from solution at a higher solids content than the materials or the prior art, resulting in increased coating efficiency; they are coatable at neutral pH and hence their use can obviate the stability problems inherent in the use of volatile, diffusible acids as coating adjuncts. Moreover, their coatings are molecularly homogeneous, resulting in more uniform image quality and freedom from mottle as compared with prior art image-receiving layers. Additionally the novel graft polymers and/or copolymers of the present invention exhibit permeability at least in part inversely dependent upon temperature.

As indicated hereinbefore, polymeric films having inverse temperature dependence with regard to alkali permeability have been disclosed for utilization as spacer layers in color diffusion transfer photographic receiving sheets. Polymers comprising such films generally 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 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.

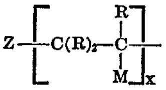
Benefits are derived from using a temperature-inverting material in a process which depends upon permeation of liquids, at a variety of temperatures, since, as the ambient temperature decreases, the polymer tends to form hydrates and swells, thus facilitating permeation as a function of the degree of 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, 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.

It will be obvious that where the image-receiving layer of the image-receiving element comprises a temperature-inverting polymeric mordant, not only is the temperature-permeation of the system enhanced, but also a technique is provided for evening out the dye uptake of the layer over an extended temperature range. Specifically, at lower temperatures where the processing composition transfer rate is slower, the increased permeability of the layer renders the mordanting sites more readily available to the diffusing image-forming components; the increase in processing composition transfer rate which takes place as the processing temperature is increased is compensated for by the corresponding decrease in permeability and availability of mordanting sites in the image-receiving layer. Thus, by means of the present invention, an image-receiving layer is provided for diffusion transfer color photographic processes wherein mordanting of dye image-forming material is substantially uniform over a wide range of temperatures.

The temperature-inverting characteristic of members of the class of graft polymers and/or 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 hydropholic-hydrophobic bonding forces.

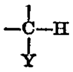
The graft polymers and/or copolymers used in the dyeable stratum or layer of the aforementioned diffusion transfer products and processes essentially conform to the following formula:



$$Z-\left[C(R)_2-\overset{\overset{R}{|}}{\underset{\underset{M}{|}}{C}}-\right]_x$$

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; M is a moiety which can provide a mordant capability; each R is the same or different substituent which will not hinder grafting of the mordant through the vinyl group such as hydrogen, hydroxy, alkyl radicals, alkanol radicals ,alkoxy, alkoxy radicals and aryl radicals with hydrogen, hydroxy, lower alkyl or alkoxy, e.g., from 1–4 carbon atoms, being the preferred substituents; and X is a positive integer.

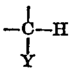
With regards to the backbone polymer or copolymer of the graft polymer, in general, any organic polymer or copolymer comprising repeating units comprising structural units containing the



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

grouping; wherein Y is selected from the group consisting of hydroxyl, amino, mercapto, acyl and aryl, amido 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 alcohols, poly-N-vinylpyrrolidone, gelatin, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, partially hydrolyzed esters of polyvinyl alcohol such as partially hydrolyzed polyvinyl acetate, polyaldehydes, polyamides, cellulose, substituted celluloses such as methyl cellulose, hydroxyethy cellulose, methy hydroxypropyl cellulose, starch, etc.

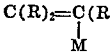
It is believed that upon oxiadtion of the



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

grouping, a free radical is formed, which attacks the graftable site of the compound providing the mordant capability thus providing the graft polymer and or copolymer.

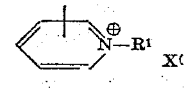
Graftable compounds which can provide the mordant capability are those which in their monomeric form, conform to the following formula:



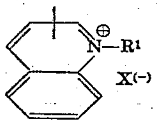
$$C(R)_2=\underset{\underset{M}{|}}{C}(R)_2$$

where, as described before, $(CR_2)=C(R_2)$ represents a graftable vinyl site and M is a moiety providing a mordant capability. Compounds of this type are known to the art and include among others those wherein the M moiety can conform to the following formulae:

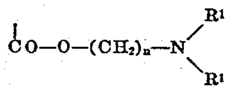
(1)



(2)

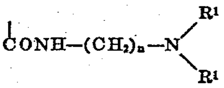


(3)



$$-\overset{|}{C}O-O-(CH_2)_n-N\begin{smallmatrix}R^1\\ \\R^1\end{smallmatrix}$$

(4)

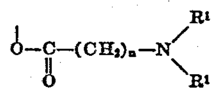


$$-\overset{|}{C}ONH-(CH_2)_n-N\begin{smallmatrix}R^1\\ \\R^1\end{smallmatrix}$$

(5)

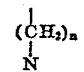
$$\overset{|}{N}\begin{smallmatrix} \\R^1\quad R^2\end{smallmatrix}$$

(6)



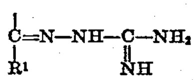
$$\overset{|}{O}-\underset{\|}{\underset{}{C}}\!\!\!\!\underset{O}{}-(CH_2)_n-N\begin{smallmatrix}R^1\\ \\R^1\end{smallmatrix}$$

(7)



$$\overset{|}{(CH_2)_n}-N\begin{smallmatrix}R^1\\ \\R^1\end{smallmatrix}$$

(8)



$$\underset{R^1}{\overset{|}{C}}{=}N-NH-\underset{NH}{\overset{}{C}}-NH_2$$

wherein *n* is an integer from 1–8; each R^1 can be hydrogen, an alkyl radical an alicyclic radical, an alkoxy radical, a saturated heterocyclic ring, and an aryl radical or substituted derivative thereof and each R^1 can be the same or different; X represents an anion such as an aryl sulfonate anion, e.g., benzenesulfonate, p-toluenesulfonate etc., an alkylsulfonate anion, e.g., methyl sulfate, ethyl sulfate, n-propyl sulfate, n-butyl sulfate etc.; or X can be a halide ion, e.g., iodide, chloride bromide or other acid anion radical.

Particular compounds conforming to the above generic formulae include the vinyl pyridines and salts thereof such as 4-vinylpyridine, 2-vinylpyridine, 5-vinyl-2-methylpyridine, etc.

