April 20, 1971 L. D. TAYLOR **3,575,700**

POLYVINYLAMIDE GRAFTS IN SPACER LAYERS FOR COLOR DIFFUSION TRANSFER LIGHT SENSITIVE UNITS

Filed Jan. 13, 1969 2 Sheets-Sheet 1

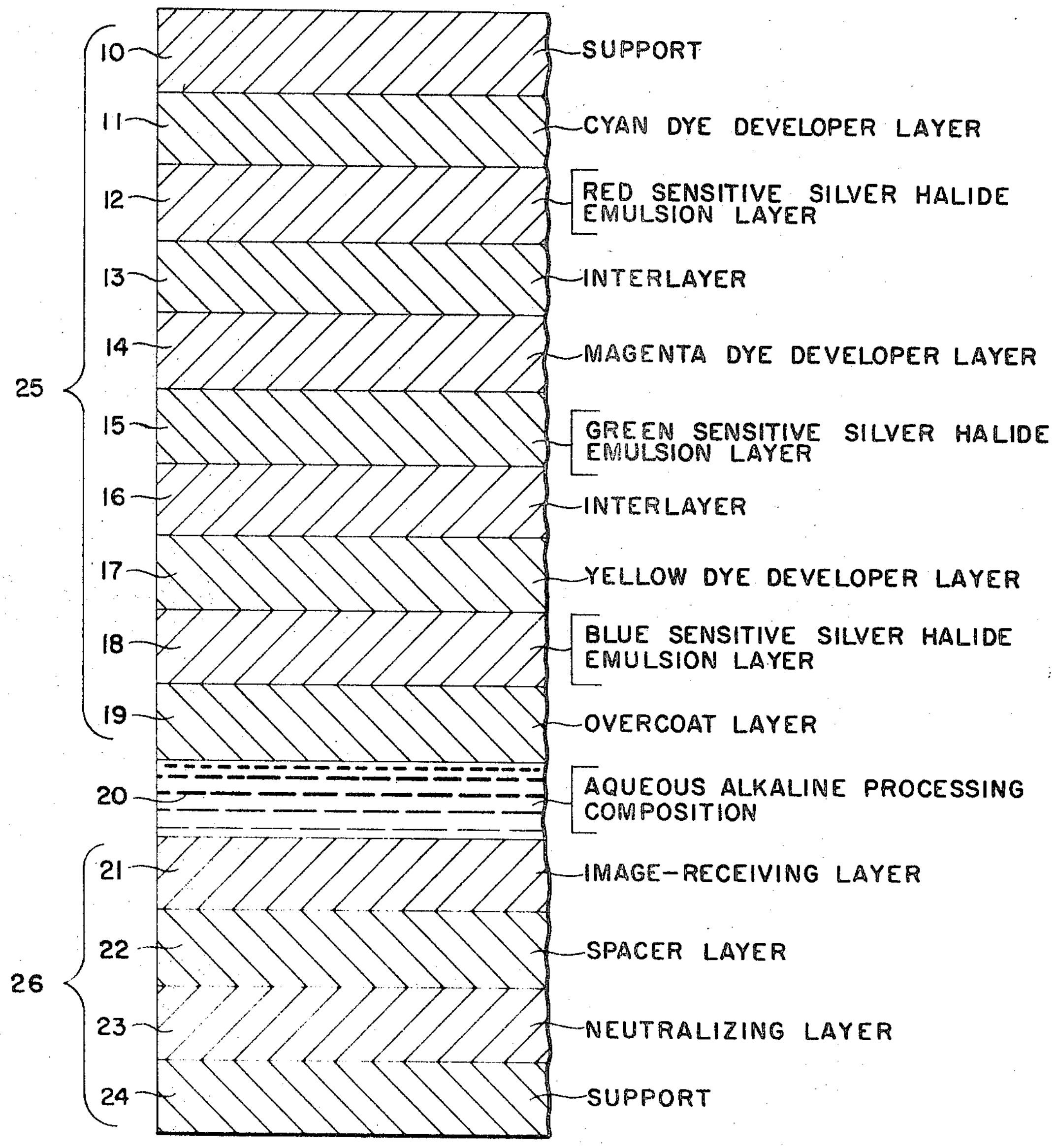

FIG. 1

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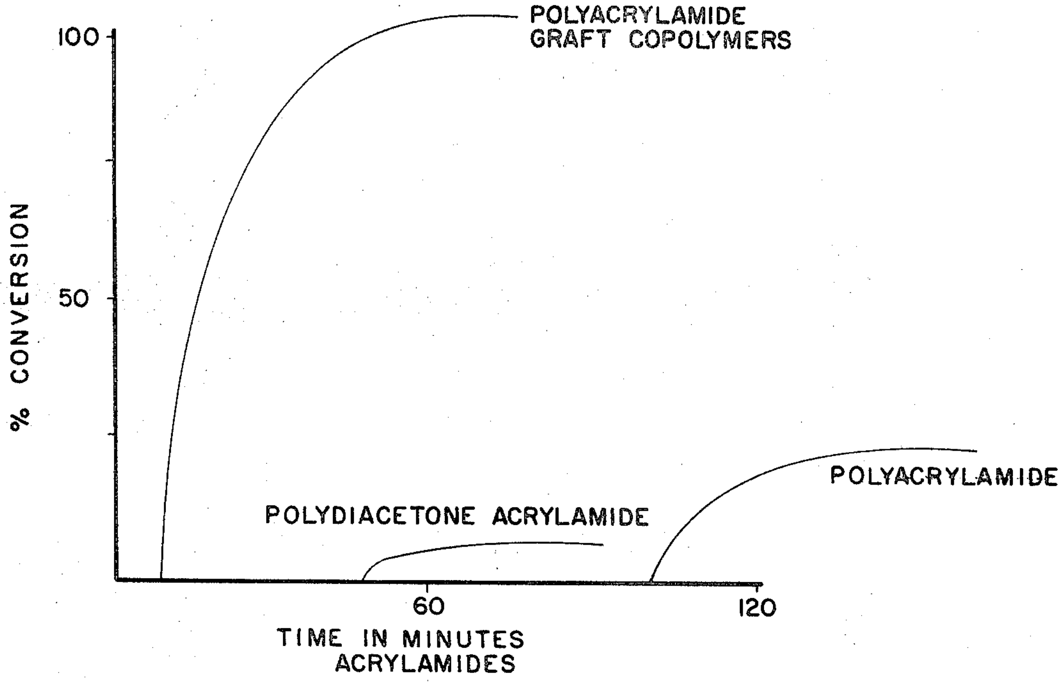

FIG. 2

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3,575,700
POLYVINYLAMIDE GRAFTS IN SPACER LAYERS FOR COLOR DIFFUSION TRANSFER LIGHT SENSITIVE UNITS

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

Continuation-in-part of application Ser. No. 641,669, May 26, 1967. This application Jan. 13, 1969, Ser. No. 790,648
Int. Cl. G03c *5/54, 7/00*
U.S. Cl. 96—3 **63 Claims**

ABSTRACT OF THE DISCLOSURE

A sensitive photographic element for diffusion transfer color systems wherein two of its sensitized layers containing dye image-forming material soluble and diffusible in alkali are separated from each other by a layer comprising polyvinyl amide graft copolymers.

This application is a continuation in part of U.S. application Ser. No. 641,669, filed May 26, 1967, now Pat. No. 3,421,892.

The present invention is concerned with polyvinyl amide graft copolymers, and, more particularly, with polyvinyl amide graft copolymers adapted for employment in photographic diffusion transfer processes.

As disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961, a photosensitive element with diffusion transfer utility, containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion, may be exposed to actinic radiation and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element may be 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, positioned intermediate the photosensitive element and the image-receiving element, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

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

Multicolor images may be obtained by diffusion transfer processes using color image-forming components such as, for example, the previously mentioned dye developers, by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, wherein at least two selectively sensitized photosensitive strata, superposed on a single, dimensionally stable support, 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 are disclosed to be optionally 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 or in the yellow dye layer. 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.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S.

applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Pats. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,136,606; 3,135,734; 3,141772; 3,142,565; and the like.

