

July 15, 1969

D. P. CARLSON ET AL

3,455,685

NOVEL PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

Filed Dec. 30, 1965

3 Sheets-Sheet 1

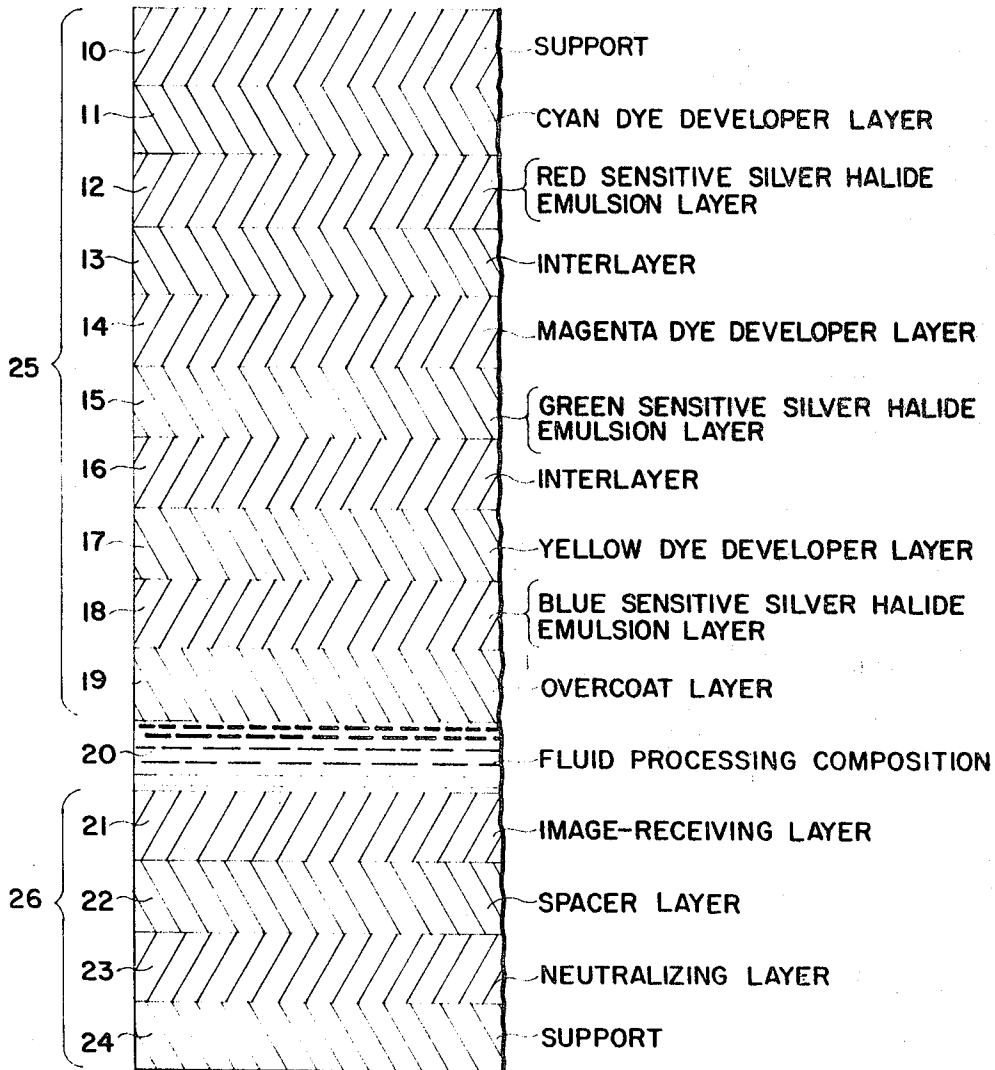


FIG. 1

INVENTORS
David P. Carlson
and
BY *Jerome L. Reid*
Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