Other compounds include 2-methyl-N-vinylimidazole B-(trimethyl amino) ethyl methacrylate nitrate, B-(trimethyl amino) ethyl methacrylate nitrate, B-(trimethyl amino) ethyl methacrylate methyl sulfate, dimethyl amino ethyl methacrylate nitrate, 5-vinyl-2 methyl-N benzyl pyridinium bromide, 4-vinyl pyridinium tosylate, p-vinyl benzyl triethylammonium chloride, 4-vinylpyridine methyl tosylate, 5-vinyl-2-methyl pyridine methyl tosylate, vinylbenzyltrimethylammoniumchloride, vinylbenzyltriethylammoniumchloride, vinylbenzylpyridiniumchloride, vinylbenzyl-N-methylmorpholiniumchloride, and the like.

Other details relating to compounds that can provide a mordant capability may be found in U.S. Pats. 2,537,924, 2,548,575, 2,564,726, 2,583,076, 2,635,535, 2,635,536, 2,753,263 3,048,487, and 3,075,841.

The graft copolymers of the present invention may be prepared, in general, by oxidizing an organic polymeric backbone containing hydroxyl, amino, mercapto, amido, acyl, or aryl groups with a transition metal ion catalyst, in the presence of the mordant monomer. Generally, a 1–10%, by weight, aqueous solution of the backbone polymer is deaerated for about 30 minutes with stirring. The monomer is then added and nitrogen is bubbled through the solution for about one hour. At this point, the nitrogen is passed over the stirred solution and the pH adjusted to around 1.5 with concentrated acid. The catalyst is dissolved in a minimum amount of water, quickly added to the polymerization mixture and stirring continued under the nitrogen atmosphere for at least two more hours with stirring times up to 24 hours, giving no adverse effect to the graft copolymer. The resulting graft copolymers are obtained from the reaction vessel in the form of aqueous solutions. They may then be coated directly from solution to provide novel image-receiving layers. However, in preferred embodiments, the pH is raised, e.g., with NH_3, to a point at which an aqueous emulsion is formed, generally a pH of around 7, depending at least in part upon the ratio of catalyst to backbone polymer and backbone polymer to mordant monomer.

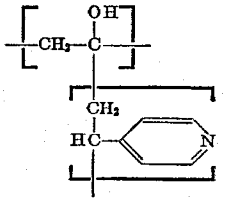
The choice of catalyst is wide ranging, with particularly good results being obtained when catalysts containing Ce^{+4}, V^{+5} and Cr^{+6} are employed in making the graft copolymers of the present invention.

Although the pH is generally adjusted to around 1.5 with concentrated nitric acid, pH's of up to about 7 have proven operative in some instances, depending at least in part on the ratio of catalyst to backbone polymer.

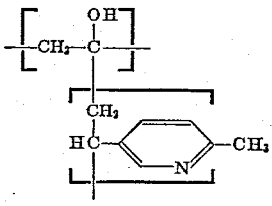
In some instances, the temperature of the polymerization mixture can be raised to around 50° C. to facilitate the reaction.

Examples of novel graft polymers which are found to be useful in the instant invention are:

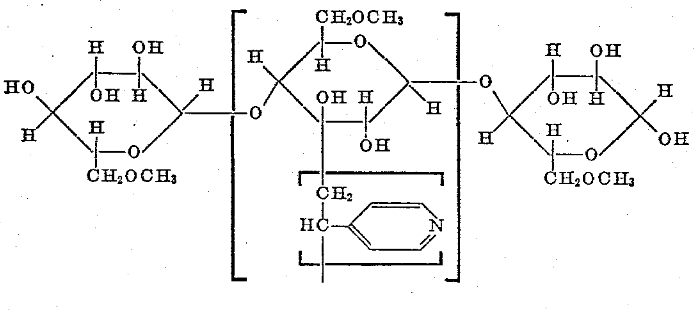
(1) 4-vinylpyridine graft on polyvinyl alcohol



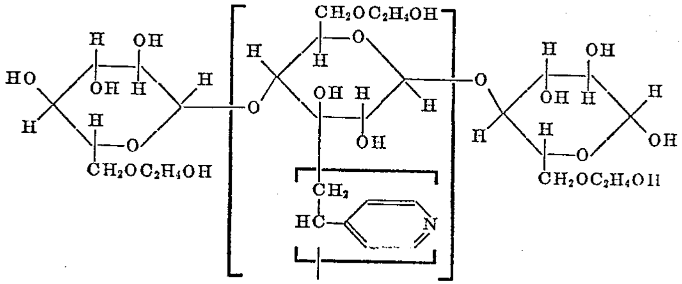
(2) 5-vinyl-2-methylpyridine graft on polyvinyl alcohol



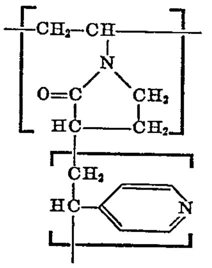
(3) 4-vinylpyridine graft on methyl cellulose



(4) 4-vinylpyridine graft on hydroxyethyl cellulose



(5) 4-vinylpyridine graft on gelatin
(6) 5-vinyl-2-methylpyridine graft on gelatin
(7) 4-vinylpyridine graft on starch
(8) 5-vinyl-2-methylpyridine graft on starch
(9) 4-vinylpyridine graft on poly-N-vinylpyrrolidone



(10) 4-vinyl pyridine graft on hydroxyethylcellulose
(11) 4-vinyl pyridine, vinylbenzyltrimethylammoniumchloride graft on hydroxyethylcellulose
(12) vinylbenzyltrimethylammoniumchloride graft on hydroxyethylcellulose
(13) vinylbenzyltrimethylammoniumchloride graft on polyvinyl alcohol
(14) 4-vinyl pyridine, vinylbenzyltrimethylammoniumchloride graft on polyvinyl amide

It has been generally found that for any given polymer, the temperature-permeability characteristics of the layers prepared therefrom 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 backbone polymer ratio, will result in layers having different diffusion characteristics if they are prepared in the presence of different backbone/catalyst ratios. In general, decreasing the amount of catalyst (and hence increasing the backbone/catalyst ratio) results in increased impermeability.

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 10 to about 130 is the most useful range irrespective of the monomers used.

From the foregoing discussion, it will be appreciated that employment of the graft copolymers of the present invention, in addition to providing an especially effective dye mordant function, can assist in evening out the temperature response characteristics of the diffusion transfer color photographic units in which they are employed, by acting at least in part as a "timing valve" for the processing composition. Ordinarily, if the processing temperature is too hot and no temperature inverting layer is used, poor dye densities and "gappiness" may be evident in the photographic image, which are believed to be due to the 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 image, causing dull, muddy colors.