As additional examples of synthetic film-forming permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl-α,β-unsaturated carboxamides and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Patent No. 3,069,263; copolymers of vinyl-phthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Patent No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxlic acids and terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-as disclosed in U.S. Patent No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, as disclosed in U.S. Patent No. 3,069,264; and the like.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric, or colloidal, matrix such as ball-milling and the like techniques, the preparation of the dye developer dispersion may also be obtained by dissolving the dye in an appropriate solvent, or mixture of solvents, and the resultant solution distributed in the polymeric binder, with optional subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic film units, reference may be made to U.S. Pat. Nos. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171; and the like.

U.S. application Ser. No. 234,864, filed Nov. 1, 1962, now U.S. Pat. 3,362,819, issued Jan. 1, 1968, in the name of Edwin H. Land, discloses image-receiving elements particularly adapted for employement in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, preferably an inert timing or spacer layer, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned application, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, nondiffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy substituted aldehydes, e.g., o-, m-, or p-benzaldehyde carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleic anhydride copolymers; etc.

The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the acid polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the polymeric acid may contain a water insoluble polymer, such as, for example, a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

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

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

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. Where this liquid processing composition is to be applied to the photosensitive emulsion stratum by being spread thereon, preferably in a relatively thin and uniform layer intermediate that stratum and a superposed image-receiving layer, it is disclosed to include 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.

For the production of the photoresponsive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or alternatively employing any of the various flocculation systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B. Photography, Its Materials and Processes, 6th ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., Photography, Its and Related Compounds.

Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of silver, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide or silver iodobromide, of varying halide ratios and varying silver concentrations.

The emulsions may include the various adjuncts, or addenda, according to the techniques disclosed in the art, such as speed-increasing compounds of the quaternary ammonium type, as described in U.S. Pats. Nos. 2,271,623; 2,288,226; and 2,334,864; or of the polyethyleneglycol type, as described in U.S. Pat. No. 2,708,162; or of the preceding combination, as described in U.S. Pat. No. 2,886,437; or the thiopolymers, as described in U.S. Pats. Nos. 3,046,129 and 3,046,134.

The emulsions may also be stabilized with the salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, as described in U.S. Pats. Nos. 2,566,245 and 2,566,263; the mercury compounds of U.S. Pats. Nos. 2,728,663; 2,728,664 and 2,728,665; the triazoles of U.S. Pat. No. 2,444,608; the azaindines of U.S. Pats. Nos. 2,444,605; 2,444,606; 2,444,607; 2,450,397; 2,444,609; 2,713,541; 2,743,181; 2,716,062; 2,735,769; 2,756,147; 2,772,164; and those disclosed by Burr in "Zwiss. Pot.," volume 47, 1952, pp. 2–28; the disulfides of Belgian Pat. No. 569,317; the benzothiozolium compounds of U.S. Pats. Nos. 2,131,038 and 2,694,716; the zinc and cadmium salts of U.S. Pat. No. 2,839,405; and the mercapto compounds of U.S. Pat. No. 2,819,965.

Hardening agents such as inorganic agents providing polyvalent metallic atoms, specifically polyvalent aluminum or chromium ions, for example, potash alum

$$[K_2Al_2(SO_4)_4 \cdot 24H_2O]$$

and chrome alum

$$[K_2Cr_2(SO_4)_4 \cdot 24H_2O]$$

and inorganic agents of the aldehyde type, such as formaldehyde, glyoxal, mucochloric, etc.; the ketone type such as diacetyl, the quinone type; and the specific agents described in U.S. Pats. Nos. 2,080,019; 2,725,294; 2,725,-295; 2,725,305; 2,726,162; 2,732,316; 2,950,197; and

2,870,013, may be incorporated, where desired and compatible, in the selected coating solution compositions.

Coating solution compositions employed to fabricate the respective strata of the film unit may contain one or more coating aids such as saponin; a polyethyleneglycol of U.S. Pat. No. 2,831,766; a polyethyleneglycol ether of U.S. Pat. No. 2,719,087; a taurine of U.S. Pat. No. 2,739,891; a maleopimarate of U.S. Pat. No. 2,823,123; an amino acid of U.S. Pat. No. 3,038,804; a sulfosuccinamate of U.S. Pat. No. 2,992,108; or a polyether of U.S. Pat. No. 2,600,831; or a gelatin plasticizer such as glycerin; a dihydroxyalkane of U.S. Pat. No. 2,960,404; a bis-glycolic acid ester of U.S. Pat. No. 2,904,434; a succinate of U.S. Pat. No. 2,940,854; or a polymeric hydrosol of U.S. Pat. No. 2,852,386.

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin, casein; or zein; or resins such as a cellulose derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in U.S. Pats. Nos. 2,253,078; 2,276,322; 2,276,323; 2,281,703; 2,310,223; 2,311,058 2,311,059; 2,414,208; 2,461,023; 2,484,456; 2,538,257; 2,579,016; 2,614,931; 2,624,674; 2,632,704; 2,642,420; 2,678,884; 2,691;582; 2,725,296; 2,753,264; and the like.

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

Another object is to provide polyvinyl amide graft copolymers having a predetermined balance of hydrophobic and hydrophilic groups in the polymer molecule, so that a proper balance is achieved, and said graft copolymer thereby imparts a built-in mechanism for achieving some degree of temperature independence in the development function of a diffusion transfer photographic process.

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

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

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

The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a diagrammatic enlarged cross sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process for the production of a multicolor positive transfer print, the thickness of the various materials being exaggerated;

FIG. 2 is a graphical representation of the relationship of the percent conversion-time characteristics of polyvinyl alcohol grafts and homopolymers of diacetone acrylamide and acrylamide.

As disclosed in copending U.S. application Ser. No. 486,862, filed Sept. 13, 1965, and now abandoned in the name of Richard J. Haberlin, it has been discovered that if one or more of the interlayers of the integral multilayer photosensitive element, described above, is specifically selected to comprise a processing composition-permeable and hydratable polymer having a dye-permeable lattice substantially only in the hydrated state and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate, significant improvement may be achieved with respect to the element's color isolation and potential photographic process speed, and with respect to the brilliance, density and hue of the transfer image color characteristics.

Specifically, employment of the detailed polymeric interlayer, during the hereinbefore described diffusion transfer process, acts to provide a barrier with respect to retardation of the positional displacement of the dye prior to establishment of substantial imagewise emulsion control of the associated dye's diffusion, with the concomitant results of providing significantly higher process speed, higher transfer image maximum densities, greater cyan and magenta dye saturation, and improved red and blue hues, in addition to, and by reason of, improved photosensitive element interimage effects. These effects result, at least in part, from prevention of the respective dye development of silver halide emulsion strata, other than the specific strata with which the individual dye is directly associated; generally characterized, respectively, as yellow, magenta, and cyan "drop-off."

The hydration with which the last-identified application is directly concerned comprises, in general, the polymer's assimilation of water molecules by hydrogen bonding. Concurrently with said hydration, the system swells and its capability regarding permeation by dye materials increases. It will also be recognized that in a given instance, the hydration and permeation of a selected specific polymer, within the photographic system context detailed, will be influenced and modulated by the polymer's relative hydrolysis, salt formation, solubility, and the like, properties.

With specific regard to selection of polymers particularly adapted for employment in accordance with the last-identified application, the respective rates of silver halide emulsion development, polymer hydration, and/or silver halide emulsion fogging may be directly measured, in accordance with any of the conventional techniques known in the art. Included among such techniques are procedures well known for the simultaneous derivation of both the development and fogging rate of a silver halide emulsion, by contemporaneous measurement of silver developed, per unit time; in exposed and unexposed portions of an emulsion stratum.

