Jan. 14, 1969 L. D. TAYLOR 3,421,892

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed May 26, 1967 Sheet 1 of 5

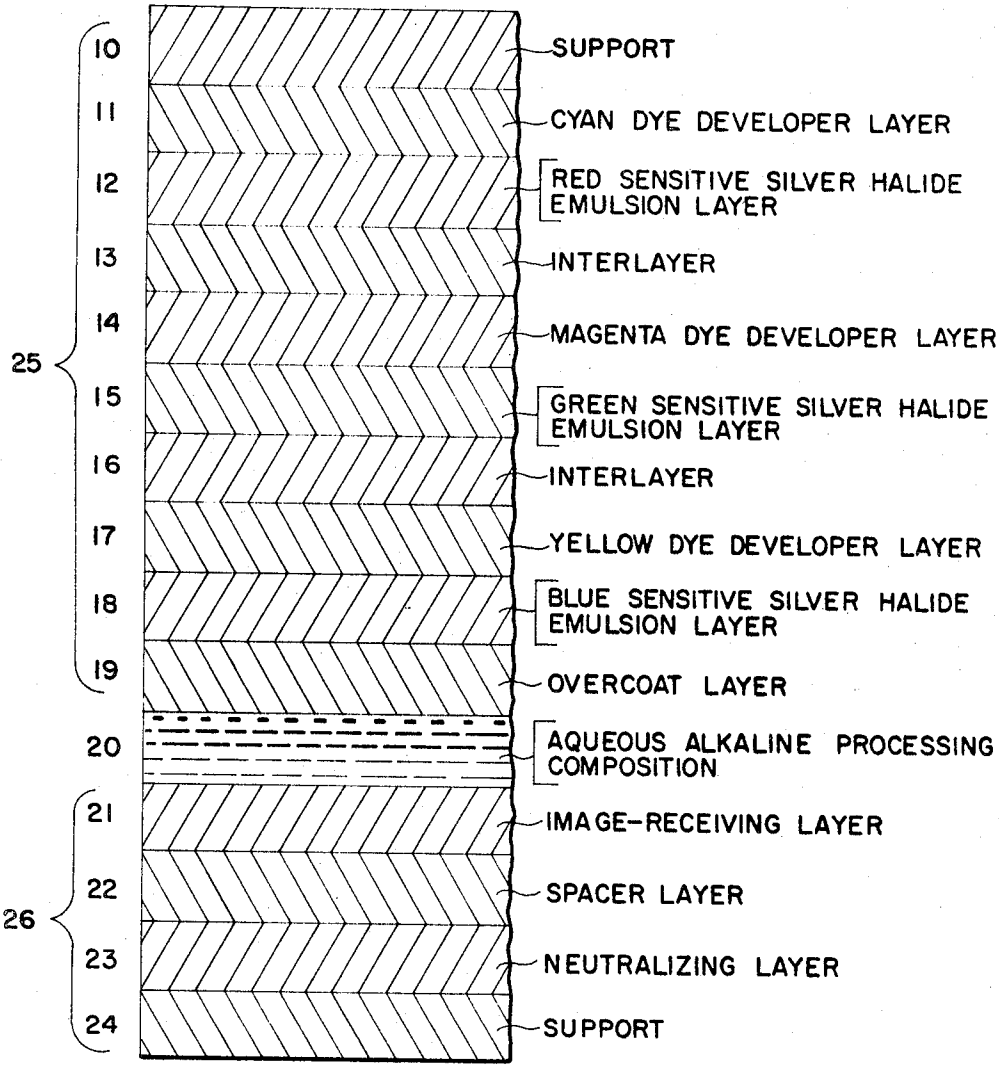

FIG. 1

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FIG. 2

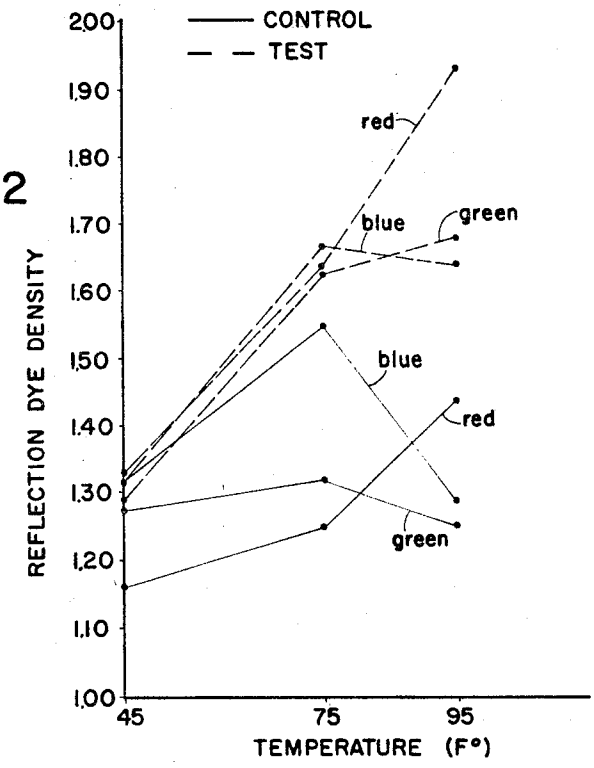
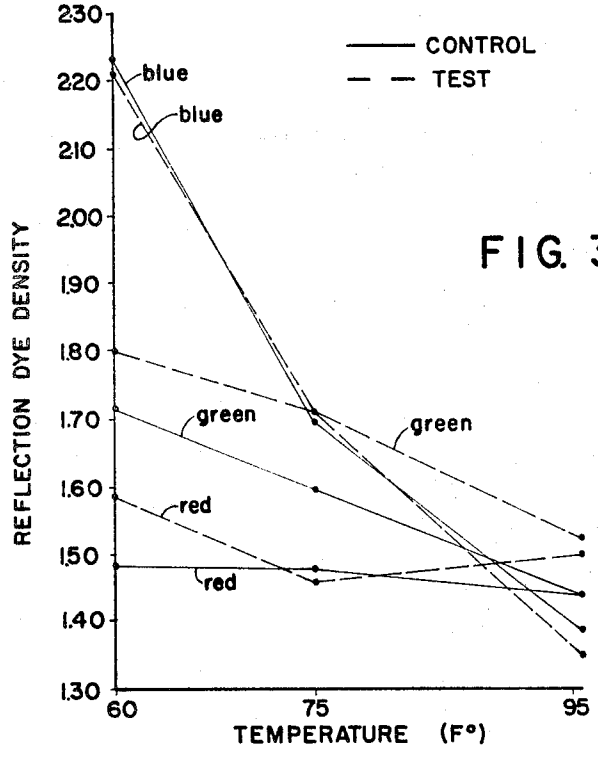