July 15, 1969

D. P. CARLSON ET AL

3,455,685

NOVEL PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

Filed Dec. 30, 1965

3 Sheets-Sheet 2

FIG. 2

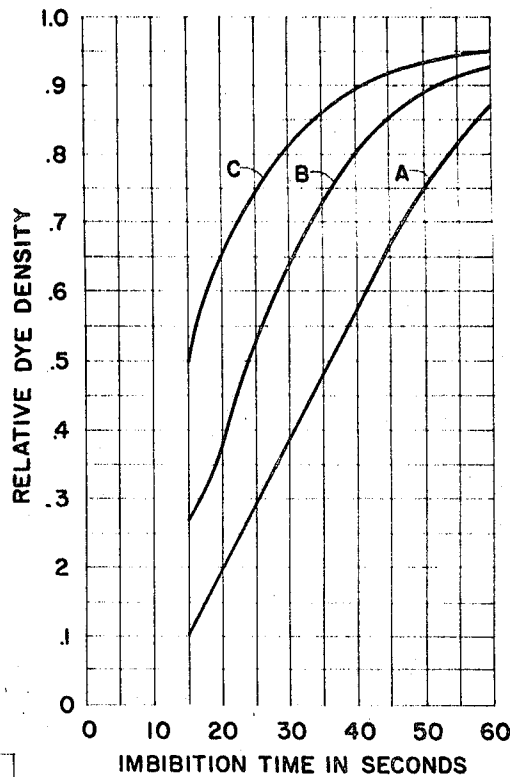
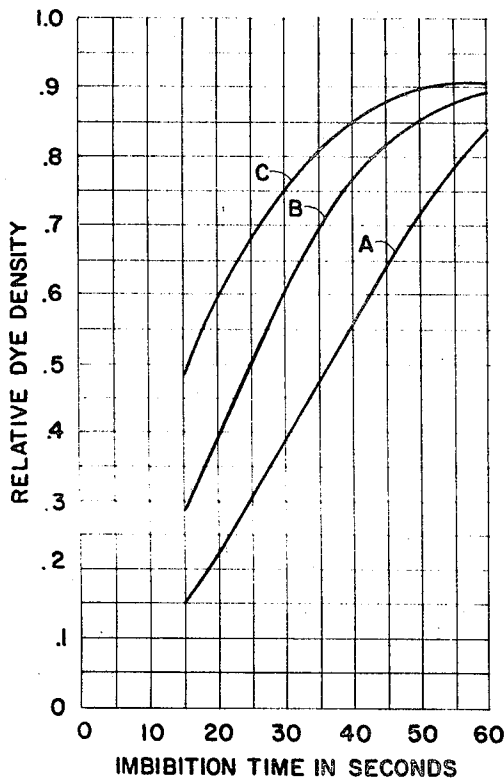


FIG. 3

INVENTORS
David P. Carlson
and
BY Jerome X. Reid
Brown and Mikelka
and
Robert M. Ford
ATTORNEYS

July 15, 1969

D. P. CARLSON ET AL

3,455,685

NOVEL PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

Filed Dec. 30, 1965

3 Sheets-Sheet 3

FIG. 4

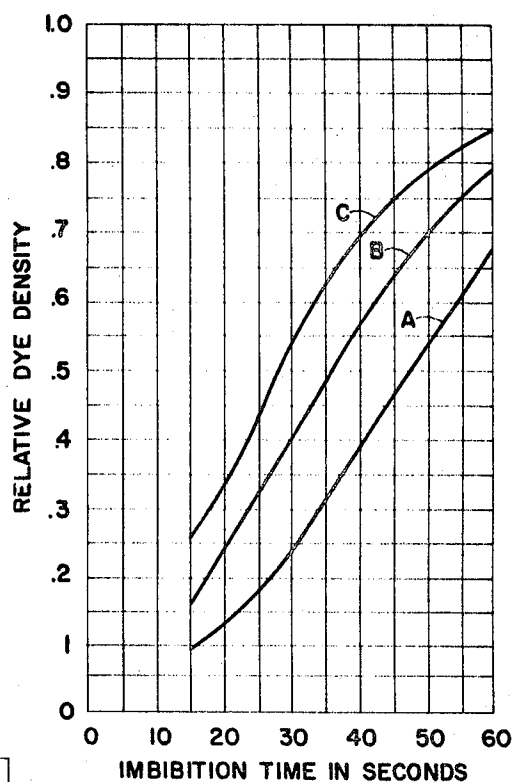
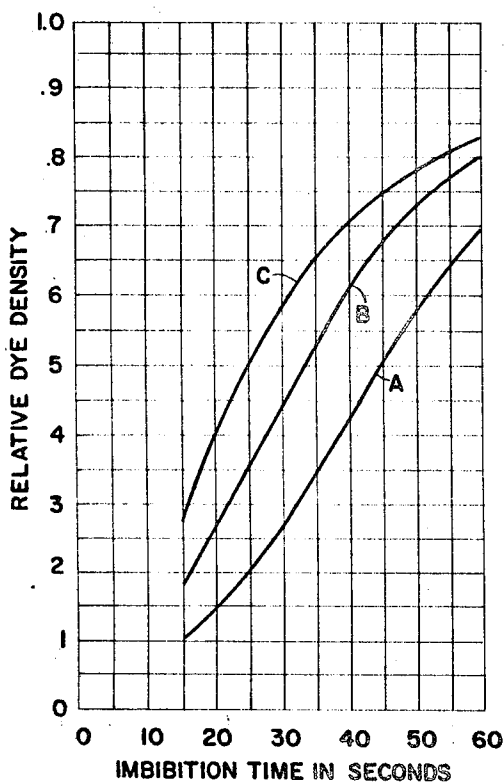