The fogging rate of the silver halide emulsions employed may be suitably modulated by incorporation of a conventional antifoggant, such as those hereinbefore detailed, in the emulsion layer itself and/or associated layers and/or processing composition, and permeation of such agent, or agents, into the respective emulsion layer to be controlled.

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

The instant invention is directly concerned with a photosensitive element which comprises a common support having, positioned on one surface, at least two selectively sensitized photosensitive silver halide emulsion strata, for example, having predominant spectral sensitivity to separate regions of the spectrum, each having a dye image-forming material which is soluble and diffusible in alkali, associated therewith, preferably a dye of predetermined color, for example, a dye which is a silver halide developing agent and which most preferably possesses a spectral absorption range substantially complimentary to the predominant sensitivity range of the associated emulsion, separated by a spacer or interlayer comprising the aforementioned polyvinyl amide graft copolymer alone or in combination with one or more additional polymers, such as gelatin, polyvinyl alcohol, and the like, and retaining photographic processing adjuncts where desired.

Preferably, the selected graft copolymer is aqueous alkaline solution permeable and hydratable, and, most preferably, substantially instantaneously permeable by molecules having a geometric size less than the geometric size of the transfer image forming dye, such as, for example, auxiliary silver halide developing agents, antifoggants, accelerators, arrestors, and the like, in order that photographic development, and the like, may proceed, with respect to the emulsion next adjacent the film base, within the earliest time sequence possible. It is important to note that interlayers prepared from the selected polymers actually act as molecular sieves, since, after a finite time, depending upon the needs of the system, in order to achieve maximum dye transfer, the interlayer should offer no resistance to the transfer of dye materials.

Specifically, as a preferred embodiment, employment of polyvinyl amide graft copolymers which are processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate, in the manner detailed above and below, produced increased photographic speed and far better color isolation and temperature independence when employed as multilayer photosensitive element interlayers. After satisfying the dye diffusion control requirements of the system, the interlayer becomes dye permeable to allow unrestricted diffusion of the dye that is positioned next adjacent the film base. There is thus provided an effective restriction of each dye's developing function to the specific silver halide emulsion with which it is associated, and thereby color isolation selectively determined by the incident spectral energy distribution per unit area of the respective photoresponsive silver halide emulsion's exposure.

As has been disclosed in my copending application Ser. No. 641,670, filed May 26, 1967, now U.S. Pat. No. 3,421,893 compounds have been found to possess temperature inverting properties; that is, their swellability, and utility as barriers, are inversely proportional to the temperature at which the development process is carried out when the hydrophiles and hydrophobes thereof are appropriately balanced and the thicknesses utilized fall within a rather broad range. The use of temperature inverting materials provides the system with a built-in mechanism for achieving some degree of temperature independence of the processing function. Specifically, utilization of instant temperature-inverting compounds in the environment of the present invention in the manner described gives particularly good cold and hot temperature processing characteristics, somewhat increased photographic speed, and improved color isolation. It should be emphasized that the precise temperature-swell characteristics of such temperature-inverting compounds must be tailored to the photographic system selected as a whole and is dependent upon the relative dye diffusion constants and development times of the various constituents of the system throughout a wide temperature range. In this respect the determination of particularly suitable materials for use as interlayers, as hereinbefore described, is substantially empirical.

Temperature-inverting polymers useful in the practice of the instant invention are prepared by incorporating into each polymer molecule a predetermined amount of hydrophilic and hydrophobic groups so that a proper balance is achieved which results in the desired barrier-permeation characteristics throughout a desired temperature range.

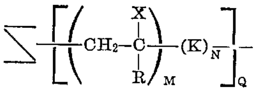
As indicated in copending U.S. application Ser. No. 664,503, filed Aug. 30, 1967, now U.S. Pat. No. 3,455,686 inverse temperature dependence of a polymeric film with regard to alkali permeability is not unknown phenomenon, the use of this property having been disclosed for utilization in diffusion transfer photographic receiving sheets. Benefits are derived from using a temperature-inverting material in a process which depends upon permeation of liquids, at a variety of temperatures, since, as the ambient temperature decreases, the polymer tends to form hydrates and swells, thus facilitating permeation as a function of the degree of swell of the polymer—dehydration being inherent with an increase in temperature. It is well known that the diffusion rate of a liquid, for example, a solution containing a dye, 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 apparent. The desired result is to have the temperature inverting material approximately counteract changes in diffusion rate of the permeating material with 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 photosensitive element interlayer, therefore, should provide the system which it comprises with the proper dye permeation-temperature properties so that dye may diffuse from the photosensitive part of the system to the receiving sheet, as a function of development, in order to form a positive image in the receiving sheet within a predetermined time, irrespective of the processing temperature employed.

The temperature-inverting characteristic of members of the class of polyvinylamide graft copolymers useful in the instant invention is probably attributable to the presence of a predetermined balance of hydrophobic groups to hydrophilic groups in the polymer molecule. The probable mechanism through which temperature inversion occurs is by the formation of hydrogen bonds between the hydrophilic portion of the polymer and the hydrogen of the solvent at low temperatures; the hydrogen bonding being discouraged as the temperature of the material is raised due to thermal destruction. The system thereupon takes the form of a less-hydrated, less-swollen, therefore, less-permeable polymer as a function of the increase in temperature. It may then be said that the preferred graft copolymers 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 defininte ratio of hydrophilic to hydrophobic groups, the resultant compound will have temperature-inverting properties. It may further be concluded, that the interactions responsible for temperature inversion are forces such as hydrogen-bonding and hydrophobic-hydrophobic bonding forces.

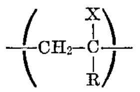
It has unexpectedly been found that a class of polyvinyl amide graft copolymers represented by the formula:

I



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

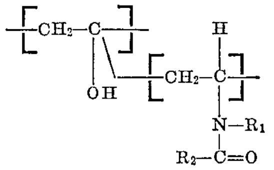
wherein Z is an organic polymeric backbone comprising repeating units comprising structural units capable of being oxidized by a transition metal ion catalyst of a first oxidation state; said catalyst having an oxidation potential, in acidic solution, of at least about 1 volt when the transition metal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

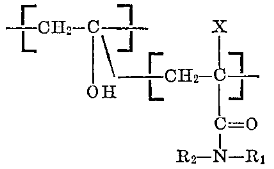


$$\left(-CH_2-\overset{X}{\underset{R}{C}}-\right)$$

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

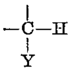
Preferred graft polymers within the scope of the present invention comprise polyvinyl amides grafted onto polyvinyl alcohol backbones, said preferred graft polymers being represented by the formulae:





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

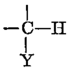
With regards to the backbone polymer of the graft copolymer, in general, any organic polymer comprising repeating units comprising structural units containing the



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

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

It is believed that upon oxidation of the



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

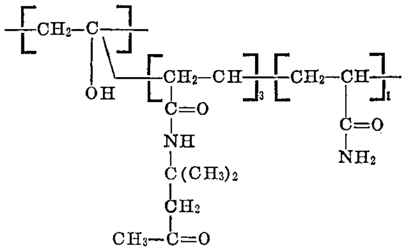
grouping, the free radical is formed, which attacks the double bond of the vinyl amide monomer, thus initiating polymerization.