The present invention will be illustrated in greater detail in conjunction with the following procedures and processes utilized in providing the novel graft copolymers of the present invention, and which set out representative photographic products and processes employing the novel graft copolymers, which, however, are not of limiting effect and are intended to be illustrative only.

Example I

A graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 227 was prepared as follows:

To a deaerated solution of 20 g. of polyvinyl alcohol in 500 cc. of water was added 10 g. of 4-vinylpyridine, with stirring under an atmosphere of nitrogen. Nitrogen was bubbled through the solution for one hour, after which the temperature of the solution was raised to 50° C., the pH was adjusted to 1.5 with concentrated nitric acid, and 1.1 g. of $Ce(NH_4)_2(NO_3)_6$ in 20 cc. of water was added. Stirring was continued for two more hours, at the end of which the desired copolymer was obtained as an aqueous solution; the pH of the solution was raised to a point at which an aqueous emulsion was formed with concentrated NH_3. The product polymer was dialyzed to remove any excess ammonium nitrate salt.

Example II

A graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 57 was prepared by the procedure of Example I using 4.4 g. of $Ce(NH_4)_2(NO_3)_6$, except that the reaction was carried out at room temperature and terminal stirring was continued overnight.

Example III

A graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 45 was prepared by the procedure of Example II, using 5.5 g. $Ce(NH_4)_2(NO_3)_6$.

Example IV

A graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/vinylpyridine mole ratio of 1/3 and a polyvinyl alcohol/catalyst mole ratio of 22.5 was prepared by the procedure as outlined in Example II using 20 g. of polyvinyl alcohol, 60 g. of 4-vinylpyridine, and 11.0 g. of $Ce(NH_4)_2(NO_3)_6$ in 25 cc. of water.

Example V

Two graft copolymers of 4-vinylpyridine on hydroxyethyl cellulose were prepared by the procedure described in Example I, except as follows:

(a) Graft copolymer having a hydroxyethyl cellulose/4-vinylpyridine weight ratio of 2/1 and a hydroxyethyl cellulose/catalyst weight ratio of 20 was prepared using 22 g. of hydroxyethyl cellulose, 11 g. of 4-vinylpyridine, and 1.1 g. $Ce(NH_4)_2\ (NO_3)_6$ in 10 cc. of water.

(b) Graft copolymer having a hydroxyethyl cellulose/4-vinylpyridine weight ratio of ⅓ and a hydroxyethyl cellulose/catalyst weight ratio of 10 was prepared using 22 g. of hydroxyethyl cellulose, 66 g. of 4-vinylpyridine, and 1.1 g. of $Ce(NH_4)_2\ (NO_3)_6$ in 10 cc. of water.

Example VI

Graft copolymers of 4-vinylpyridine on methyl cellulose were prepared as follows:

An aqueous solution of 10 g. of methyl cellulose in 500 cc. of water (Methocel HG 60, 4000 cps., available commercially from Dow Chemical Co., Midland, Mich.) was purged from nitrogen for two hours, after which 10 g. of 4-vinylpyridine was added. The pH was adjusted to 1.5 with concentrated nitric acid, and 0.6 g. of $Ce(NH_4)_2(NO_3)_6$ was added. The mixture was reacted at 30° C. for 1.5 hours and at 50° C. for 1.5 hours, after which NH_3 was added to bring the pH to 7. The resulting precipitated polymer was washed with water and acetone, and recovered as an off-white powder.

A second graft copolymer of 4-vinylpyridine on methyl cellulose was prepared by the same procedure, but using a lower viscosity methyl cellulose (Methocel MC, 400 cps., available commercially from Dow Chemical Co.). Upon addition of NH_3, a white latex was obtained, which was dialyzed for two days to yield the product polymer.

A third graft copolymer of 4-vinylpyridine on methyl cellulose was prepared by dissolving 50 g. of methyl cellulose (Methocel MC, 10 cps., available commercially from Dow Chemical Co.) in 500 cc. of hot water. 700 cc. of cold water and 100 g. of 4-vinylpyridine, and about 100 g. of concentrated nitric acid, to give a pH of 1.5, were added. After stirring under an atmosphere of nitrogen at room temperature for two hours, the solution became cloudy. 300 cc. of water were added, and the temperature was raised to 45° C. The mixture was repeatedly evacuated and vented into nitrogen. Upon addition of 3.0 g. of $Ce(NH_4)_2(NO_3)_6$ in 15 cc. of water, the mixture gradually became translucent. Stirring was continued overnight at 45–50° C. after which the reaction product was recovered as a white latex. The copolymer was purified by dialysis and centrifugation, yielding a clear 4.4 weight percent aqueous solution.

Example VII

A graft copolymer of 5-vinyl-2-methyl pyridine on gelatin having a gelatin/5-vinyl-2-methyl pyridine weight ratio of ½ was prepared by the procedure of Example II, using 10 g. of gelatin in 460 cc. of water, 20 g. of 5-vinyl-2-methyl pyridine, and 3.3 g. of $Ce(NH_4)_2(NO_3)_6$ in 10 cc. of water. The copolymer was recovered in the form of an aqueous emulsion.

Example VIII

A graft copolymer of 4-vinylpyridine on poly-N-vinylpyrrolidone was prepared by the procedure of Example I, using 30 g. of poly-N-vinylpyrrolidone in 500 cc. of water, 15 g. of 4-vinylpyridine, and 10.0 g. of $Ce(NH_4)_2(NO_3)_6$ in 20 cc. of water. The copolymer was recovered in the form of an aqueous emulsion.

Example IX

A graft copolymer of 4-vinylpyridine on starch was prepared by the procedure of Example I, using 20 g. of soluble starch dissolved in 500 cc. of water, 40 g. of 4-vinylpyridine, and 4.4 g. of $Ce(NH_4)_2(NO_3)_6$. A second copolymer having a lower starch/catalyst ratio was similarly prepared, with the exception that 8.8 g. of $Ce(NH_4)_2(NO_3)_6$ was employed.