FIG. 5

INVENTORS
David P. Carlson
and
Jerome X. Reid
Brown and Mikulka
and
Robert M. Ford
ATTORNEY

1

2

3,455,685

NOVEL PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

David P. Carlson, Westborough, and Jerome L. Reid, Watertown, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

Continuation-in-part of application Ser. No. 488,355, Sept. 20, 1965. This application Dec. 30, 1965, Ser. No. 517,572

Int. Cl. G03c 7/20, 5/54, 7/28

U.S. Cl. 96—3

18 Claims

ABSTRACT OF THE DISCLOSURE

A process for forming diffusion transfer images in color which comprises the steps of exposing a photosensitive element comprising a plurality of layers; applying to said photosensitive element an aqueous alkaline processing composition which comprises, in solution, alkali metal hydroxide, lead, triethanolamine, and hydroxyalkyl ether substituted polymer; effecting thereby development of said exposed photosensitive element; forming thereby an imagewise distribution of mobile dye; at least a portion of said mobile dye being transferred by imbibition to a superposed image-receiving element comprising a plurality of layers; and separating said image-receiving element from superposed relationship with said photosensitive element, subsequent to dye image formation.

This application is a continuation-in-part of our co-pending U.S. application Ser. No. 488,355, filed Sept. 20, 1965 and now abandoned.

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

The primary objects of the present invention are to provide photographic products and compositions particularly adapted for employment in diffusion transfer photographic color processes; to provide photographic products which include a photosensitive element which comprises at least one photosensitive emulsion having preferably associated therewith, as a color image-forming component, a dye of predetermined color which is a silver halide developing agent and a fluid photographic transfer composition specified hereinafter; to provide photographic diffusion transfer products comprising a photosensitive element and a fluid photographic transfer composition, of the last-identified type, in combination with a photographic diffusion transfer image-receiving element comprising a plurality of essential layers including a common support carrying a solution dyeable polymeric layer, as detailed hereinafter.

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

The invention accordingly comprises the products and compositions 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; and

FIGS. 2, 3, 4, and 5 are each graphic illustrations of the density versus processing time relationship of each dye constituting a multicolor transfer image, wherein the transfer image employed for each of FIGS. 2 and 3 was prepared according to the present invention and the transfer image employed for each of FIGS. 4 and 5 was prepared according to the procedures of the prior art.

U.S. Patents Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1963; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; 2,802,735, issued Aug. 13, 1957, disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized which comprise, at least in part, reacting one or more developing agents and one or more color formers to provide a positive color image on a superposed image-receiving layer. U.S. Patent No. 3,019,124, issued Jan. 30, 1962, disclosed the manufacture of photographic color screen elements; and U.S. Patents Nos. 2,968,554, issued Jan. 17, 1961 and 2,983,606, issued May 9, 1961 disclose diffusion transfer processes wherein a color screen element is utilized to provide a multicolor positive image to a superposed image-receiving layer. U.S. Patent No. 2,774,668, issued Dec. 18, 1956, the copending U.S. application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956, now U.S. Patent No. 3,345,135 and the previously cited U.S. Patent No. 2,983,606 disclose diffusion transfer processes wherein complete dyes are utilized to provide a positive color image to a superposed image-receiving layer.

As disclosed in U.S. Patent No. 2,983,606, issued May 9, 1961, a photosensitive element containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion may be exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition, positioned intermediate the photosensitive element and the image-receiving layer, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain

agents adapted to mordant or otherwise fix the diffused un-oxidized 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 using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer 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 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. 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.

Another technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the previously noted U.S. Patents Nos. 2,968,554 and 2,983,606. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen prepared in accordance with the disclosures of said patents, comprises minute red-sensitized emulsion elements, minute green-sensitized elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

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 additional 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; 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 sulfolbenzal 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-aldyl- α,β -carboxamides with N-hydroxyalkyl- α,β -unsaturated carboxamides, as disclosed in U.S. Patent No. 3,069,263; copolymers of vinyl-phthalimide and α,β -unsaturated carboxylic acids, as disclosed in U.S. Patent No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β -unsaturated 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-cycloaldyl- 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 solution distributed in the polymeric binder, with appropriate solvent, or mixture of solvents, and the resultant subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic 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 No. 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 comprises a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, preferably an inert timing or spacer layer, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

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

The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the 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 terminat-

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

The inert spacer layer of the aforementioned 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-vinylpyridine, 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 gelatin 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, alternately, employing any of the various floc 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 Neblette, C. B. Photography Its Materials and Processes, 6th Ed., 1962.