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

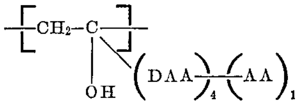
Monomers of interest which are useful in making graft copolymers with the necessary hydrophilic-hydrophobic balance include: acrylamide; N-methyl acrylamide, methacrylamide; N-methyl methacrylamide; ethyl acrylate; N-ethyl acrylamide; N - methylolacrylamide; N,N-dimethyl acrylamide; N,N - dimethyl methacrylamide; N-(n-propyl)acrylamide; N - isopropyl acrylamide; N - (β-hydroxyl ethyl)acrylamide; N - [β - (dimethylamino)ethyl] acrylamide; N - t - butyl acrylamide; β-(acrylamido)ethyl trimethyl ammonium p-toluene sulfonate; N-[β-(dimethylamino)ethyl]methacrylamide; 2 - [2′-(acrylamido)ethoxy]ethanol; N - [3′ - methoxy propyl]acrylamide; 2-hydroxy - 3 - methacryloxy propyl trimethyl ammonium chloride; 2 - acrylamido - 3 - methyl butyramide; acrylamido acetamide; methacrylamido acetamide; 2-[2′-methacrylamido - 3′ - methyl butyramido]acetamide; N-vinyl pyrrolidone; diacetone acrylamide; dimethylamino ethyl methacrylate; dimethylamino ethyl acrylate; vinyl acetate, p-styrene sulfonamide; N-isopropyl ethylene sulfonamide, etc.

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

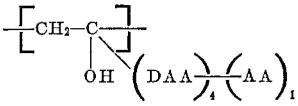
(1) Acrylamide-diacetone acrylamide graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.67/1.



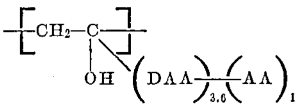
(2) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol. DAA/AA=4/1; monomer/PVA=2.67/1.



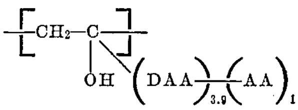
(3) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=4/1; monomer/PVA=3.33/1.



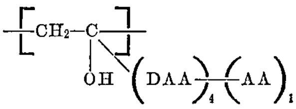
(4) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.9/1; monomer/PVA=3.30/1.



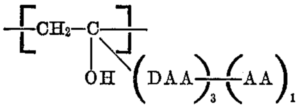
(5) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.9/1; monomer/PVA=3.30/1.



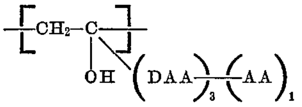
(6) Acylamide (AA)-diacetone acylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=4/1; monomer/PVA=3.56/1.



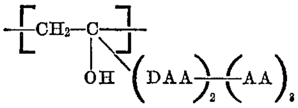
(7) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.0/1.



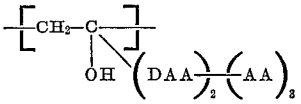
(8) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.2/1.



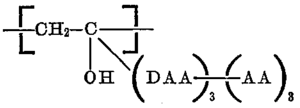
(9) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/3; monomer/PVA=5.3/1.



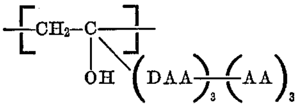
(10) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/3; monomer/PVA=2.67/1.



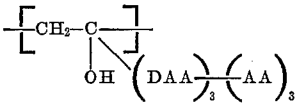
(11) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3; monomer/PVA=1.75/1.



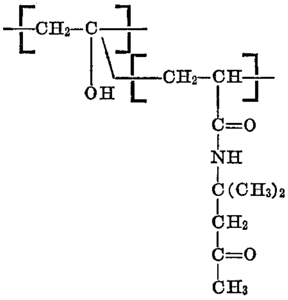
(12) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3; monomer/PVA=5.3/1.



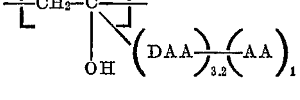
(13) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/3 monomer/PVA=3.33/1.



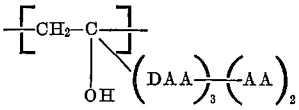
(14) Diacetone acrylamide (DAA) graft or polyvinyl alcohol (PVA). Monomer/PVA=2.0/1.



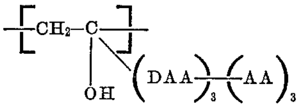
(15) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.2/1; monomer/PVA=2.8/1.



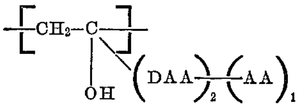
(16) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/2; monomer/PVA=3.3/1.



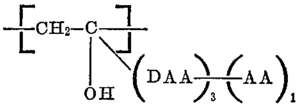
(17) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3.3; monomer/PVA=0.4/1.



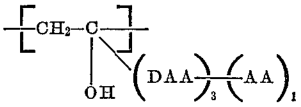
(18) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/1; monomer/PVA=3.0/1.



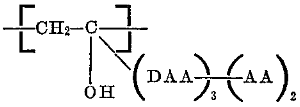
(19) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=1.4/1.



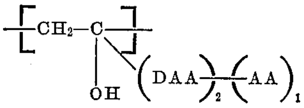
(20) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=4.0/1.



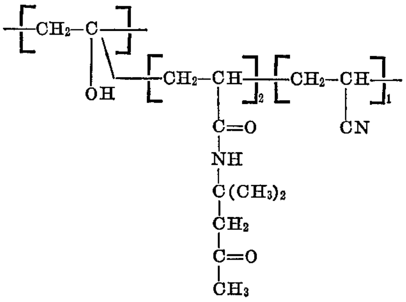
(21) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=3/2; monomer/PVA=2.67/1.



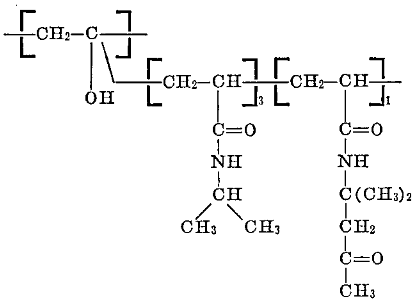
(22) Acrylamide (AA)-diacetone acrylamide (DAA) graft on polyvinyl alcohol (PVA). DAA/AA=2/1; monomer/PVA=4.1/1.



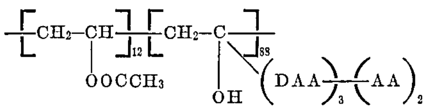
(23) Diacetone acrylamide (DAA) acrylonitrile graft on polyvinyl alcohol (PVA). DAA/acrylonitrile=2/1; monomer/PVA=3.5/1.



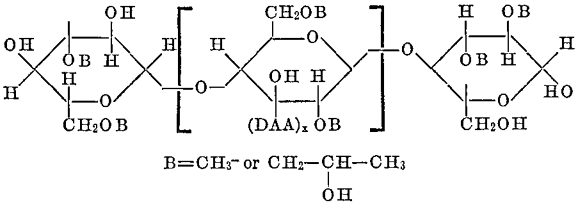
(24) Acrylamide (AA)-Isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA). IspAA/AA=3/1; monomer/PVA=1/1.1.



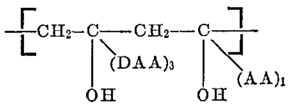
(25) Acrylamide (AA)-diacetone acrylamide (DAA) graft on partially hydrolyzed polyvinyl acetate. DAA/AA=3/2; monomer/partially hydrolyzed polyvinyl acetate=1/1.



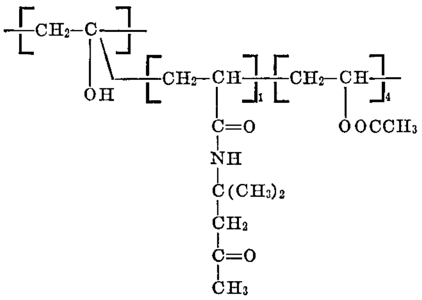
(26) Diacetone acrylamide (DAA) graft on methyl hydroxy propyl cellulose.



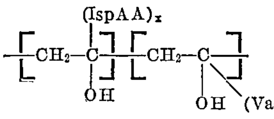
(27) Acrylamide (AA) and diacetone acrylamide (DAA) sequentially grafted on polyvinyl alcohol (PVA). DAA/AA=3/1; monomer/PVA=2.66/1.



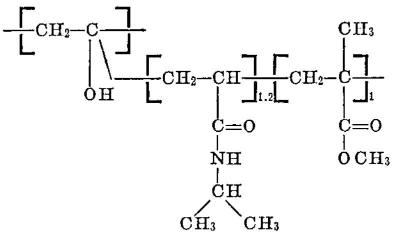
(28) Diacetone acrylamide (DAA)-vinyl acetate (Vac) graft on polyvinyl alcohol (PVA). DAA/Vac=1/4; monomer/PVA=5.1/1.