Example X

To a solution of 11 g. of hydroxyethyl cellulose in 250 ml. H_2O was added 5.5 g. 4-vinylpyridine, 5.41 g. concentrated HNO_3 and 7.6 g. vinylbenzyltrimethylammoniumchloride. Nintrogen was bubbled through the mixture for one hour and the temperature was raised to 50° C. then 1.1 g. $Ce(NH_4)_2(NO_3)_6$ in 10 ml. H_2O was added and stirring continued overnight. The pH of the polymerization mixture was then adjusted to 7.0 with concentrated NH_4OH. The graft copolymer of hydroxyethyl cellulose having 4 vinylpyridine vinylbenzyltrimethylammoniumchloride grafted thereto was recovered in the form of an aqueous emulsion having 9.1% solids by weight. The mole ratio of hydroxyethyl cellulose (HEC) to 4 vinylpyridine (4VP) to vinylbenzyltrimethylammoniumchloride was 2/1/1.4.

Example XI

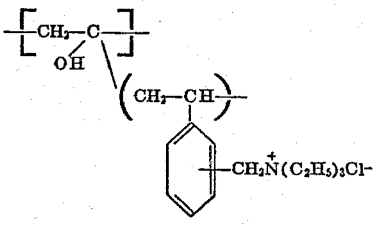
A graft copolymer of vinylbenzyltrimethylammoniumchloride on hydroxyethyl cellulose was prepared in accordance with the procedure of Example X but no 4-vinylpyridine was used and only 0.5 g. concentrated HNO_3 was used.

Example XII

The following example illustrates a method for preparing a graft copolymer of p-vinylbenzyltriethylammoniumchloride on polyvinyl alcohol wherein the mole ratio of polyvinyl alcohol to p-vinylbenzyltriethylammoniumchloride is 1:1.

To a solution of 11 g. polyvinyl alcohol in 200 ml. H_2O was added 11 g. vinylbenzyltriethylammoniumchloride. Nitrogen was bubbled through the mixture for 1 hour and the temperature raised to 60° C. then 0.5 g. concentrated NHO_3 and 1.6 g. $CE(NH_4)_2(NO_3)_6$ in 10 mls. H_2O was added. Stirring continued for 2½ hours and the graft copolymer was recovered in the form of an aqueous solution having a pH of 5.0 and containing 9.4% solids by weight.

The graft copolymer prepared above conforms to the following structure:



Example XIII

A graft copolymer of vinylbenzyltrimethylammoniumchloride, 4-vinylpyridine on polyvinyl alcohol wherein the mole ratio of polyvinyl alcohol to vinyl benzyltrimethylammoniumchloride to 4 vinylpyridine was 2/2/1 was prepared in accordance with the procedure of Example XII except that vinylbenzyltrimethylammoniumchloride was used together with 5 g. 4-vinylpyridine, 4.8 g. concentrated HNO_3. 2.2 g. $CE(NH_4)_2(NO_3)_6$ and the polymerization was run overnight at 60° C. The graft copolymer was recovered as an aqueous emulsion having a pH of 5.0 and containing 11% solids by weight.

Example XIV

A series of four image-receiving elements was prepared as follows:

A cellulose nitrate subcoated baryta paper was coated with the partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 g. of a DX-840-31 resin (trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity polyethylene/maleic anhydride), 140 g. 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 comprising of a graft copolymer of diacetone acrylamide and acrylamide on polyvinyl alcohol at a coverage of 750 mg./ft.^{2} to provide a spacer layer. (Spacer layers for diffusion transfer color image-receiving elements comprising graft vinylamide copolymers and procedures for preparing such polymers are described in U.S. Pat. Nos. 3,575,700 and 3,575,701 both to Lloyd D. Taylor.) The first element so prepared was then coated, on the external surface of the spacer layer, with the vinylpyridine graft copolymer of Example I at a pH of 7.4, and the second and third elements were coated at a pH of 6.0 with the vinylpyridine graft copolymers of Examples II and III, respectively, all at coverages of 1000 mg./ft.^{2}. The fourth element was similarly coated at a pH of 4.5 with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, to serve as a control. The thus-prepared image-receiving elements were baked at 180° F. for 30 minutes and then allowed to cool.

The negative component of the photographic film distributed by Polaroid Corporation, Cambridge, Mass., under the trade designation of Polacolor film Type 108, was employed as the photosensitive element for the image-receiving elements prepared above. Such multicolor, multilayer photosensitive elements 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 may comprise a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive 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 stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive element 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-hexylcarbamyl-4-(p-[hydroquinonyl-ethyl]-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.

Each of four photosensitive elements were exposed and processed at room temperature by spreading an aqueous liquid processing composition at a pH of not less than about 12 which comprised:

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

between each exposed multicolor element and its respective image-receiving element as they are brought into superposed relationship. After an imbibition of approximately 60 seconds, the image-receiving elements were separated from the remainder of the film assembly.

The following is a tabulation of D_{max} values obtained in the resulting photographic image:

TABLE 1

PVA/catalyst ratio in image-receiving layer	Red $D_{max.}$	Green $D_{max.}$	Blue $D_{max.}$
Control	2.47	2.48	2.44
227 (Example I)	2.55	2.55	2.55
57 (Example II)	2.50	2.55	2.55
45 (Example III)	2.44	2.55	2.55

It can be seen that the novel graft copolymers of the present invention provide images of excellent dye density over a wide polyvinyl alcohol/catalyst ratio range even when coated at relatively high pH's.

Example XV

In order to evaluate the light stability of photographic images prepared utilizing graft copolymers of the present invention, a series of four photographic images were prepared as in Example XIV, except that the graft copolymers were diluted by half (on a weight basis) with polyvinyl alcohol prior to coating. The images so prepared were subjected to a Xenon arc lamp for specified periods of time, at the end of which the change in D_{max} (magenta image) was measured. The following is a tabulation of the percent change (fading) in each of the test images:

TABLE 2

PVA/catalyst ratio in image-receiving layer	After—			
	24 hrs.	48 hrs.	9 hrs.	144 hrs.
Control	22	36	51	58
227 (Example I)	14	31	41	48
57 (Example II)	14	24	36	43
45 (Example III)	9	23	32	38

Example XVI

A series of six image-receiving elements was prepared, each comprising, in sequence, a transparent cellulose nitrate-subcoated baryta support, and a polymeric acid layer and spacer layer as described in Example XIV. A mordant layer was applied at a coverage of 1000 mg./ft.^{2} to the first two elements comprising a graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 45 (prepared in Example III supra and coated at a pH of 6.0); to the second two elements comprising a graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 76 (prepared by the same procedure except using 3.3 g. of $Ce(NH_4)_2(NO_3)_6$, and coated at a pH of 6.0); and to the remaining two elements as controls, a 2/1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine (coated at a pH of 4.5). The thus-prepared image-receiving elements were baked at 180° F. for 30 minutes and then allowed to cool.