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

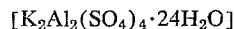
The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of silver, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, or silver iodobromide,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

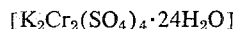
The emulsions may also be stabilized with the salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, as described in U.S. Patents Nos. 2,566,245 and 2,566,263; the mercury compounds of U.S. Patents Nos. 2,728,663; 2,728,664 and 2,728,665; the triazoles of U.S. Patent No. 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.," vol. 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



and chrome alum



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, 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 bis-glycolic 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 the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivative, as described in U.S. 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 has now been quite unexpectedly discovered that if the processing composition employed to effect the photographic diffusion transfer color process previously described is specifically formulated to comprise an aqueous processing composition which includes, in solution, alkali metal hydroxide, lead, triethanolamine, and a hydroxyalkyl ether substituted polymer, wherein the alkali metal hydroxide is present in a concentration sufficient to provide a pH in excess of about 13 to the composition, the hydroxyalkyl ether substituted polymer and soluble lead are each present in a concentration sufficient to provide to the composition an apparent viscosity of at least 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m., and at a temperature of 25° C., at termination of transfer processing, in general, at a pH below about 13, and the triethanolamine is present in a concentration sufficient to inhibit cross-linking of the polymer by the soluble lead at the concentration of hydroxyl ions initially present in the processing composition, at a pH above about 13, then significant improvements in brilliance, density, hue and saturation of the transfer image color characteristics are achieved, when compared with prior art processing compositions providing substantially identical rheological properties, at the termination of the transfer processing time interval.

In addition, it has been further found that when the last-described processing composition additionally

contains soluble zinc, still further such significant improvements may be achieved with reference to the last-identified transfer image.

Specifically, employment of the instant formulated fluid processing composition provides significantly higher transfer image, maximum dye densities, greater cyan, magenta and yellow dye saturation and improved red, green and blue hues, per unit processing time employed for the production of color transfer images, when employed in the previously described dye diffusion transfer processes employing an image-receiving element possessing the above-described polymeric acid layer, as compared with prior art fluid processing compositions, at termination of transfer processing, which, at the same processing temperature, possess substantially identical rheological properties.

In general, the processing formulation previously described will be specifically formulated to comprise, by weight, an aqueous solution containing about 2 to 5% hydroxyalkyl ether substituted polymer, 4 to 15% alkali metal hydroxide, 0.05 to 1.5% lead, and 0.1 to 2% triethanolamine, in combination, and preferably additionally contains 0.05 to 1.5% zinc.

As examples of hydroxyalkyl ether substituted polymers, mention may be made of hydroxyalkyl ether substituted cellulose polymers such as hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, etc.; hydroxyalkyl ether substituted vinyl polymers such as hydroxyethyl polyvinyl alcohol, hydroxypropyl polyvinyl alcohol, etc.; and the like. Of the preceding polymers hydroxyethyl cellulose has been found to comprise the preferred water-soluble hydroxyalkyl ether substituted polymer.

As is well known to those skilled in the art, the processing composition adapted to effect diffusion transfer processing of a photographic film unit should possess such rheological properties, for example, sufficiently high viscosity, as to provide the processing composition with the requisite dimensional stability to facilitate the stripping, or removal, of the composition from contact with the transfer image-carrying element, subsequent to transfer image formation. Specifically, as previously mentioned, when the fluid processing composition is to be applied to the photosensitive emulsion stratum by being spread thereon, generally as a relatively thin and uniform layer intermediate that stratum and a superposed image-receiving layer, it is disclosed to preferably include a viscosity increasing compound comprising a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and stable film with sufficient dimensional stability to facilitate the stripping of same. Such film-forming materials generally comprise relatively high molecular weight polymeric substances distributed in the processing composition. However, in order to obtain a processing composition with the dimensional stability desirable for separation or stripping, it has been traditionally recognized that a sacrifice in dye transfer image formation characteristics, per unit processing time, must be acceded to. The distribution of a film-forming polymeric substance within the processing composition, in a sufficient concentration to provide the desired rheological properties, in effect provides an impediment to the transfer of dye components through the polymer containing processing composition. Specifically, the addition of the film-forming polymers traditionally employed in the diffusion transfer art in their customary concentrations generally provides, in effect, a physical and/or chemical barrier to the imbibition transfer of the dye through the processing compositions, which, in turn, results in decreased transfer image-dye maximum density, saturation, hue, process speed, and the like, per unit processing time, as a necessary concomitant of achieving the processing composition dimensional stability desired for effecting separation of the positive print from contact with the composition.

However, as previously mentioned, it has now been found that a processing composition formulated in accordance with the instant disclosure provides, subsequent to transfer processing, substantially the same rheological properties as that provided by prior art processing compositions employing a concentration of the designated polymer considerably in excess of that necessitated by the instant invention, for example, a concentration containing approximately double the percentage, by weight, of polymer, and substantially ameliorates the above-described disadvantages inherent in the employment of viscosity increasing agents, with respect to the positive transfer image's characteristics.