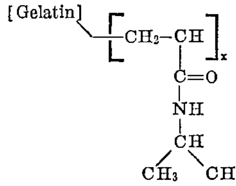
(29) Vinyl acetate graft (Vac) on isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA).



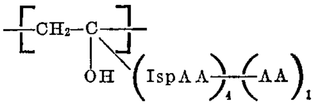
(30) Isopropyl acrylamide (IspAA)-methyl methacrylate (MM) graft on polyvinyl alcohol (PVA). IspAA/MM=1.2/1; monomer/PVA=1.3/1.



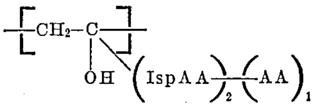
(31) Isopropyl acrylamide graft on gelatin.



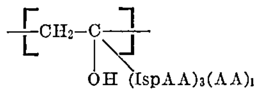
(32) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=4/1; monomer/PVA=3/1.



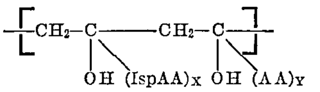
(33) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=2/1; monomer/PVA=3.5/1.



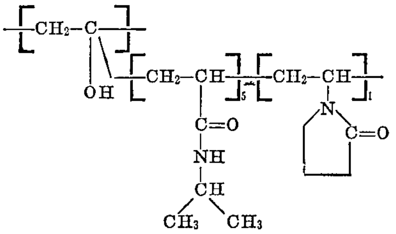
(34) Isopropyl acrylamide (IspAA)-acrylamide (AA) graft on polyvinyl alcohol (PVA). IspAA/AA=3/1; monomer/polymer=3/1.



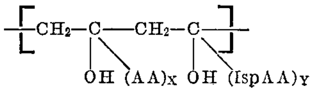
(35) Acrylamide (AA) graft on Isopropyl acrylamide (IspAA) graft on polyvinyl alcohol (PVA).



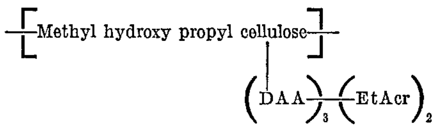
(36) Isopropyl acrylamide (IspAA)-N-Vinyl pyrrolidone on polyvinyl alcohol (PVA). IspAA/N-Vinyl pyrrolidone=5/1; monomer/PVA=2.6/1.



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



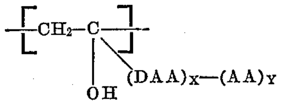
(38) Diacetone acrylamide (DAA)-ethyl acrylate (EtAcr) copolymer graft on methyl hydroxy propyl cellulose. DAA/EtAcr=3/2.

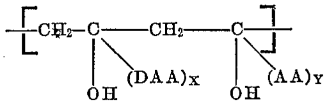


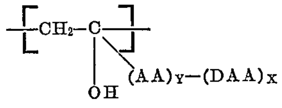
Throughout the above listing of graft polymers, certain ratios have been used. These are molar ratios, with 44 grams of polyvinyl alcohol being equal to one mole. In light of the numerous examples cited, it is apparent that the R groups on a backbone can be different or the same, the only requirement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

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

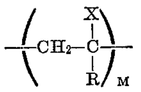
From the hereinbefore set out list of graft polymers, one sees that R can either change or be the same throughout the backbone. Also, any two or more monomers can be grafted onto a particular backbone in a number of ways. For example, an acrylamide-diacetone acrylamide graft on polyvinyl alcohol could,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





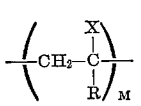


The same type of reasoning holds true when one has a K type of compound incorporated into the graft copolymer. This is borne out by reference to hereinbefore set out graft copolymers 28 and 29. In copolymer 28, vinyl acetate is directly attached to the



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

group, whereas in copolymer 29 the vinyl acetate is grafted directly onto the backbone. In this latter type of compound, (K) is directly attached to the backbone Z, and not to the

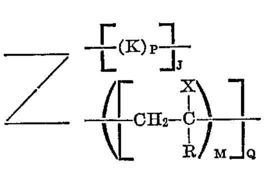


$$-\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M-$$

group as depicted in Formula I.

Graft copolymers of this class are represented by the formula:

(II)



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

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

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

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

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

The thickness of the temperature inverting layer will be somewhat critical since the hydration mechanism of the layer may form tunnels in the film through which processing composition may preferentially diffuse. In the case of graft copolymers, diffusion takes place not only through the film, but can also take place at the interface of the polymer balls, when the polymer is cast in film form of the selected thickness. In order to maintain uniformity in processing time, the thickness of the individual polymer layers utilized should be predetermined to achieve uniform permeation time throughout the operative temperature range. As a rule, coverages from 10–200 milligrams per square foot in the case of multilayer photosensitive element interlayers, is the range in which desired processing times for permeation of the processing solution found in, for example, Polaroid Type 108 film packs, is achieved.

The present invention has also been specifically found to possess certain distinct advantages, when compared with the multilayer photosensitive element interlayer systems of the prior art which employ so-called "barrier" system interlayers, in order to effect processing in a stepwise, or layerwise, manner. Specifically, the prior art teaches the employment of a barrier interlayer to separate an outer emulsion layer and associated dye from an inner emulsion layer and its associated dye, in order that processing may be effected in the stepwise manner. The barrier layer comprises, in general, a polymeric layer which is permeated, by the fluid processing composition, at a rate sufficienly slow so as to insure that permeation of the fluid composition, from an outer emulsion layer into the next inner emulsion layer, is deferred, until processing of the outer emulsion layer is substantially complete. In general, barrier interlayers of this type comprise two distinct types. The first type comprises impermeable polymeric interlayers which possess a solution rate, upon contact with the fluid processing composition, during photographic processing, such that the interlayer requires a longer time span to be rendered permeable than the time interval necessitated to effect development of the outer emulsion stratum. The second type comprises impermeable polymeric interlayers which possess a hydrolysis rate, upon contact with the fluid processing composition, such that the interlayer requires a time interval for the occurrence of hydrolysis, sufficient as to provide processing composition permeability, in excess of that required to effect devlopment of the outer emulsion.

As will be appreciated from the above description of the prior art barrier interlayers, the present invention possesses, when compared with such prior art systems, the specific advantage of providing the previously stated control of dye diffusion during substantially contemporaneous development of all the emulsion strata constituting the integral multilayer photosensitive element as well as providing, when desired, increased temperature latitude. It thus avoids the prior art's necessity of conducting development in relatively insulated steps, with such processes' concomitant increase in the necessary processing time interval and the resultant propensity for image degradation, for example, from fog buildup and the like, in the outer emulsion strata remaining in processing composition contact for an overly extended period, or conducting substantially contemporaneous development of all the emulsion strata, with resultant loss of color isolation, due to undesirable migration of dye preceding effective control, or an empirical system combining the above systems in such a manner as is designed to effect a balance between the undesirable effects of each and to thus minimize the effects to at least some effective extent.

In accordance with the teachings of the art, the positioning of the respective silver halide emulsion/dye developer units of the tripack configuration detailed above may be varied. However, it is generally preferred to constitute the tripack configuration in accordance with the general scheme set forth in the drawing, that is, the cyan dye developer/red-sensitive emulsion unit next contiguous the support surface and the yellow dye developer/blue-sensitive emulsion unit most distant from the support surface.

As detailed in the illustrative drawing, a selectively exposed photosensitive element **25** comprises: a support **10**; a layer **11** containing a cyan dye developer; a layer **12** comprising a red-sensitive silver halide emulsion; a photosensitive element interlayer **13** comprising the graft copolymer detailed above; a layer **14** containing a magenta dye developer; a layer **15** comprising a green-sensitive silver halide emulsion; an interlayer **16** comprising the graft copolymer detailed above; a layer **17** containing a yellow dye developer; a layer **18** comprising a blue-sensitive silver halide emulsion; and a protective overcoat layer **19**.