Each of the above image-receiving elements was processed by spreading an aqueous liquid processing composition at a pH of not less than about 12 which comprised water, potassium hydroxide, hydroxyethyl cellulose thickener, and thymolphthalein, between each image-receiving element and a superposed stripping sheet comprising a support having a layer of gelatin coated thereon at a coverage of 600 mg./ft.^{2}, after which the image-receiving element and stripping sheet were stripped apart. In each instance, the permeability of the image-receiving element was evaluated by visual determination of the length of time required for the thymolphthalein color to clear (indicating that a pH of 10.5 had been reached).

The following is a tabulation of the permeation times in seconds at various temperatures of each of the various image-receiving elements:

TABLE 3

PVA/catalyst ratio in image-receiving layer	40° F.	100° F.
Control	340	270
56	390	410
76	715	705

It can be readily seen that the novel graft vinylpyridine copolymers of the present invention may be used to provide image-receiving elements having more uniform alkali permeability over a wide temperature range, as compared with prior image-receiving elements.

Example XVII

A graft copolymer of 4-vinylpyridine on gelatin having a gelatin/4-vinylpyridine weight ratio of 1/2 and a gelatin/catalyst weight ratio of 3 was prepared by adding 20 g. of 4-vinylpyridine to a deaerated solution of 10 g. of gelatin in 500 cc. of water, with stirring under an atmosphere of nitrogen. Nitrogen was bubbled through the solution for three hours, after which the pH was adjusted to 1.5 with concentrated nitric acid, and 3.3 g. of $Ce(NH_4)_2(NO_3)_6$ in 20 cc. of water was added. Stirring was continued overnight, at the end of which the desired copolymer was obtained as an aqueous solution. The pH was raised to 4.7 with aqueous NH_3, resulting in the formation of an aqueous emulsion. The polymer was dialyzed to remove any excess ammonium nitrate salt.

Three image-receiving layers were prepared by coating the thus-prepared copolymer to a thickness of 0.30 mil on the external surface of a polymeric acid layer as described in Example XIV, which had been coated on a cellulose nitrate subcoated baryta paper. Control image-receiving layers were similarly prepared, using a 2/1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine (at a thickness of 0.32 mil) in place of the graft copolymer.

The alkali permeability time (in seconds) of the respective elements was determined by the same procedure detailed in Example XVI, with the following results:

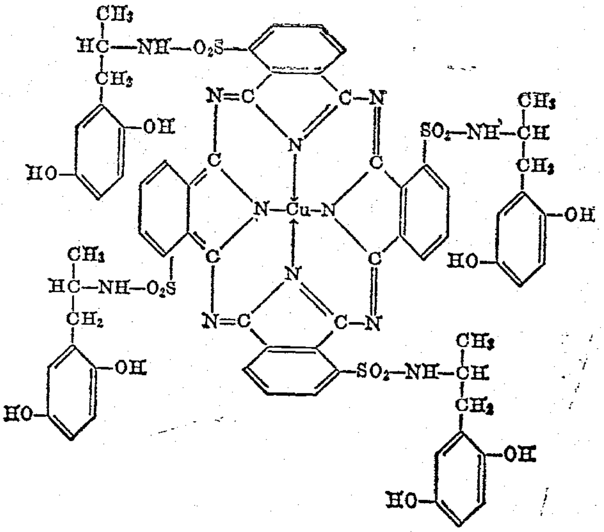
TABLE 4

	40°	75°	100°
Control	33	15.8	8.6
Gelatin/4-vinylpyridine	5	4.5	8

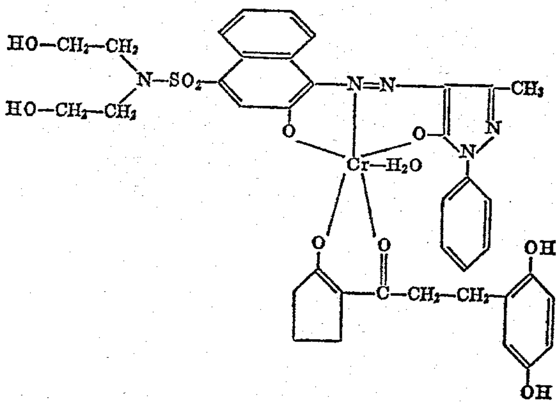
Example XVIII

A series of five image-receiving elements was prepared, each comprising, in sequence, a cellulose-nitrate-subcoated baryta support, a polymeric acid layer as described in Example XIV, and a spacer layer comprising a graft copolymer of diacetone acrylamide and acrylamide on polyvinyl alcohol as described in Example XVI. The image-receiving layers of the first four elements all comprised a graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 2/1 and a polyvinyl alcohol/catalyst mole ratio of 46, prepared as in Example III, and coated at pH's of 4.5, 7.1, 8.3 and 10.0, respectively. The fifth image-receiving element comprised an image-receiving layer comprising a 2/1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, coated at a pH of 4.5, as a control.

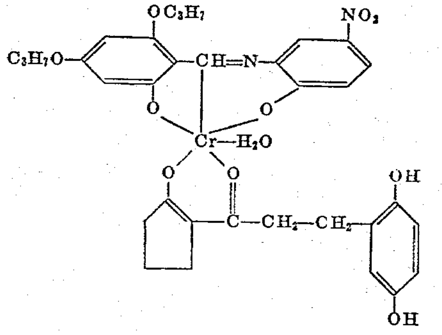
Photosensitive elements of the general type described with reference to Example XIV were provided, with the major exception that the particular dye developers employed were metal-complexed dye developers of the following formulae:



a cyan dye developer:



a magenta dye developer; and



a yllow dye developer. Metallized dye developers of the foregoing types are described in U.S. Pat. No. 4,482,972, issued Dec. 9, 1969, and in U.S. Pats. Nos. 3,563,739; 3,551,406 and 3,597,200 all to Martin Idelson and in copending applications Ser. No. 851,525 filed June 30, 1969 by Martin Idelson and Ser. No. 830,489 filed June 4, 1969 by Arthur G. Goulston and Paul S. Huyeffer, now U.S. Pat. No. 3,704,301.