FIG. 3



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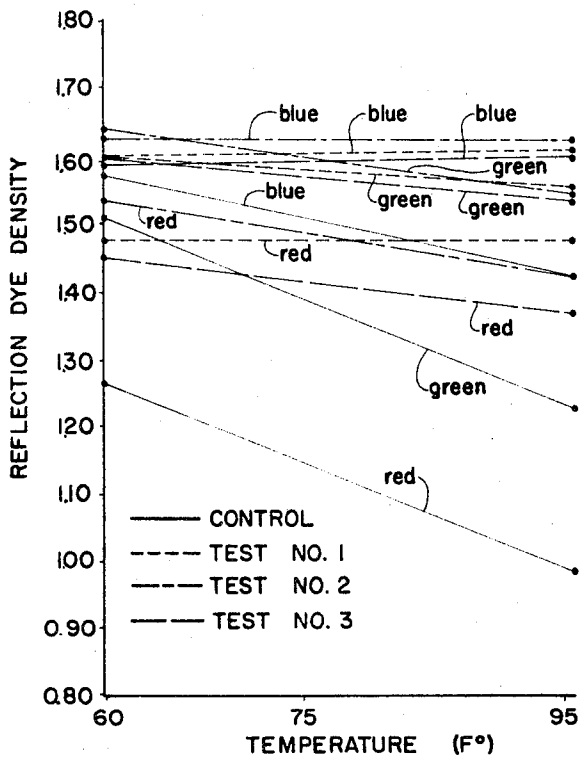

FIG. 4

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United States Patent Office 3,421,892 Patented Jan. 14, 1969

3,421,892

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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Filed May 26, 1967, Ser. No. 641,669
U.S. Cl. 96—3 42 Claims
Int. Cl. G03c 7/00

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 a polyvinyl amide.

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

As disclosed in U.S. Patent 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, position 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 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 image-wise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this image-wise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The 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 multi-layer photosensitive element, such as is disclosed in the aforementioned U.S. Patent 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. Patent 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 addi-

tional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Patents 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; 3,135,-606; 3,135,734; 3,141,772; 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. Patent No. 2,992,-104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Patent 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 vinylphthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Patent No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of α,β-unsaturated carboxylic acids, 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 extensivee compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic color-providing materials in polymeric binders, specifically for the formation component layers of photographic film units, reference may be made to U.S. Patents Nos. 2,269,158, 2,322,027, 2,304,939, 2,304,940, 2,801,-171, and the like.

Copending U.S. application Ser. No. 234,864, filed Nov. 1, 1962 now U.S. Patent 3,362,819, in the name of Edwin H. Land discloses image-receiving elements particularly adapted for employment in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, 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 acide 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 copending application, by (a) a

mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the polymeric acid may contain a water insoluble polymer, 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 combination of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

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

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as 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-vinylpridine, as disclosed in U.S. Patent 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. Patents 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. Patents 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 C. B. Neblette, 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 F. M. Hammer, The Cyanine Dyes 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. Patents Nos. 2,271,623; 2,288,226; and 2,334,864; or of the polyethyleneglycol type, as described in U.S. Patent No. 2,708,162; or of the preceding combination, as described in U.S. Patent No. 2,886,437; or the thiopolymers, as described in U.S. Patents 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. Patents Nos. 2,566,245 and 2,566,263; the mercury compounds of U.S. Patents Nos. 2,728,663, 2,728,664 and 2,728,665; the triazoles of U.S. Patent No. 2,444,608; the azindines of U.S. Patents 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, pages 2–28; the disulfides of Belgian Patent No. 569,317; the benzothiazolium compounds of U.S. Patents Nos. 2,131,038 and 2,694,716; the zinc and cadmium salts of U.S. Patent No. 2,839,405; and the mercapto compounds of U.S. Patent 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. Patents 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. Patent No. 2,831,766; a polyethyleneglycol ether of U.S. Patent No. 2,719,087; a taurine of U.S. Patent No. 2,739,891; a maleopimarate of U.S. Patent No. 2,823,123; an amino acid of U.S. Patent No. 3,038,804; a sulfosuccinamate of U.S. Patent No. 2,992,108; or a polyether of U.S. Patent No. 2,600,831; or a gelatin plasticizer such as glycerin; a dihydroxyalkane of U.S. Patent No. 2,960,404; a bisglycolic acid ester of U.S. Patent No. 2,904,434; a succinate of U.S. Patent No. 2,940,854; or a polymeric hydrosol of U.S. Patent No. 2,852,386.