As shown in the drawing, the multilayer exposed photosensitive element **25** is shown in processing relationship with an image-receiving element **26** and a layer **20** of processing composition distributed intermediate elements **25** and **26**.

Image-receiving element **26** comprises: a support **24**; a neutralizing layer **23**; a spacer layer **22**; and an image-receiving layer **21**.

As previously discussed, liquid processing composition **20** is effective to initiate development of the latent images in the respective silver halide emulsion strata and hydration of the polymeric interlayers. After a suitable imbibition period, during which at least a portion of the dye developer associated with unexposed areas of each of the emulsions is transferred to superposed image-receiving element **26**, the latter element is separated to reveal the positive multicolor image.

The present invention will be illustrated in greater detail in conjunction with the following procedures which set out representative embodiments and photographic utilization of the novel photosensitive elements of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

A photosensitive element may be prepared by coating in succession on a gelatin subbed cellulose triacetate base the following layers:

(1) A layer of cyan dye developer 1,4-bis(β-[hydroquinonyl - α - methyl]-ethylamino)-5,8-dihydroxy-anthraquinone dissolved in diethyl lauramide dispersed in gelatin and coated at a coverage of about 125 mg. of dye per square foot.

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 200 mg. of silver per square foot.

(3) A layer of an isopropyl acrylamide-acrylamide graft on polyvinyl alcohol at a coverage of 50 mg. per square foot.

(4) A layer of magenta dye developer 2-(p-[α-hydroquinonyl ethyl]-phenylazo)-4-isopropoxy-1-naphthol dissolved in diethyl lauramide dispersed in gelatin and coated at a coverage of about 75 mg. of dye per square foot.

(5) A green-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 115 mg. of silver per square foot.

(6) A layer of gelatin coated at a coverage of about 140 mg. per square foot.

(7) A layer of yellow dye developer 4-(p-[β-hydroquinonylethyl] - phenylaxo) - 3 - (N-n-hexyl carboxamido)-1 phenyl-5-pyrazolone dissolved in diethyl lauramide dispersed in gelatin and coated at a coverage of about 50 mg. of dye per square foot.

(8) A blue-sensitive gelatino silver iodobromide emulsion coated at a coverage of about 61 mg. of silver per square foot.

(9) A layer containing 4'-methyl phenyl hydroquinone dissolved in diethyl lauramide dispersed in gelatin and coated at a coverage of about 30 mg. 4'-methyl phenyl hydroquinone per square foot.

The isopropyl acrylamide-acrylamide graft on polyvinyl alcohol, and the other polyvinyl amide graft copolymers, can be prepared by the method disclosed in copending application of Stanley F. Bedell, Ser. No. 790,714, filed concurrently herewith.

With regards to the isopropyl acrylamide-acrylamide graft on polyvinyl alcohol, the preparation is as follows:

To a solution of 11 g. (0.25 m) of polyvinyl alcohol in 500 cc. of H_2O under stirring and nitrogen, 63 g. (0.56 m) of isopropyl acrylamide and 10 g. (0.14 m) of acrylamide were added, and stirring continued under the nitrogen atmosphere for 1 hour. The temperature was raised to 50° C., the pH was adjusted to 1.5 with concentrated HNO_3, and 0.55 g. of $Ce(NH_4)_2(NO_3)_6$ in 10 cc. of water was added. Stirring was continued for 2 hours at 50° C., the heat was removed, and stirring continued overnight.

For purposes of comparison a photosensitive element substantially of the above-identified type may be fabricated employing, as layer 3, gelatin coated at a coverage of 240 gms. per square foot.

The required number of image-receiving elements may be prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 grams of high viscosity poly-(ethylene/maleic anhydride), 140 grams of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.75 mil thick. The external surface of the acid layer may be coated with a 4% solution of polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.3 mil thick. The external surface of the spacer layer may be then coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs. per square foot, to provide a polymeric image-receiving layer approximately 0.40 mil thick. The thus-prepared image-receiving element may be then baked at 180° F. for 30 minutes and then allowed to cool.

The photosensitive elements may then be exposed and processed at various temperatures by spreading an aqueous liquid processing composition comprising:

Water—100 cc.
Potassium hydroxide—11.2 gm.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250]—3.9 gm.
Potassium thiosulfate—0.5 gm.
Benzotriazole—3.5 gm.
N-benzyl-α-picolinium bromide—2.0 gm.
Lithium hydroxide—0.5 gm.

between an individual image-receiving element and each of the exposed multicolor elements, as they are brought into superposed relationship in a Polaroid Land camera. After an imbibition period of 60 seconds or 120 seconds, for tests conducted at 75° F. and 95° F. or 45° F. and 60° F., respectively, the image-receiving sheet may be separated from the photosensitive element.

Visual observation of the test and control materials will demonstrate that the negative prepared with an interlayer of the instant invention provides improved transfer image color balance, greatly improved magenta density and better saturation and color isolation characteristics. It will likewise be found that the film demonstrated improved stability to varying gaps which might occur between the photosensitive sheet and the image-receiving sheet.

The procedure outlined above may be repeated except that layer **3** of the above test negative may be replaced with isopropyl acrylamide-methyl methacrylate graft on polyvinyl alcohol coated at a coverage of 50 mg. per square foot and layer **3** of the control may contain a vinyl acetate-crotonic acid copolymer containing 2% by weight crotonic acid coated at a coverage of 187 gms. per square foot, and in each case the 4'-methyl phenyl hydroquinone may be coated in the sixth layer at a coverage of 14 gms. per square foot, instead of in the ninth layer.

The isopropyl acrylamide-methyl methacrylate graft on polyvinyl alcohol may be prepared as follows:

To a solution of 11 g. of polyvinyl alcohol in 500 cc. of H_2O, under stirring and nitrogen, 20 g. of isopropyl acrylamide and 15 g. of methacrylate were added. The pH was then adjusted to 1.5 with HNO_3, and 1.1 g. of $Ce(NH_4)_2(NO_3)_6$ in 10 cc. of H_2O was added. The stirring under nitrogen was continued for 2 more hours at 50° C. The isopropyl acrylamide-methyl methacrylate interlayer was observed to provide improved color balance, greatly improved magenta density and better saturation and color characteristics in a like manner as the graft copolymer outlined above.

Graft copolymers of isopropyl acrylamide-N-vinyl pyrrolidone on polyvinyl alcohol and isopropyl acrylamide on gelatin coated at various coverages in the range 50–100 mg./ft.^{2} have been found to give a like improvement when compared to gelatin and the vinyl acetate-crotonic acid copolymer mentioned hereinbefore.

In a preferred embodiment of the present invention, the gelatino silver halide emulsion layers are about 0.6 to 6 microns thick, the gelatino dye-retaining layers are about 1 to 7 microns thick, and the graft copolymer photosensitive element interlayers are cast at a coverage of 10–200 mg. per square foot. With respect to a preferred image-receiving element, the image-receiving layer is about 0.25 to 0.4 mil thick, and the polymeric acid layer is about 0.3 to 1.5 mils thick, and the spacer layer is about .05 to 0.5 mil thick. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

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

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

Although the transition metal ion catalysts hereinbefore described will initiate the homopolymerization of monomers such as diacetone acrylamide, acrylamide, etc., the induction periods are so long and the rates so slow, that under grafting conditions, little or no such polymerization can occur. The results of such a study are graphically shown in FIG. 2, which sets out the percent-conversion-time characteristics of a typical acrylamide-diacetone acrylamide graft on polyvinyl alcohol, and the homopolymers of the respective monomers.