Each of the photosensitive elements were exposed and processed at room temperature with one of the above-prepared image-receiving elements.

The following is a tabulation of the D_{max} values obtained in the resulting photographic images:

TABLE 5

Receiving layer	pH	Red $D_{max.}$	Green $D_{max.}$	Blue $D_{max.}$
Control	4.5	2.08	2.12	2.14
PVA/4-VP graft	4.5	2.55	2.35	2.32
Do	7.1	2.55	2.53	2.42
Do	8.3	2.55	2.35	2.32
Do	10.0	2.52	2.24	2.22

It can readily be seen that the graft copolymers of the present invention can be coated over a wide pH range without adversely affecting image densities.

Example XIX

An image-receiving element was preparedas in Example XVIII but the image-receiving layer comprised the graft copolymer of Example X, e.g., a graft copolymer of 4-vinylpyridine, vinyl benzyl trimethyl ammonium chloride on hydroxyethyl cellulose. Another image-receiving element comprised an image-receiving layer comprising a 2/1 mixture by weight of polyvinyl alcohol and poly-4-vinylpyridine as a control.

Photosensitive elements of the type used in Example XVIII, e.g., employing metallized dye developers were exposed and processed with each of the above prepared image-receiving elements at room temperature and with the same processing composition.

The following table presents a comparison of the d max data after two minutes and after 24 hours.

TABLE 6

	$D_{max.}$ after two minutes		
Receiving layer	Red	Green	Blue
Control	1.5	1.25	1.4
Graft copolymer of Example X	3.1	2.1	2.0
	$D_{max.}$ after 24 hours		
Control	2.5	2.3	2.15
Graft copolymer of Example X	3.0	2.45	2.35

Example XX

A graft copolymer of 4-vinylpyridine on polyvinyl alcohol having a polyvinyl alcohol/4-vinylpyridine mole ratio of 1/2 and a polyvinyl alcohol/catalyst mole ratio of 23 was prepared as described in Example II, using 20 g. of polyvinyl alcohol, 40 g. of 4-vinylpyridine, and 11.0 g. $Ce(NH_4)_2(NO_3)_6$ in 25 cc. of water. The graft copolymer so prepared was coated at a pH of 5.1 as the image-receiving layer of an image-receiving element prepared as in Example XVIII.

A photosensitive element substantially identical to that of Example VIII was employed, and was exposed and ment as described in Example VIII, resulting in an image having a red D_{max} of 2.50, green D_{max} of 2.41 and blue D_{max} of 2.23

Example XXI

A graft copolymer of 5-vinyl-2-methylpyridine on polyvinyl alcohol having a polyvinyl alcohol/5-vinyl-2-methyl-pyridine mole ratio of 1/2 and a polyvinyl alcohol/catalyst mole ratio of 22.5 was prepared by the method of Exampe I using 20 g. of polyvinyl alcohol, 40 g. of 5-vinyl-2-methyl-pyridine and 1.1 g. of $Ce(NH_4)_2(NO_3)_6$ in 10 cc. of water. The graft copolymer so prepared was coated as the image-receiving layer of an image-receiv- transparent support and a spacer layer comprising a graft copolymer of diacetone acrylamide and acrylamide on polyvinyl alcohol as described in Example XIV.

Example XXII

A graft copolymer of 4-vinylpyridine on hydroxyethyl cellulose having a hydroxyethyl cellulose/4-vinylpyridine weight ratio of 1/2 and a hydroxyethyl cellulose/catalyst weight ratio of 10 was prepared by the method Example 1 using 1.1 g. of hydroxyethyl cellulose, 22 g. of 4-vinylpyridine, and 1.1 g. of $Ce(NH_4)_2(NO_3)_6$ in 10 cc. of water. The graft copolymer so prepared was coated as the image-receiving layer of an image-receiving element as described in Example XXI.

Example XXIII

A series of three photosensitive elements prepared as in Example XIV were exposed and processed with, respectively, the image-receiving elements of Example XXI, Example XXII, and a control element identically prepared except that the image-receiving layer thereof comprised a 2/1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine. A processing composition as described in Example XIV was employed, but which contained additionally a titanium dioxide reflecting material in sufficient quantity to mask the photosensitive element subsequent to exposure and processing; subsequent to processing, the photosensitive element and image-receiving element were not stripped apart, but were maintained in superposed relationship, the final images being viewable through the transparent supports of the respective image-receiving elements. The images resulting from the two graft copolymer image-receiving layers gave excellent, mottle-free images of high density as compared with the control. Moreover, the dye densities were more rapidly achieved with the former than with the control. It was observed, for example, that while the control element required 7 minutes to reach a dye density of 2.0, the same dye density was reached in the element comprising the graft copolymer of 4-vinylpyridine on hydroxyethyl cellulose in less than two minutes.

The resulting images were examined for darkening or stain, as determined by D_{min} readings, initially at 24 hours after processing, and again after 22 days, with the following results:

TABLE 7

	Stain			Stain (after 22 days)		
Receiving layer	Red	Green	Blue	Red	Green	Blue
Control	0.22	0.24	0.29	0.20	0.26	0.45
5-vinyl-2-methyl-pyridine on polyvinyl alcohol	0.20	0.21	0.24	0.21	0.25	0.37
4-vinylpyridine on hydroxyethyl cellulose	0.20	0.21	0.24	0.22	0.27	0.39

It was noted that the D_{min} areas in the images prepared with the graft copolymer image-receiving layers appeared considerably whiter than those of the control emulsion to an even greater extent than would be expected from the above D_{min} readings.

Example XXIV

To a solution of 11 g. polyacrylamide in 250 g. H_2O was added 5.5 g. 4-vinylpyridine, 5.3 g. conc. HNO_3 and 2.75 g. vinylbenzyltrimethylammoniumchloride. Nitrogen was bubbled through the solution for 1 hour; the temperature raised to 50° C. and 0.55 g. $Ce(NH_4)_2(NO_3)_6$ in 10 cc. H_2O was added. Stirring was continued for 16 hours. The pH of the mixture was then adjusted to 8.5 with NH_3 and dialyzed to remove ammonium nitrate. An aqueous emulsion is obtained which has a pH of 8.0 the ratio of polyacrylamide to 4-vinylpyridine to vinylbenzyltrimethylammoniumchloride is 2:1:0.25 in the graft copolymer so obtained.