In explanation of the effect provided by the processing composition of the present invention, but not bound by the accuracy of the proposed theoretical explanation, it is believed that the triethanolamine compound inhibits the plumbite ion component from cross-linking the hydroxyalkyl ether cellulose polymer, at the concentration of hydroxyl ions present in the processing formulation, as applied to the photoexposed photosensitive element. However, during processing, hydroxyl ions are removed from the processing composition, upon contact with the polymeric acid stratum of the image-receiving layer as previously described, which, in turn, is believed to decrease the inhibitory effects of the triethanolamine with respect to the plumbite ion, and which, in turn, at that stage of processing, that is, toward the termination of processing, effectually cross-links the hydroxyalkyl ether substituted polymer, thereby providing the requisite dimensional stability necessary to effect separation of the processing composition from contact with the print-receiving element.

In addition, when, during processing, the hydroxyl ions are removed from the processing composition by the polymeric acid stratum of the image-receiving layer to such an extent that the pH of the processing composition falls below about 13, the previously soluble zinc ion forms a relatively insoluble zinc hydroxide which, in turn, precipitates from the solution as a fibrous filamentary material physically entrained within the polymeric matrix. Thus, in addition to the potential decrease in the concentration of free hydroxyl ions present by reason of the formulation of the insoluble zinc hydroxide precipitate and the resultant decrease in the inhibitory effects of the triethanolamine, with its concomitant cross-linking of the polymer by the plumbite ion, the presence of the fibrous filamentary zinc hydroxide precipitate entrained within the cross-linked polymeric matrix additionally enhances the dimensional stability of the resultant polymeric structure and thus additionally facilitates separation of the processing composition from contact with the print-receiving element.

The alkali metal hydroxide, designated for employment in the processing composition, may comprise any one or more of such hydroxides including, singly or in combination, sodium, potassium, lithium, cesium, etc., hydroxides.

The lead detailed for employment in the processing composition may be provided by any one or more of the various conventional soluble lead salts which do not deleteriously affect the photographic system such as lead nitrate, oxide, sulfate, and the like.

The zinc detailed for employment may be provided by any one or more of the various conventional soluble zinc salts which do not deleteriously affect a photographic system, such as zinc nitrate, oxide, sulfate, chloride, and the like.

As detailed in FIG. 1 of 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; a layer 14 containing a magenta dye developer; a layer 15 comprising a green-sensitive silver halide emulsion; an interlayer 16; 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 FIG. 1, the multilayer exposed photosensitive element 25 is shown in processing relationship with an image-receiving element 26 and a layer 20 of the previously described 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. After a suitable imbibition period, generally in the order of about one minute at room temperature, during which at least a portion of the dye developer associated with unexposed areas of each of the emulsions is transferred to superposed image-receiving element 26, the latter element is separated to reveal the positive multicolor image.

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

A series of photosensitive elements were prepared by coating, in succession, on a gelatin subbed cellulose triacetate film base, the following layers:

(1) A layer of the cyan dye developer 1,4-bis-(β -[hydroquinonyl - α - methyl]-ethylamino) - 5,8 - dihydroxy-anthraquinone dissolved in diethyl lauramide dispersed in gelatin and coated at a coverage of 159 mgs./ft.² of dye and 119 mgs./ft.² of gelatin;

(2) A red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of 245 mgs./ft.² of silver, and 147 mgs./ft.² of gelatin;

(3) A layer of gelatin coated at a coverage of 240 mgs./ft.²;

(4) A layer of the 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 69 mgs./ft.² of dye and 104 mgs./ft.² of gelatin;

(5) A green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of 116 mgs./ft.² of silver and 70 mgs./ft.² of gelatin;

(6) A layer of gelatin coated at a coverage of 126 mgs./ft.²;

(7) A layer of the yellow dye developer 4-(p[β -hydroquinonyl-ethyl] - phenylazo) - 3 - (N-n-hexylcarboxamido) - 1 - phenyl - 5 - pyrazolone, dissolved in diethyl lauramide, dispersed in gelatin and coated at a coverage of 58 mgs./ft.² of dye and 58 mgs./ft.² of gelatin;

(8) A blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of 71 mgs./ft.² of silver and 43 mgs./ft.² of gelatin; and

(9) A layer containing 4'-methylphenyl hydroquinone dissolved in diethyl lauramide, dispersed in gelatin and coated at a coverage of 26 mgs./ft.² of 4'-methylphenyl hydroquinone and 26 mgs./ft.² of gelatin.

The required number of image-receiving elements were 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 was 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 was then coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinyl-pyridine, at a coverage of approximately 600 mgs./ft.², to provide a polymeric image-receiving layer approximately 0.40 mil thick. The

thus-prepared image-receiving element was then baked at 180° F. for 30 minutes and then allowed to cool.