As the binder for 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. Patents Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Patent No. 2,541,474; vinyl polymers such as described in U.S. Patents 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 a primary object of the present invention to provide novel photographic diffusion transfer color processes and novel photosensitive elements particularly adapted for employment in such processes.

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

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

A further object of the present invention is to provide products for use in photographic diffusion transfer color processes which include a photosensitive element which comprises a plurality of essential layers superposed upon a common support including at least two selectively sensitized photosensitive layers, each having associated therewith as a dye image-forming material which is soluble and diffusible in alkali, wherein at least two of said sensitized layers and associated dyes are separated from each other by a layer comprising a polyvinyl amide, as described more fully below.

Another object of the present invention is to provide a product for use in a photographic diffusion transfer color process comprising a photosensitive element, as described above, in combination with a photographic diffusion transfer image-receiving composite structure comprising a plurality of essential layers including a solution-dyeable polymeric layer.

Finally, it is an object of the present invention to provide a product for use in a diffusion transfer photographic color process which product comprises a photosensitive element and transfer image-receptive composite structure each as identified above and a fluid photographic processing composition.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

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

FIG. 2 is a graphical representation of the relationship between temperature and reflection dye density for photosensitive sheets containing N-isopropyl acrylamide as compared to sheets containing gelatin in the third layer, according to the layer-sequence scheme recited in Example 1, below.

FIG. 3 is a graphical representation of the relationship between temperature and reflection dye density for photosensitive sheets containing N-ethyl acrylamide as compared to sheets containing a vinyl acetate-crotonic acid copolymer in the third layer, according to the layer-sequence scheme recited in Example 1, below.

FIG. 4 is a graphical representation of the relationship between temperature and reflection dye density for photosensitive sheets containing a copolymer of N-isopropyl acrylamide and N(β-dimethylamino) ethyl acrylamide with 1%, 2% and 4%, respectively of polyacrylamide added, after 6 days of aging at 75° F. and 120° F., respectively, when compared to a sheet containing a vinyl acetate-crotonic acid copolymer in the third layer according to the layer-sequence scheme recited in Example 1, below.

As disclosed in copending U.S. application Ser. No. 486,862, now abandoned, filed Sept. 13, 1965, 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 preferably less than the development and greater than the fogging rates of the dye associated silver halide next adjacent the photosensitive element's film base, 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."

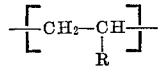
The hydration with which the last-identified application is directly concerned comprises, in general, the polymer's assimilation of water molecules by hydrogen bonding. Concurrently with said hydration, the system swells and its capability regarding permeation by dye materials increases. It will also 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

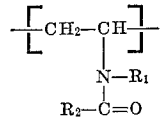
halide emulsion fogging may be directly measured, in accordance with any of the conventional techniques known in the art. Included among such techniques are procedures well known for the simultaneous derivation of both the development and fogging rate of a silver halide emulsion, by contemporaneous measurement 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.

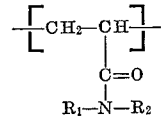
It has now unexpectedly been discovered that the use of a certain class of polymers as negative interlayers produces far better color isolation and temperature dependence than compounds described in the prior art. The class of processing composition permeable polymers which are particularly adapted for employment in accordance with the instant invention are polyvinyl amides, that is, processing composition permeable polymers within the formula:



where R is selected from the group consisting of carboxamido groups and amino carbonyl groups. Preferred polymers within the scope of the present invention comprise polyvinyl amides within the formulae:



and



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 both R_1 and R_2 are intended to encompass equivalents thereof and accordingly may comprise substituted or unsubstituted alkyl or aryl groups, etc., to conform to the desires of the operator. In general, then, R_1 and R_2 may be any group which functionally contributes a desired property such as, for example, hydrophilicity or hydrophobicity, to the polymer.

The instant invention is thus 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 complementary to the predominant sensitivity range of the associated emulsion, separated by a spacer or interlayer comprising the aforementioned polyvinyl amide polymer 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.

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 polymer interlayers are 0.1 to 5 microns thick. With respect to a preferred image-receiving element, the image-receiving layer is about 0.25 to 0.4 mil thick, the polymeric acid layer is about 0.3 to 1.5 mils thick, and the spacer layer is about 0.1 to 0.7 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.

Preferably, however, the selected polymer 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.