Example XXV

A series of two photosensitive elements were prepared, exposed and processed in the manner described in Example XXIII. One element had as the image-receiving layer, a coating of the graft copolymer of Example XXIV while the other had a coating of a 2:1:0.25 mixture of polyacrylamide, 4-vinylpyridine, vinylbenzyltrimethylammoniumchloride as the image-receiving layer.

The following table presents a comparison of the $D_{max.}$ data for the element having the layer containing the graft copolymer and the element having the layer containing a mixture of the ingredients of the graft copolymer composition.

TABLE 8

Receiving layer	$D_{max.}$ after two minutes		
	Red	Green	Blue
Graft copolymer	2.20	2.11	2.11
Mixture	1.7	1.62	1.88

Example XXVI

The procedure of Example XXIV was repeated but 1.2 g. of $Ce(NH_4)_2(NO_3)_6$ were employed as catalyst rather than the 0.55 g. of Example XXIV.

Example XXVII

The procedure of Example XXIV was repeated but 2.2 g. of $Ce(NH_4)_2(NO_3)_6$ were employed as catalyst rather than the 0.55 g. of Example XXIV.

Example XXVIII

A series of two photosensitive elements were prepared, exposed and processed in the manner described in Example XXIII. One element had as the receiving layer a coating of the graft copolymer of Example XXVI while the other had a coating of the graft copolymer of Example XXVII.

The following table presents a comparison of the $D_{max.}$ data for the elements and shows that significant improvements in $D_{max.}$ can be obtained by increasing the catalyst concentration.

TABLE 9

Receiving layer	$D_{max.}$ after two minutes		
	Red	Green	Blue
Graft copolymer of Example XXVI	1.96	1.74	1.61
Graft copolymer of Example XXVII	2.49	2.13	2.06

In preferred embodiments of this invention wherein a polymeric acid layer is included as a component of the novel image-receiving element, the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg./ft.^{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 ml. thick, and the image-receiving element spacer layer is preferably about 0.05 to 0.5 mils thick.

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 imbibition to be completed outside of a camera, i.e., in an area exposed to light actinic to the silver halide emulsions.

Use of the novel image-receiving elements of this invention makes feasible the use, over an extended range of ambient 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.

In diffusion transfer color processes employing dye developers, 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, certain embodiments of this invention contemplate 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.

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.

The graft copolymers of the present invention provide stable aqueous emulsions having low viscosity and high solids content. The preferred range is 18–25% solid, with the resulting emulsion having a viscosity of 200–400 centipoises. Depending upon the use, the solids content can vary ± 10%. They may be coated at fast coating machine speeds, and result in clear films.

The method of preparation of the graft polymers is generally the same as that outlined in the hereinbefore stated examples; the pH, however, may vary from 1.5 to about 7 depending upon the catalyst/backbone polymer ratio. Although the transition metal ion catalysts hereinbefore described will initiate homopolymerization of vinylpyridine monomers, for example, the induction periods are so long and the rates so slow that under grafting conditions, little or no such polymerization can occur. As a rule, however the vinyl-pyridine graft polymers of the present invention are usually obtained in greater than 99% conversion, and most often in the order of 99.9% conversion, with essentially no residual vinylpyridine homopolymer.

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.

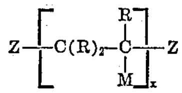
Although the invention has been illustrated in connection with dye developers, and the invention is particularly applicable to dye developers because of their susceptibility to aerial oxidation at high pH, the novel image-receiving elements of this invention may be used in other diffusion transfer processes such as those previously decribed to obtain tranfer 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.

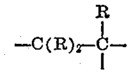
What is claimed is:

1. An image-receiving element for use in a photographic diffusion transfer color process including an alkaline solution permeable and dyeable layer within which a dye image is adapted to be formed and said layer comprises a graft copolymer represented by the formula:



$$Z-\left[C(R)_2-\overset{R}{\underset{M}{C}}\right]_x-Z$$

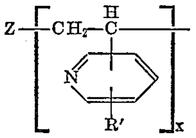
wherein Z is an organic polymeric backbone comprising repeating units which comprise structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state, said catalyst having an oxidation potential, in acidic solution, of at least about one volt when the transition metal is reduced to the next lowest acidic solution stable oxidation state;



$$-C(R)_2-\overset{R}{\underset{|}{C}}-$$

represents the residue of a graftable vinyl group wherein each R is the same or different substituent which will not hinder grafting of the residue to the backbone; M is a moiety that can provide a mordant capability; and *x* is a positive integer.

2. An element of claim **1** wherein said graft copolymer is a graft copolymer represented by the formula:



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; R′ is selected from the group consisting of hydrogen and lower alkyl; and *x* is a positive integer.

3. An element of claim **1** wherein said organic polymeric backbone is selected from the group consisting of cellulosic polymers, vinyl polymers and gelatin.

4. An element of claim **1** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl, and aryl.

5. An element of claim **1** wherein said organic polymeric backbone comprises polyvinyl alcohol.

6. An element of claim **1** wherein said organic polymeric backbone comprises hydroxyethyl cellulose.

7. An element of claim **1** wherein said organic polymeric backbone comprises methyl cellulose.

8. An element of claim **1** wherein said organic polymeric backbone comprises poly-N-vinylpyrrolidone.

9. An element of claim **1** wherein said organic polymeric backbone comprises starch.

10. An element of claim **1** wherein said organic polymeric backbone comprises polyacrylamide.

11. An element of claim **1** wherein said grafted moiety comprises 4-vinylpyridine.

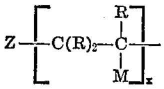
12. An element of claim **1** wherein said grafted moiety comprises 5-vinyl-2-methylpyridine.

13. An element of claim **1** wherein said grafted moiety comprises a vinylbenzyltrimethylammoniumchloride.

14. An element of claim **1** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4} and Cr^{+6}.

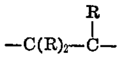
15. An element as defined in claim **1** comprising a plurality of substantially discret layers including, in sequence, a support layer, a permeable polymeric acid layer adapted to neutralize alkali contacted therewith, an alkaline solution permeable polymeric spacer layer, and an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed comprising a graft copolymer wherein the grafted moiety provides a mordant capability.