A plurality of photosensitive elements were then individually exposed and processed, at room temperature (75° F.), by spreading an aqueous liquid processing composition comprising:

Water	cc	100
Potassium hydroxide	g	11.2
Hydroxyethyl cellulose (3200 cps.)	g	2.0
Lithium nitrate	g	0.7
Potassium thiosulfate	g	0.45
Benzotriazole	g	3.5
Benzyl- α -picolinium bromide	g	2.0
Triethanol amine	g	0.7
Lead nitrate	g	1.0

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 15 seconds, the picture door of the camera was opened and the image-receiving element separated from the remainder of one film assembly. After an imbibition period of 30 seconds a second image-receiving element was separated. After an imbibition period of 45 seconds a third image-receiving element was separated. After an imbibition period of 60 seconds the fourth image-receiving element was separated.

The last-identified procedure was then repeated employing a processing composition comprising:

Water	cc	100
Potassium hydroxide	g	11.2
Hydroxyethyl cellulose (3200 cps.)	g	2.0
Lithium nitrate	g	0.7
Potassium thiosulfate	g	0.45
Benzotriazole	g	3.5
Benzyl- α -picolinium bromide	g	2.0
Triethanol amine	g	0.7
Lead nitrate	g	1.0
Zinc nitrate	g	0.5

For the purpose of providing comparative, or control, data, the preceding procedure was first repeated employing a processing composition comprising:

Water	cc	100
Potassium hydroxide	g	11.2
Hydroxyethyl cellulose (3200 cps.)	g	3.8
Lithium nitrate	g	0.7
Potassium thiosulfate	g	0.45
Benzotriazole	g	3.5
Benzyl- α -picolinium bromide	g	2.0
Zinc nitrate	g	0.5

and then repeated employing a processing composition comprising:

Water	cc	100
Potassium hydroxide	g	11.2
Hydroxyethyl cellulose (3200 cps.)	g	3.8
Lithium nitrate	g	0.7
Potassium thiosulfate	g	0.45
Benzotriazole	g	3.5
Benzyl- α -picolinium bromide	g	2.0

which latter processing composition exhibited substantially the same rheological properties, at termination of the optimum transfer processing interval, that is 60 seconds, as the test formulation.

The resultant test and comparative maximum dye density versus imbibition time relationship of each dye constituting the multicolor transfer images are represented by the graphic illustrations detailed in FIGS. 2, 3, 4 and 5. In each of the figures, Curves A, B and C represent, respectively, the cyan, magenta and yellow dye maximum density versus imbibition time relationship of the respective multicolor transfer images. FIG. 2 represents the maximum dye density versus imbibition time relationship of each dye constituting the multicolor transfer images pro-

vided employing the processing composition detailed above containing lead and triethanolamine. FIG. 3 represents the dye maximum dye density versus imbibition time relationship of each dye constituting the multicolor transfer images provided by the employment of the above described processing composition containing lead, triethanolamine and zinc. FIG. 4 represents the maximum dye density versus imbibition time relationship of each dye constituting the multicolor transfer images prepared employing the above described control processing composition containing zinc and sufficient additional hydroxyethyl cellulose as to insure analogous rheological properties to the preceding test materials. FIG. 5 represents the maximum dye density versus imbibition time relationship of each dye constituting the multicolor transfer images prepared employing the control processing composition detailed above containing neither zinc nor lead, but retaining sufficient additional hydroxyethyl cellulose to provide the same rheological properties, at termination of the optimum processing interval, that is, 60 seconds, as the test formulations. Comparative examination of the resultant curves for each individual dye forming the test and control transfer images clearly details the magnitude of the effects achieved employing the present invention. It should also be noted that the advantages achieved by reason of the instant detailed procedure are effective at relatively low photographic process temperatures, that is, 45° F., with a magnitude corresponding to that achieved at room temperature. Direct visual observation of the multicolor transfer images provided by means of the instant detailed procedure reveals that such images have improved color brilliance, hue, saturation and isolation, when compared with control subject materials.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Patent No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary 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 processing composition or they may be initially incorporated, at least in part, in any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in U.S. 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 photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera ap-

paratus 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. Patent 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 apredetermined 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 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. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various latter 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 supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminums; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

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

The rupturable containers may be constructed in accordance with the disclosures set forth in U.S. Patent No. 2,634,888. The containers employed are, in general, constructed from a blank comprising a flexible, deformable, three-ply sheet material comprising, respectively, an outer layer of kraft paper, a layer of metal foil and an inner layer or liner of a thermoplastic resin, or two-ply sheet material comprising the latter two strata. The container blank is folded upon itself such as to provide a fluid-containing cavity and exhibiting a sealed passage adjacent to an edge thereof which may be substantially uniformly unsealed throughout a predetermined length of the sealed passage upon application of stress to the container.