As a rule, the graft polymers of the present invention are usually obtained in greater than 99% conversion, and most often in the order of 99.9% conversion. Batches of acrylamide-diacetone acrylamide grafts on polyvinyl alcohol were prepared, with the original charges of monomer being 181 g./l. of DAA and 23.6 g./l. of AA. At the end of each batch run, the residual monomer concentration was determined by vapor phase chromatographic analysis, the results of which are set out below in Table 1.

TABLE I

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

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

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethyleneimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated at least in part, in any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in U.S. Pat. No. 3,173,786.

In products employed in the diffusion transfer processes of this invention, it may be preferable to expose from the emulsion side. It may, therefore, be desirable to hold the photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera apparatus suitable for processing film of the type just mentioned is provided by the Polaroid Land camera, sold by Polaroid Corporation, Cambridge, Mass., or similar camera structure such, for example, as the roll film type camera forming the subject matter of U.S. Pat. No. 2,435,717 or the film pack type camera forming the subject matter of U.S. Pat. No. 2,991,702. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which require a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, silver halide solvents, etc., other than those specifically mentioned, provided that the pH of the composition is initially in excess of at least 10, for most favorable results, and most preferably in excess of 12. When desirable, it is also contemplated to include in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The support layers referred to may comprise any of the various types of conventional rigid or flexible dimensionally stable 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.

The nature and construction of rupturable containers is well understood in the art; see, for example, U.S. Pat. No. 2,543,181, issued Feb. 27, 1951, and U.S. Pat. No. 2,634,886, issued Apr. 14, 1953.

It will be apparent that, by appropriate selection of the image-receiving element materials from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency.

While a rupturable container provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition, as by coating the composition on said photosensitive element or otherwise wetting said element with the composition, following which the permeated, exposed photosensitive element, still, without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

Although the invention has been discussed in detail throughout employing dye developers, the preferred dye image-providing materials, it will be readily recognized that other, less preferred, dye image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; and 2,802,735, issued Aug. 13, 1957, 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. Pat. No. 2,774,668, issued Dec. 18, 1956, 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.

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

The present invention also includes the employment of a black dye developer and the use of a mixture of dye developers adapted to provide a black and white transfer image, for example, the employment of dye developers of the three subtractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

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.

It also will be recognized that, where desired, the film unit structure may also comprise an integral positive/negative construction carried on a single support.

In addition to the described essential layers, it will be recognized that the film unit 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, and that any one or more of the described layers may comprise a composite of two or more of the same, or different, components, and which may be contiguous, or separated from each other as, for example, two or more neutralizing layers, or the like, any one of which may be dispersed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable base.

Since certain changes may be made in the above products and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An integral multilayer photosensitive element which comprises, in combination:

(a) a support layer;

(b) at least two selectively sensitized silver halide emulsion layers each having associated therewith a dye image-forming material;

(c) a layer intermeditae said emulsion layers comprising a polyvinyl amide graft copolymer.

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

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

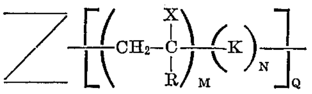
4. The integral multilayer photosensitive element of claim **1** which comprises, in combination:

(a) a support layer;

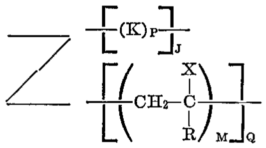
(b) at least two selectively sensitized silver halide emulsion layers each having associated therewith a dye image-forming material;

forming material;

(c) a layer intermediate said emulsion layers comprising a polyvinyl amide graft copolymer represented by the formulae:

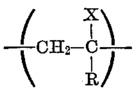


$$Z\left[\left(CH_2-\underset{R}{\overset{X}{C}}\right)_M\left(K\right)_N\right]_Q$$



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

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



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

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

5. The invention of claim **4** wherein said dye image-forming material is a dye which is a silver halide developing agent.

6. The invention of claim **5** wherein said photosensitive element comprises selectively sensitized silver halide emulsions having predominant spectral sensitivity to separate regions of the spectrum.

7. The invention of claim **6** wherein said dye associated with each of said silver halide emulsion layers possesses a spectral absorption range, subsequent to processing, substantially complementary to the predominant sensitivity range of its associated emulsion layer.

8. The invention of claim **5** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state.

9. The invention of claim **8** wherein said polyvinyl amide graft copolymer layer has a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate.

10. The invention of claim **5** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state, and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion next adjacent said support layer, and preceding substantial fogging of the dye associated silver halide emulsion next adjacent said support layer.

11. The invention of claim **5** wherein said organic polymeric backbone is selected from the group consisting of cellulosic and vinyl polymers.

12. The invention of claim **5** wherein said organic polymeric backbone is selected from the group consisting of polymeric polyols, gelatin, polyvinyl alcohol, polysaccharides, polyalkyleneimines, partial acetals of polyvinyl alcohol, and polyaldehydes.

13. The invention of claim **5** wherein said structural units are comprised of a member selected from the group consisting of hydroxyl, amino, mercapto, acyl and aroyl.

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

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

16. The invention of claim **14** wherein said polyacrylamide graft copolymer contains hydrophobic and hydrophilic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

17. The invention of claim **16** wherein said organic polymeric backbone is polyvinyl alcohol.

18. The invention of claim **5** wherein at least one of said dyes is present in a separate layer adjacent its associated silver halide emulsion layer.

19. The invention of claim **18** wherein said separate layer comprises gelatin.

20. The invention of claim **5** wherein at least one of said silver halide emulsion layers comprises gelatin.

21. The invention of claim **14** wherein said polyacrylamide graft copolymer is characterized by decreased hydratability with increased temperature.

22. The invention of claim **14** wherein said polyacrylamide graft copolymer is selected from the group consisting of polyacrylamide graft copolymers having the same backbone to monomer and monomer to monomer ratios, but having different backbone to catalyst ratios.

23. The invention of claim **14** wherein said polyacrylamide copolymer layer is an isopropyl acrylamide-acrylamide graft on polyvinyl alcohol.

24. The invention of claim **5** wherein said organic polymeric backbone is cellulosic.

25. The invention of claim **14** wherein said polyacrylamide graft copolymer is an isopropyl acrylamide graft on gelatin.

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

27. The invention of claim **14** wherein said polyacrylamide graft copolymer is an isopropyl acrylamide graft on a backbone comprised of diacetone acrylamide graft on polyvinyl alcohol.

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

29. The invention of claim **14** wherein K is selected from the group consisting of vinyl acetate, acrylonitrile, methyl methacrylate and ethyl acrylate.

30. A photographic film unit which comprises, in combination, a photosensitive element having a diffusion transfer image-receiving element superposed thereto, said photosensitive element comprising as essential layers:

(a) a support layer carrying on one surface at least two selectively sensitized silver halide emulsion layers each having a dye, which is a silver halide developing agent, of predetermined color associated therewith, and

(b) a layer, intermediate at least two of said silver halide emulsion layers comprising a processing composition-permeable polyvinyl amide graft copolymer;

said diffusion transfer image-receiving element comprising a plurality of substantially discrete layers including, in sequence:

(a) a support layer;

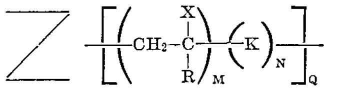
(b) a permeable polymeric acid layer adapted to neutralize alkali contacted therewith; and

(c) an alkaline solution permeable and dyeable polymeric layer within which a dye image is adapted to be formed; wherein said photosensitive element and said image-receiving element are superposed whereby said silver halide emulsion is in overlying relationship with said dyeable polymeric layer.

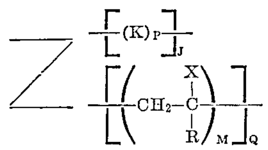
31. The photographic film unit of claim **30** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

32. The photographic film unit of claim **31** wherein said polyacrylamide graft copolymer is comprised of an acrylamide grafted onto a polyvinyl alcohol backbone.