In a preferred embodiment, the selected polyvinyl amide possesses a processing composition hydration rate sufficiently less than the development and greater than the fogging rate of the respective dye-associated silver halide emulsion possessing the slowest development and the most rapid fogging rate of the two emulsions intermediate which the polymer is positioned, in order to simultaneously retard rearward diffusion of the dye associated with the silver halide emulsion next adjacent the element's surface and forward diffusion of the dye associated with the silver halide emulsion next adjacent the film base, until the respective imagewise emulsion development and control of each dye is substantially established. 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 copending application of Lloyd D. Taylor, Ser. No. 641,670 filed concurrently herewith, compounds of the instant class 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 development function. Specifically, utilization of the 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 hydro-

philic and hydrophobic groups so that a proper balance is achieved which results in the desired barrier-permeation characteristics throughout a desired temperature range. Such polymers include graft as well as random copolymers. In the former category might be, for example, the product obtained by grafting vinyl amide groups onto a polyvinyl alcohol backbone. Also useful in the present invention are homopolymers wherein various moieties present in the monomer lend varying degrees of hydrophilicity and hydrophobicity to the polymer.

As indicated in copending U.S. application Ser. No. 447,100 now abandoned, filed Apr. 9, 1965 in the names of Leonard G. Farney, Howard G. Rogers, and Richard W. Young, inverse temperature dependence of a polymeric film with regard to alkali permeability is not an unknown phenomenon, the use of this property having been disclosed for utilization in diffusion transfer photographic receiving sheets. Benefits are derived from using a temperature-inverting material in a process which depends upon permeation of liquids, at a variety of temperatures, since, as the ambient temperature decreases, the polymer tends to form hydrates and swells, thus facilitating permeation as a function of the degree of swell of the polymer—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.

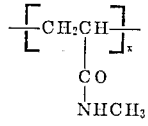
Extreme inverse temperature characteristics are generally not particularly desirable since the development of the photosensitive part of the system and the dye transfer are temperature dependent processes and should be functionally compatible with the temperature-permeation properties of the receiving sheet. An ideal interlayer, therefore, should provide the system which it comprises with the proper 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, substantially irrespectively of the processing temperature employed.

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

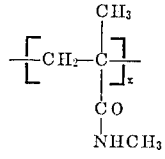
Monomers of interest which are useful in making copolymers or terpolymers with the necessary hydrophilic-hydrophobic balance include: acrylamide; N-methyl acrylamide, methacrylamide; N-methyl methacrylamide; ethyl acrylate; N-ethyl acrylamide; N-methylolacrylamide; N,N-dimethyl acrylamide; N,N-dimethyl methacrylamide; N-(n-propyl) acrylamide; N-isopropyl acrylamide; N-(β-hydroxy 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, etc.

Polymers which are found to be useful in the practice of the present invention are:

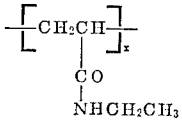
(1) Poly N-methylacrylamide:



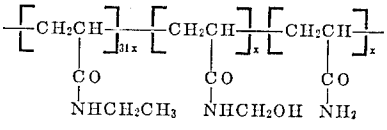
(2) Poly N-methylmethacrylamide:



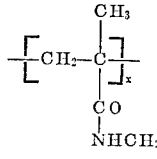
(3) Poly N-ethylacrylamide:



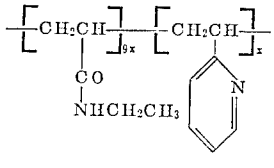
(4) 31:1:1 terpolymer of N-ethylacrylamide:N-methylolacrylamide:acrylamide



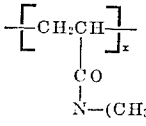
(5) Poly N-ethylmethacrylamide:



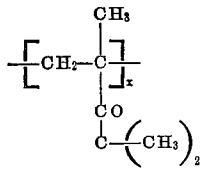
(6) 9:1 copolymer of N-ethylacrylamide:2-vinyl pyridine



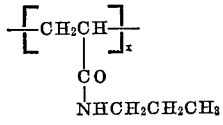
(7) Poly N,N-dimethylacrylamide:



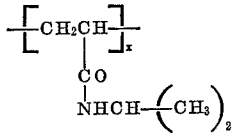
(8) Poly N,N-dimethylmethacrylamide:



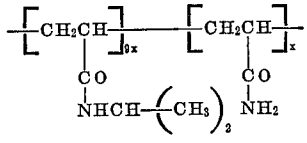
(9) Poly N-(n-propyl)acrylamide:



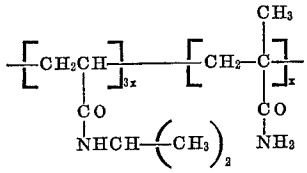
(10) Poly N-isopropylacrylamide:



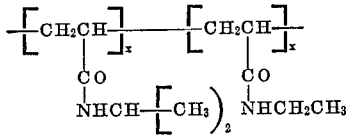
(11) 9:1 copolymer of N-isopropylacrylamide:acrylamide:



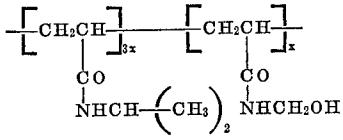
(12) 3:1 copolymer of N-isopropylacrylamide: methacrylamide:



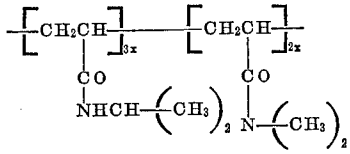
(13) 1:1 copolymer of N-isopropylacrylamide: N-ethylacrylamide



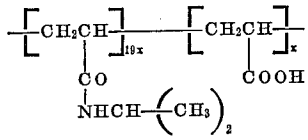
(14) 3:1 copolymer of N-isopropylacrylamide: N-methylol-acrylamide:



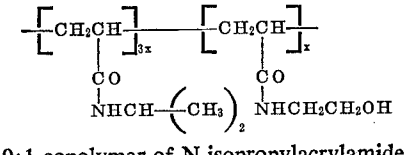
(15) 3:2 copolymer of N-isopropylacrylamide N,N-dimethylacrylamide



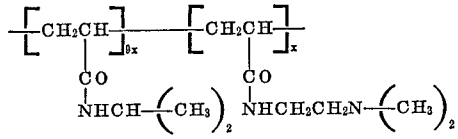
(16) 19:1 copolymer of N-isopropylacrylamide: acrylic acid



(17) 3:1 copolymer of N-isopropylacrylamide: N-(β-hydroxyethyl)acrylamide

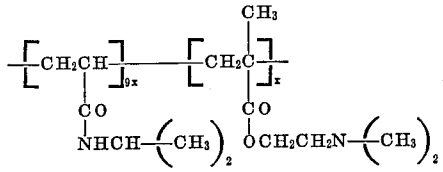


(18) 9:1 copolymer of N-isopropylacrylamide: N[β-(dimethylamino)ethyl]acrylamide

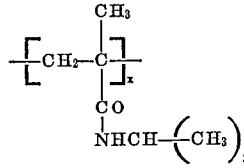


(19) 9:1 copolymer of N-isopropylacrylamide: dimethylamino ethyl acrylate

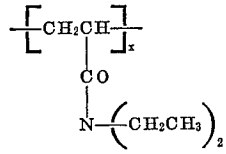
(20) 9:1 copolymer of N-isopropylacrylamide: dimethylamino ethyl methacrylate



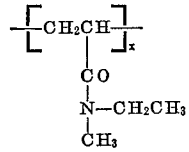
(21) Poly N-isopropylmethacrylamide



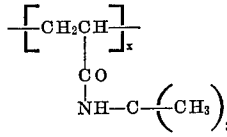
(22) Poly N,N-diethylacrylamide



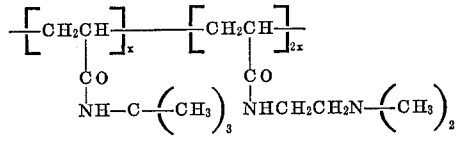
(23) Poly N-ethyl-N-methyl acrylamide



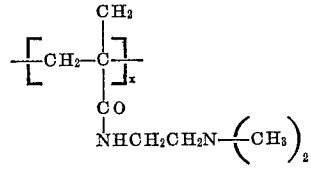
(24) Poly N-t-butylacrylamide



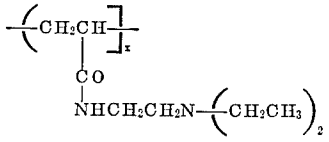
(25) 1:2 copolymer of N-t-butylacrylamide: N[β-(di-methylamino)ethyl]acrylamide



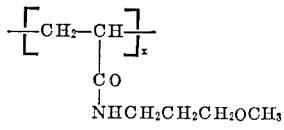
(26) Poly N[β-(dimethylamino)ethyl]methacrylamide



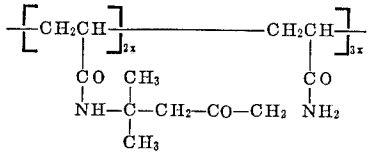
(27) Poly N[β-(diethylamino)ethyl]acrylamide



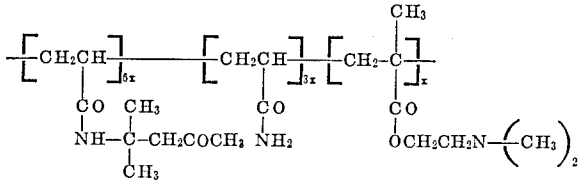
(28) Poly N[3'-methoxypropyl]acrylamido



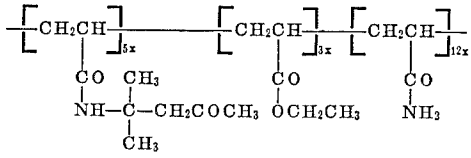
(29) 2:3 copolymer of diacetone acrylamide and acrylamide



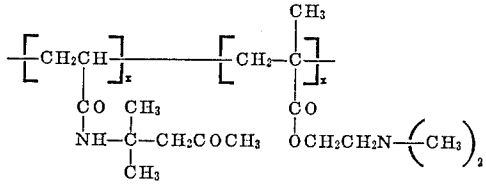
(30) 6:3:1 terpolymer of diacetone acrylamide: acrylamide: dimethylamino ethyl methacrylate



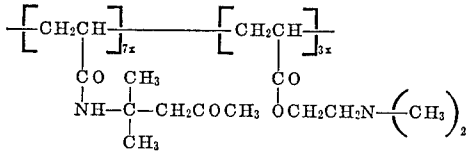
(31) 5:3:12 terpolymer of diacetone acrylamide: ethylacrylate: acrylamide



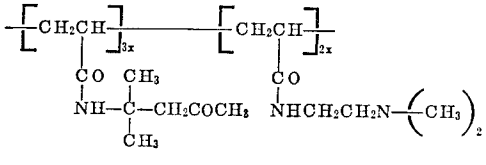
(32) 1:1 copolymer of diacetone acrylamide and dimethylamino ethyl methacrylate