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 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.

Throughout the specification and appended claims, the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive element. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive element will be a positive and the image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

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.

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

What is claimed is:

1. A process of forming diffusion transfer images in color which comprises the steps of exposing a photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent; applying to said photosensitive element an aqueous alkaline processing composition which comprises, in solution, alkali metal hydroxide, lead ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide being present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at termination of transfer processing, said triethanolamine being present in a concentration sufficient to inhibit cross-linking of said polymer by said lead ions at the concentration of hydroxyl ions initially present in said processing composition; effecting thereby development of said exposed photosensitive element; forming thereby an image-wise distribution of mobile dye, as a function of the point-to-point degree of exposure of said element; transferring by imbibition, at least a portion of said image-wise distribution of mobile dye to a superposed image-receiving element comprising a plurality of layers including a processing composition permeable and dyeable polymeric layer and a processing composition permeable polymeric hydroxyl ion acceptor layer, to provide to said dyeable polymeric layer a dye image; and separating said

image-receiving element from superposed relationship with said photosensitive element, subsequent to dye image formation.

2. A process of forming diffusion transfer images in color as defined in claim 1, wherein said hydroxyalkyl ether substituted polymer is hydroxyethyl cellulose.

3. A process of forming diffusion transfer images in color which comprises the steps of exposing a photosensitive layer comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent; applying to said photosensitive element an aqueous alkaline processing composition which comprises, in solution, about 2 to 5% hydroxyalkyl ether substituted cellulose, 4 to 15% alkali metal hydroxide, 0.05 to 1.5% lead ions and 0.1 to 2% triethanolamine, by weight; effecting thereby development of said exposed photosensitive element; forming thereby an image-wise distribution of mobile dye, as a function of the point-to-point degree of exposure of said element; transferring by imbibition, at least a portion of said image-wise distribution of mobile dye to a superposed image-receiving element comprising a plurality of layers including a processing composition permeable and dyeable polymeric layer and a processing composition permeable polymeric acid layer, to provide to said dyeable polymeric layer a dye image; and separating said image-receiving element from superposed relationship with said photosensitive element, subsequent to transfer dye image formation.

4. A process of forming diffusion transfer images in color which comprises the steps of exposing a photosensitive layer comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent; applying to said photosensitive element an aqueous alkaline processing composition which comprises, in solution, alkali metal hydroxide, lead ions, zinc ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at termination of transfer processing, said triethanolamine being present in a concentration sufficient to inhibit cross-linking of said polymer by said lead ions at the concentration of hydroxyl ions initially present in said processing composition; effecting thereby development of said exposed photosensitive element; forming thereby an image-wise distribution of mobile dye, as a function of the point-to-point degree of exposure of said element; transferring, by imbibition, at least a portion of said image-wise distribution of mobile dye to a superposed image-receiving element comprising a plurality of layers including a processing composition permeable and dyeable polymeric layer and a processing composition permeable polymeric hydroxyl ion acceptor layer, to provide to said solution dyeable polymeric layer a dye image; and separating said image-receiving element from superposed relationship with said photosensitive element, subsequent to dye image formation.

5. A process of forming diffusion transfer images in color as defined in claim 4, wherein said hydroxyalkyl ether substituted polymer is hydroxyethyl cellulose.

6. A process of forming diffusion transfer images in color which comprises the steps of exposing a photosensitive layer comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent; applying to said photosensitive element an aqueous alkaline processing composition which comprises, in solution, about 2 to 5% hydroxyalkyl ether substituted cellulose.

lose, 4 to 15% alkali metal hydroxide, 0.05 to 0.5% zinc ions, and 0.1 to 2% triethanolamine, by weight; effecting thereby development of said exposed photosensitive element; forming thereby an imagewise distribution of mobile dye, as a function of the point-to-point degree of exposure of said element; transferring, by imbibition, at least a portion of said imagewise distribution of mobile dye to a superposed image-receiving element comprising a plurality of layers including a processing composition permeable and dyeable polymeric layer and a processing composition permeable polymeric hydroxyl ion acceptor layer, to provide to said solution dyeable polymeric layer a dye image; and separating said image-receiving element from superposed relationship with said photosensitive element, subsequent to dye image formation.