33. The photographic film unit of claim **30** wherein said polyvinyl amide graft copolymer is represented by the formulae:

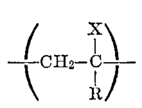


$$Z\left[\left(\mathrm{CH_2}-\underset{\substack{|\\ R}}{\overset{\substack{X\\ |}}{C}}\right)_M(K)_N\right]_Q$$



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

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



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

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

34. The invention of claim **33** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state, and has a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate.

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

36. The invention of claim **35** wherein said polyvinyl amide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

37. The invention of claim **36** wherein said polyacrylamide graft copolymer layer is characterized by decreased hydratability with increased temperature.

38. A photographic film unit as defined in claim **35** including a rupturable container containing an aqueous alkaline processing solution affixed at least one edge of one of said photosensitive and said image-receiving elements, and adapted to rupture and distribute its contents intermediate said photosensitive element and said image-receiving element.

39. A photographic film unit as defined in claim **38** wherein said aqueous alkaline solution has a pH of not less than 12.

40. A photosensitive element as defined in claim **6** which comprises, in combination, a plurality of essential layers including, in sequence:

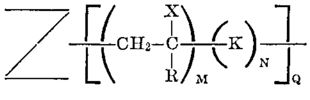
(a) a support layer;
(b) a cyan dye-containing layer;
(c) a red-sensitive silver halide emulsion layer;
(d) an interlayer;
(e) a magenta dye-containing layer;
(f) a green-sensitive silver halide emulsion layer;
(g) an interlayer;
(h) a yellow dye-containing layer; and
(i) a blue-sensitive silver halide emulsion layer;

wherein each of said cyan, magenta and yellow dyes are silver halide developing agents, and at least one of said interlayers comprises a processing composition permeable and hydratable polyvinyl amide graft copolymer.

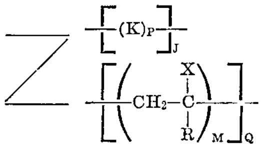
41. The invention of claim **40** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

42. The invention of claim **41** wherein said polyacrylamide graft copolymer is comprised of an acrylamide grafted onto a polyvinyl alcohol backbone.

43. The invention of claim **40** wherein said polyvinyl amide graft copolymer is represented by the formulae:

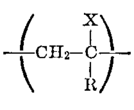


$$Z\left[\left(\mathrm{CH_2}-\underset{\substack{|\\ R}}{\overset{\substack{X\\ |}}{C}}\right)_M(K)_N\right]_Q$$



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

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



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

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

44. The invention of claim **43** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state, and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion next adjacent said support layer, and preceding substantial fogging of the dye associated silver halide emulsion next adjacent said support layer.

45. The invention of claim **43** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

46. The invention of claim **45** wherein said polyacrylamide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics, and is characterized by decreasing hydratability with increased temperature.

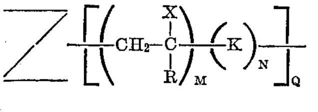
47. A process of forming transfer images in color which comprises the steps of:

- (a) exposing to actinic radiation a photosensitive element comprising at least two selectively sensitized silver halide emulsion strata, each of said silver halide emulsions having associated therewith a dye image-forming material; and a layer intermediate at least two of said silver halide emulsion strata, comprising a processing composition permeable polyvinyl amide graft copolymer;
- (b) applying an aqueous alkaline processing composition to said exposed photosensitive element;
- (c) effecting development of the latent images contained in each of said silver halide emulsions;
- (d) immobilizing the dye image-forming material associated with each of said emulsions as a result of development;
- (e) forming an imagewise distribution of mobile dye image-forming material, as a function of the point-to-point degree of exposure thereof; and
- (f) transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye image-forming material to a superposed image-receiving layer to provide thereto a multicolor dye image.

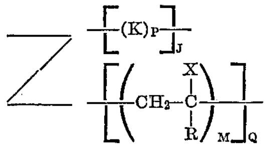
48. The invention of claim **47** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

49. The invention of claim **48** wherein said polyacrylamide graft copolymer comprises an acrylamide grafted onto a polyvinyl alcohol backbone.

50. The invention of claim **47** wherein said polyvinyl amide graft copolymer is represented by the following formulae:

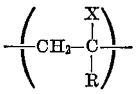


$$Z\left[\left(CH_2-\overset{X}{\underset{R}{C}}\right)_M\left(K\right)_N\right]_Q$$



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

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



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

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

51. The invention of claim **50** wherein said dye image-forming material is a silver halide developing agent.

52. The invention of claim **51** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state, and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion next adjacent said support layer, and preceding substantial fogging of the dye associated silver halide emulsion next adjacent said support layer.

53. The invention of claim **50** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer.

54. The invention of claim **53** wherein said polyacrylamide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics, and is characterized by decreasing hydratability with increased temperature.

55. The invention of claim **53** wherein said polyacrylamide graft copolymer is selected from the group consisting of isopropyl acrylamide-acrylamide graft on polyvinyl alcohol, isopropyl acrylamide graft on gelatin and acrylamide-diacetone acrylamide graft on polyvinyl alcohol.

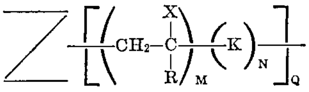
56. A process of forming multicolor transfer images which comprises the steps of:

- (a) exposing a photosensitive element which comprises blue-sentitive, green-sensitive and red-sensitive silver halide emulsion layers mounted on a common dimensionally stable support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsions having associated therewith, respectively, yellow, magenta and cyan dyes, each of said dyes being a silver halide developing agent and being dispersed in a separate layer next adjacent its associated emulsion and intermediate said emulsion and said support, at least two of said emulsion and associated dye-containing layers having, intermediate same, a layer comprising an alkali solution-permeable and hydratable polyvinyl amide graft copolymer;
- (b) applying an aqueous alkaline processing composition to said exposed photosensitive element;
- (c) effecting development of the latent images contained in said emulsions;
- (d) immobilizing said yellow, magenta and cyan dyes, as a result of development of the exposed areas of their associated silver halide emulsion;
- (e) forming an imagewise distribution of mobile yellow, magenta and cyan dye, in unexposed areas of their associated emulsions, as a function of the point-to-point degree of emulsion exposure; and
- (f) transferring, by imbibition, at least a portion of each of said imagewise distributions of dye to a superposed image-receiving layer to provide thereto a multicolor dye image.

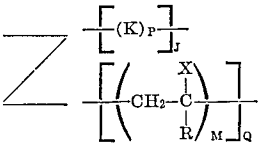
57. The invention of claim **56** wherein said polyvinyl amide graft copolymer is a polyacrylamide graft copolymer layer.

58. The invention of claim **57** wherein said polyacrylamide graft copolymer is comprised of an acrylamide grafted onto a polyvinyl alcohol backbone.

59. The invention of claim **56** wherein said polyvinyl amide graft copolymer is represented by the formulae:

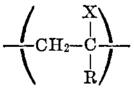


$$Z\left[\left(\mathrm{CH_2}-\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\right)_M(K)_N\right]_Q$$



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

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



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

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

60. The invention of claim **59** wherein said polyvinyl amide graft coploymer is a polyacrylamide graft copolymer.

61. The invention of claim **59** wherein said polyvinyl amide graft copolymer layer is processing composition-permeable and hydratable, with a dye permeable lattice substantially only in the hydrated state, and a hydration rate effective to provide a dye permeable lattice subsequent to substantial development of the dye associated silver halide emulsion possessing the slowest development rate, and preceding substantial fogging of the dye associated silver halide emulsion possessing the most rapid fogging rate.

62. The invention of claim **60** wherein said polyacrylamide graft copolymer contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics, and is characterized by decreasing hydratability with increased temperature.

63. The invention of claim **60** wherein said polyacrylamide graft copolymer is selected from the group consisting of isopropyl acrylamide-acrylamide graft on polyvinyl alcohol, isopropyl acrylamide graft on gelatin, and acrylamide-diacetone acrylamide graft on polyvinyl alcohol.

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A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—29; 260—8