16. A process for forming photographic diffusion transfer images in color which comprises the step of developing an exposed photosensitive element comprising at least one silver halide emulsion layer having associated therewith a dye image-providing material by contacting said element with an aqueous alkaline solution, 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 of a superposed image-receiving element comprising a solution dyeable and permeable image-receiving layer which comprises a graft copolymer represented by the formula:



$$Z-\left[C(R)_2-\overset{R}{\underset{M}{C}}\right]_x-$$

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,

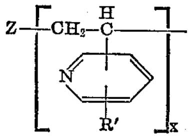


$$-C(R)_2-\overset{R}{C}-$$

represents the residue of a graftable vinyl group wherein each R isthe same or different substituent which will not hinder grafting of the residue to the backbone; M is a moiety that can provide a mordant capability and *x* is a positive integer.

17. A process of claim **1** wherein said image-receiving element includes a polymeric acid layer adapted to neutralize alkali contacted therewith, and wherein, subsequent to substantial dye image formation in said image-receiving layer, at least a portion of the ions of said alkaline solution are transferred by imbibition to said polymeric acid layer to thereby reduce the alkalinity of said image-receiving element.

18. A process of claim **16** wherein said graft copolymer is a vinylpyridine graft copolymer represented by the formula:



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; R′ is selected from the group consisting of hydrogen and lower alkyl; and *x* is a positive integer.

19. A process of claim **16** wherein said organic polymeric backbone is selected from the group consisting of cellulosic polymers, vinyl polymers, and gelatin.

20. A process of claim **16** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl, aryl and amido.

21. A process of claim **16** wherein said organic polymeric backbone is polyvinyl alcohol.

22. A process of claim **16** wherein said organic polymeric backbone is hydroxyethyl cellulose.

23. A process of claim **16** wherein said organic polymeric backbone is methyl cellulose.

24. A process of claim **16** wherein said organic polymeric backbone is poly-N-vinylpyrrolidone.

25. A process of claim **16** wherein said organic polymeric backbone is starch.

26. A process of claim **16** wherein said organic polymeric backbone comprises polyacrylamide.

27. A process of claim **16** wherein said grafted moiety comprises 4-vinylpyridine.

28. A process of claim **16** wherein said grafted moiety comprises 5-vinyl-2-methylpyridine.

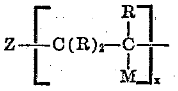
29. A process of claim **16** wherein said grafted moiety comprises vinylbenzyltrimethylammoniumchloride.

30. A process of claim **16** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4}, and Cr^{+6}.

31. A process for forming diffusion transfer images in color as defined in claim **16**, 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, an alkaline solution permeable polymeric spacer layer, and an alkaline solution permeable and dyeable polymeric layer comprising a graft copolymer wherein the grafted moiety provides a mordant capability to receive 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.

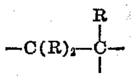
32. A process for forming diffusion transfer images in color as defined in claim **16**, which comprises, in combination, the steps of exposing a photosensitive element including blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers mounted on a common support, said blue-sensitive, 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; 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 comprising a graft copolymer within which a dye image is adapted to be formed, an alkaline solution permeable spacer layer, and an alkaline solution permeable polymeric acid layer adapted to neutralize alkali contacted therewith, mounted on a common support, to provide to said alkaline solution permeable and dyeable polymeric layer a multicolor dye image; and transferring, by diffusion, subsequent to substantial transfer image formation, a sufficient portion of the ions of said aqueous alkaline composition to said alkaline solution permeable polymeric acid layer to thereby reduce the alkalinity of said image-receiving element.

33. A photographic film unit for diffusion transfer color processes which comprises, in combination, a photosensitive element having an image receiving element affixed in a superposed position thereto, said photosensitive element comprising at least one silver halide emulsion layer having associated therewith a dye image providing material, and said image-receiving element comprising an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed and said layer comprises a graft copolymer represented by the formula:



$$Z-\left[C(R)_2-\overset{R}{\underset{M}{C}}-\right]_x$$

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

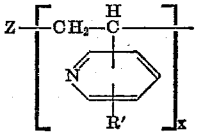


$$-C(R)_2-\overset{R}{\underset{|}{C}}-$$

represents the residue of a graftable vinyl group wherein each R is the same or different substituent which will not hinder grafting of the residue to the backbone; M is a moiety that can provide a mordant capability and *x* is a positive integer.

34. A film unit as defined in claim **33** wherein said image-receiving element includes a permeable polymeric acid layer adapted to neutralize alkali contacted therewith.

35. A film unit of claim **33** wherein said graft copolymer is a graft copolymer represented by the formula:



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; R′ is selected from the group consisting of hydrogen and lower alkyl; and *x* is a positive integer.

36. A film unit of claim **33** wherein said organic polymeric backbone is selected from the group consisting of cellulosic polymers, vinyl polymers and gelatin.

37. A film unit of claim **33** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl, aryl and amido.

38. A film unit of claim **33** wherein said organic polymeric backbone comprises polyvinyl alcohol.

39. A film unit of claim **33** wherein said organic polymeric backbone comprises hydroxyethyl cellulose.

40. A film unit of claim **33** wherein said organic polymeric backbone comprises methyl cellulose.

41. A film unit of claim **33** wherein said organic polymeric backbone comprises starch.

42. A film unit of claim **33** wherein said organic polymeric backbone comprises starch.

43. A film unit of claim **33** wherein said organic polymeric backbone comprises polyacrylamide.

44. A film unit of claim **33** wherein said grafted moiety comprises 4-vinylpyridine.

45. A film unit of claim **33** wherein said grafted moiety comprises 5-vinyl-2-methyl-pyridine.

46. A film unit of claim **33** wherein said grafted moiety comprises vinylbenzyltrimethylammoniumchloride.

47. A film unit of claim **33** wherein said transition metal ion catalyst is comprised of a member selected from the group consisting of V^{+5}, Ce^{+4}, and Cr^{+6}.

48. A film unit of claim **33** wherein said photosensitive element comprises 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.

49. A film unit of claim **48** wherein said photosensitive element comprises a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and red-sensitive silver halide emulsion layer 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.

50. A film unit of claim **33** wherein said image-receiving element comprises a plurality of substantially discrete layers including, in sequence, an alkaline solution permeable and dyeable polymeric layer within which a dye is adapted to be formed and said layer comprises a graft copolymer wherein the grafted moiety can provide a mordant capability, an alkaline solution permeable polymeric acid layer adapted to neutralize alkali contacted therewith, mounted on a common support.

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U.S. Cl. X.R.

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