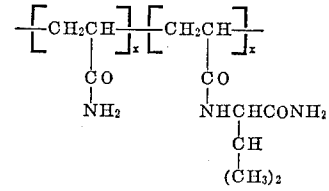
(33) 7:3 copolymer of diacetone acrylamide and dimethylamino ethyl acrylate



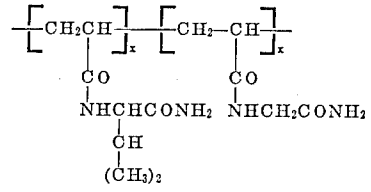
(34) 3:2 copolymer of diacetone acrylamide and N-[β-(dimethylamino)ethyl]acrylamide



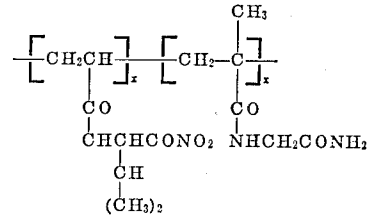
(35) 1:1 copolymer of acrylamide and 2-acrylamido-3-methylbutyramide



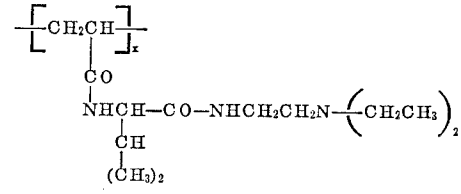
(36) 1:1 copolymer of 2-acrylamido-3-methyl butyramide and acrylamidoacetamide



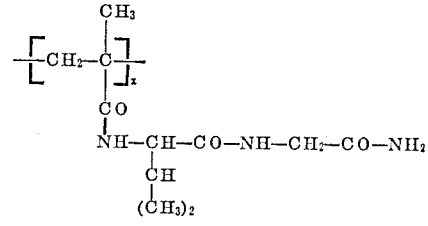
(37) 1:1 copolymer of 2-acrylamido-3-methylbutyramide and methacrylamidoacetamide



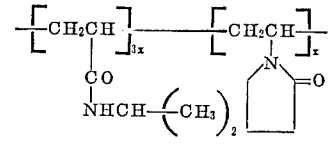
(38) Poly 2-acrylamido-3-methyl-N-[β-(diethylamino)ethyl]butyramide



(39) Poly 2-[2'-methacrylamido-3'-methylbutyramido]acetamide



(40) 3:1 copolymer of N-isopropylacrylamide and N-vinylpyrrolidone



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

As might be expected 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 flow. 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, thicknesses from 0.1 to 5.0 microns 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 been specifically found to possess certain distinct advantages, when compared with the 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 sufficiently 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 development 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; an interlayer **13** comprising the polymer 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 polymer 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.

Example 1

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 die 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 poly-N-isopropyl acrylamide coated at a coverage of 30 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-hydroquinonyl ethyl]-phenylazo)-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 iodo-bromide 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 poly-N-isopropyl acrylamide was prepared by adding 113.16 gms. of N-isopropyl under nitrogen to 1 l. of distilled water in a 2 l. flask. 5 ml. of isopropanol were added. The pH was adjusted to 6.4 with NaOH and 0.1 g. of $NaHSO_3$ and 0.1 g. of $K_2S_2O_8$ were added. The solution was stirred until viscous and dialyzed for 24 hours.

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 were then exposed and processed at various temperatures by spreading an aqueous liqiud processing composition comprising:

Water	cc. 100
Potassium hydroxide	gm__ 11.2
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Del., under the trade name Natrasol 250]	gm__ 3.9
Potassium thiosulfate	gm__ 0.5
Benzotriazole	gm__ 3.5
N-benzyl-α-picolinium bromide	gm__ 2.0
Lithium hydroxide	gm__ 0.5

between an individual image-receiving element and each of the exposed multicolor elements, as they were 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 was separated from the photosensitive element.

Examination of the resultant images showed the following differential maximum densities which comprise the difference between the maximum and minimum densities recorded for the various colors of the film with a Quantalog MacBeth densitometer.

Temp., ° F.	$\Delta D_{max.}$ Test Sheet Wherein Layer 3 Contains Poly-N-isopropyl Acrylamide			$\Delta D_{max.}$ Control Wherein Layer 3 Contains Gelatin		
	Red	Green	Blue	Red	Green	Blue
45	1.33	1.29	1.32	1.16	1.27	1.32
75	1.64	1.63	1.67	1.25	1.32	1.55
95	1.93	1.68	1.64	1.44	1.25	1.29

Visual observation of the test and control materials demonstrates that the negative prepared with an interlayer of the instant invention provides improved color balance, greatly improved green density and better saturation and color isolation characteristics. It was likewise found that the film demonstrated improved stability to varying gaps which might occur between the photosensitive sheet and the image-receiving sheet. Additionally an improvement in $D_{min.}$ was observed for the test at all temperatures as compared to the control.

The test results tabulated above, correspond to the graphical presentation of FIG. 2 of the drawings.

Example 2

The procedure of Example 1 was carried out except that layer 3 of the test negative comprised poly-N-ethyl acrylamide coated at a coverage of 71 mg. per square foot and layer 3 of the control contained 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 was coated in the sixth layer at a coverage of 14 gms. per square foot, instead of in the ninth layer.

The poly-N-ethyl acrylamide was prepared as follows: 330 gms. of N-ethyl acrylamide was dissolved in 3.3 l. of distilled water and 17 ml. of isopropanol under nitrogen. The solution was cooled at 8° C. and 0.111 g. of concentrated H_2SO_4, 0.377 g. of $NaBrO_3$ and 0.288 g. of Na_2SO_3 was added. The solution was stirred for 24 hours and then dialyzed for 24 hours.

A comparison was made with a control formulated substantially as above. Examination of the resultant images showed the following differential maximum densities:

Temp., ° F.	$\Delta D_{max.}$ Test Sheet Wherein Layer 3 Contains Poly-N-Ethyl Acrylamide			$\Delta D_{max.}$ Control Wherein Layer 3 Contains Vinyl Acetate-Crotonic Acid Copolymer		
	Red	Green	Blue	Red	Green	Blue
*60	1.58	1.80	2.21	1.48	1.71	2.23
75	1.46	1.71	1.71	1.48	1.60	1.70
95	1.50	1.52	1.35	1.44	1.44	1.39

*90 seconds.

The test material, i.e., poly-N-ethyl acrylamide was found to improve gap performance from 0.0044 inch to 0.0036 inch and better dye transfer was observed with the test material than with the control. Additionally it was found that 100 mg. per square foot of poly-N-ethyl acrylamide exhibits equal color isolation capabilities as the crotonic acid compolymer covered the 189 mg. per square foot.

The test results, tabulated above, correspond to the graphical presentation of FIG. 3 of the drawings.

Example 3

The procedure of Example 2 was carried out except that layer 3 of the test comprised a copolymer of N,N-(β-dimethylamino)ethyl acrylamide; N-isopropyl acrylamide, in a ratio of 1 to 19 with either 1%, 2% or 4%, respectively, by weight based on total solids, of polyacrylamide mixed therewith. Also, in addition to containing 14 mgs. per square foot of 4' methyl phenyl hydroquinone in layer 6, of both the test and control, 30 mgs. of 4' methyl phenyl hydroquinone per square foot, dispersed in gelatin, was spread in layer 9.

The copolymer was made as follows: 288.4 gms. of N-isopropyl acrylamide and 19.05 gms. of N(β-dimethylamino)ethyl acrylamide were dissolved in 2.7 l. of distilled water. 12.0 ml. of isopropanol was added and the solution was deaerated with nitrogen for one hour. The solution was adjusted to pH 6.4 by the addition of concentrated nitric acid and then 0.25 gm. of sodium bisulfite and 0.25 gm. of potassium persulfate were added simultaneously. The solution was stirred under nitrogen overnight and then dialyzed for 24 hours.

3.07 gms. of polyacrylamide was then added to the copolymer and the mixture was coated.

A comparison was made between various test sheets and the control, and produced the following differential maximum densities:

Temp., ° F.	$\Delta D_{max.}$ Test Sheet Wherein Layer 3 Contains 1% Polyacrylamide			$\Delta D_{max.}$ Test Sheet Wherein Layer 3 Contains 2% Polyacrylamide			$\Delta D_{max.}$ Test Sheet Wherein Layer 3 Contains 4% Polyacrylamide			$\Delta D_{max.}$ Control Wherein Layer 3 Contains Vinyl Acetate-Crotonic Acid Copolymer		
	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
60 (90 seconds)	1.48	1.76	2.2	1.50	1.76	1.76	1.44	1.76	2.06	1.47	1.73	2.11
75	1.53	1.65	1.65	1.59	1.69	1.68	1.50	1.65	1.54	1.31	1.56	1.63
95	1.76	1.75	1.31	1.77	1.67	1.30	1.73	1.72	1.33	1.30	1.39	1.18
120 (after 6 days aging at 120°)	1.53	1.61	1.65	1.48	1.60	1.67	1.42	1.59	1.64	0.99	1.28	1.48

The test results, tabulated above, correspond to the graphical presentation of FIG. 4 of the drawings.

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, tolu-hydroquinine, phenylhydroquinone, 4'-methylphenyl-hydroquinone, 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. Patent 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-ethylenimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processng 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 amonium compound, in accordance with the processes disclosed in U.S. Patent No. 3,173,786.

In products employed in the diffusion transfer processes of this invention, it is preferable to expose from the emulsion side. It is, therefore, desirable to hold the photosensitve 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. Patent No. 2,435,717 or the film pack type camera forming the subject matter of U.S. Paent 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 dervied 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. Patent No. 2,543,181, issued Feb. 27, 1951, and U.S. Patent 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. Patents Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; 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. Patent 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.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a

yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye developer.

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 product 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. A 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 intermediate said emulsion layers comprising a permeable polyvinyl amide.

2. The invention of claim **1** wherein said dye image-forming material is a dye which is a silver halide developing agent.

3. The invention of claim **2** wherein said polyvinyl amide possesses a dye permeable lattice substantially only in the hydrated state and a hydration rate less than the development rate and greater than the fogging rate of the dye asociated silver halide emulsion having the slowest development rate and the most rapid fogging rate.

4. The invention of claim **2** wherein said polyvinyl amide possesses a dye permeable lattice substantially only in the hydrated state and a hydration rate less than the development rate and greater than the fogging rate of the dye-associated silver halide emulsion next adjacent said support layer.

5. The invention of claim **2** wherein said polyvinyl amide is a polyacrylamide.

6. The invention of claim **5** where in said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

7. The invention of claim **2** wherein at least one of said dyes is present in a separate layer adjacent its associated silver halide emulsion layer.

8. The invention of claim **7** wherein said separate layer comprises gelatin.

9. The invention of claim **2** wherein at least one of said silver halide emulsion layers comprises gelatin.

10. The invention of claim **6** wherein said polyacrylamide polymer is characterized by decreased hydratability with increased temperature.

11. The invention of claim **10** wherein said polyacrylamide polymer is poly-N-isopropyl acrylamide.

12. The invention of claim **10** wherein said polyacrylamide ploymer is poly-N-ethyl acrylamide.

13. The invention of claim **10** wherein said polyacrylamide polymer is a 1:19 copolymer of N,N(β-dimethylamino)-ethyl acrylamide and N-isopropyl acrylamide and contains about 1% to 4% of polyacrylamide mixed therewith.

14. A photographic film unit which comprises, in combination, a photosensitive element having a diffusion transfer image-receiving element affixed upon one edge thereof, 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;

said diffusion transfer image-receiving element comprising, as essential layers, in sequence:

(a) a support layer;

(b) a polymeric acid layer; and

(c) a dyeable polymeric layer;

wherein said photosensitive element and said image-receiving element are adapted to be superposed thereby positioning said silver halide emulsion in overlying relationship with said dyeable polymeric layer.

15. The invention of claim **14** wherein said polyvinyl amide composition possesses a dye permeable lattice substantially only in the hydrated state and a hydration rate less than the development rate and greater than the fogging rate of the silver halide emulsion next adjacent said support layer.

16. The invention of claim **14** wherein said polyvinyl amide is a polyacrylamide.

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

18. The invention of claim **17** wherein said polyacrylamide is characterized by decreased hydratability with increased temperature.

19. A photographic film unit as defined in claim **14** including a rupturable container containing an aqueous alkaline solution affixed 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 upon superpositioning of said elements.

20. As a product, a photographic film unit as defined in claim **19** wherein said aqueous alkaline solution has a pH of not less than about 12.

21. As a product, a photographic film unit which comprises, in combination, a photosensitive element contain-

ing a plurality of essential layers including, in sequence:

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

wherein each of said cyan, magenta and yellow dyes being silver halide developing agents, and at least one of said spacer layers comprises a processing composition permeable and hydratable polyvinyl amide.

22. The invention of claim **21** wherein said polyvinyl amide composition possesses a dye permeable lattice substantially only in the hydrated state in a hydration rate less than the development and greater than the fogging rate of the silver halide emulsion next adjacent said support layer.

23. The invention of claim **21** wherein said polyvinyl amide polymer is a polyacrylamide.

24. The invention of claim **23** wherein said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

25. The invention of claim **24** wherein said polyacrylamide polymer is characterized by decreased hydratability with increased temperature.

26. 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;
(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 associated with each of said emulsions as a result of development;
(e) forming an imagewise distribution of mobile dye, 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 to a superposed image-receiving layer to provide thereon a multicolor dye image.

27. The invention of claim **26** wherein said dye image-forming material is a silver halide developing agent.

28. The invention of claim **27** wherein said polyvinyl amide composition possesses a dye permeable lattice substantially only in the hydrated state in a hydration rate less than the development and greater than the fogging rate of the silver halide emulsion next adjacent said support layer.

29. The invention of claim **27** wherein said polyvinyl amide is a polyacrylamide.

30. The invention of claim **29** wherein said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

31. The invention of claim **30** wherein said polyacrylamide is characterized by decreasing hydratability with increasing temperature.

32. The invention of claim **29** wherein said polyacrylamide polymer comprises poly-N-isopropyl acrylamide.

33. The invention of claim **29** wherein said polyacrylamide polymer comprises poly-N-ethyl acrylamide.

34. The invention of claim **29** wherein said polyacrylamide polymer comprises a 1:19 copolymer of N,N(β-dimethylamino)ethyl acrylamide and N-isopropyl acrylamide with about 1% to 4% of polyacrylamide mixed therewith.

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

(a) exposing a photosensitive element which comprises blue-sensitive, green-sensitive and red-sensitive gelatino-silver halide emulsion layers mounted on a common dimensionally stable support, said blue-sensitive, green-sensitive and red-sensitive gelatino-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;
(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 emulsions;
(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.

36. The invention of claim **35** wherein said polyvinyl amide composition possesses a dye permeable lattice substantially only in the hydrated state in a hydration rate less than the development rate and greater than the fogging rate of the dye associated silver halide emulsion having the slowest development rate and the most rapid fogging rate.

37. The invention of claim **35** wherein said polyvinyl amide composition is a polyacrylamide.

38. The invention of claim **37** wherein said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-permeation characteristics.

39. The invention of claim **38** wherein said polyacrylamide polymer is characterized by decreased hydratability with increased temperature.

40. The invention of claim **37** wherein said polyacrylamide polymer is poly-N-isopropyl acrylamide.

41. The invention of claim **37** wherein said polyacrylamide polymer is poly-N-ethyl acrylamide.

42. The invention of claim **37** wherein said polyacrylamide polymer is a 1:19 copolymer of N,N(β-dimethylamino)ethyl acrylamide and N-isopropyl acrylamide and contains about 1% to 4% of polyacrylamide mixed therewith.

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