7. A multicolor diffusion transfer process which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers having positioned contiguous, respectively, yellow, magenta and cyan dyes, each of said yellow, magenta and cyan dyes being silver halide developing agents, by permeating said photosensitive element with a fluid processing composition which comprises, in solution, alkali metal hydroxide, lead ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide being present in a concentration efficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at termination of transfer processing, said triethanolamine being present in a concentration sufficient to inhibit cross-linking of said polymer by said lead ions at the concentration of hydroxyl ions initially present in said processing composition; immobilizing said yellow, magenta and cyan dyes, as a function of development; forming thereby an imagewise distribution of mobile yellow, magenta and cyan dyes, as a function of the point-to-point degree of exposure of said element; transferring by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element comprising a plurality of essential layers including, in sequence, a support layer, a solution permeable polymeric hydroxyl ion acceptor layer, and a solution dyeable and permeable polymeric layer, to provide to said dyeable polymeric layer a multicolor transfer dye image, and subsequent to substantial transfer dye image formation, transferring, by imbibition, at least a sufficient portion of said hydroxyl ions of said processing composition to said polymeric hydroxyl ion acceptor layer to provide a reduction of the pH of said composition to less than about 13; and then separating said image-receiving element from said superposed relationship with said photosensitive element.

8. A multicolor diffusion transfer process which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers having positioned contiguous, respectively, yellow, magenta and cyan dyes, each of said yellow, magenta and cyan dyes being silver halide developing agents, by permeating said photosensitive element with a fluid processing composition which comprises, in solution, alkali metal hydroxide, lead ions, zinc ions, triethanolamine, and ether substituted polymer, said alkali metal hydroxide being present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead

ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at termination of transfer processing; said triethanolamine being present in a concentration sufficient to inhibit cross-linking of said polymer by said lead ions at the concentration of hydroxyl ions initially present in said processing composition; immobilizing said yellow, magenta and cyan dyes, as a function of development; forming thereby an imagewise distribution of mobile yellow, magenta and cyan dyes, as a function of the point-to-point degree of exposure of said element; transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element comprising a plurality of essential layers including, in sequence, a support layer, a solution permeable polymeric hydroxyl ion acceptor layer, and a solution dyeable and permeable polymeric layer, to provide to said dyeable polymeric layer a multicolor transfer dye image, and subsequent to substantial transfer image formation, transferring, by imbibition, at least a sufficient portion of said hydroxyl ions of said processing composition to said polymeric hydroxyl ion acceptor layer to provide a reduction of the pH of said composition to less than about 13; and then separating said image-receiving element from said superposed relationship with said photosensitive element.

9. A photographic processing composition which comprises an aqueous alkaline solution containing, in solution, alkali metal hydroxide, lead ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide being present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at a pH less than about 13, said triethanolamine being present in a concentration sufficient to inhibit the cross-linking of said polymer by said lead ions at a pH greater than about 13.

10. A photographic processing composition which comprises, in solution, about 2 to 5% hydroxyalkyl ether substituted cellulose, 4 to 15% alkali metal hydroxide, 0.03 to 1.5% lead ions, and 0.1 to 2% triethanolamine, by weight.

11. A photographic processing composition as defined in claim 10, wherein said hydroxyalkyl ether substituted cellulose comprises hydroxyethyl cellulose.

12. A photographic processing composition which comprises an aqueous alkaline solution containing, in solution, alkali metal hydroxide, lead ions, zinc ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide being present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at a pH less than about 13, said triethanolamine being present in a concentration sufficient to inhibit the cross-linking of said polymer by said lead ions at a pH greater than about 13.

13. A photographic processing composition which comprises, in solution, about 2 to 5% hydroxyalkyl ether substituted cellulose, 4 to 15% alkali metal hydroxide, 0.05 to 1.5% lead ions, 0.05 to 0.5% zinc ions, and 0.1 to 2% triethanolamine, by weight.

14. A photographic processing composition as defined in claim 13, wherein said hydroxyalkyl ether substituted cellulose comprises hydroxyethyl cellulose.

19

15. A photographic film assembly for the performance of a diffusion transfer process for the formation of a color transfer image which comprises, in combination, a photo-sensitive element, an image-receiving element and container means for releasably retaining a fluid processing composition, said elements and said container means being operatively secured together so that said container is capable of releasing its fluid contents, upon superpositioning of said elements, intermediate the opposed surfaces of said elements, said photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent, said image-receiving element comprising a plurality of layers including a processing composition permeable and dyeable polymeric layer and a processing composition permeable polymeric hydroxyl ion acceptor layer, and said processing composition comprising, in solution, alkali metal hydroxide, lead ions, triethanolamine, and hydroxyalkyl ether substituted polymer, said alkali metal hydroxide being present in a concentration sufficient to provide a pH in excess of about 13 to said composition, said hydroxyalkyl ether substituted polymer and said lead ions being present in a concentration sufficient to provide to said composition an apparent viscosity of at least about 100,000 cps., as measured by a Brookfield Viscosimeter, Model LVT, using a No. 4 spindle at 0.3 r.p.m. and a temperature 25° C., at a pH

20

less than about 13, said triethanolamine being present in a concentration sufficient to inhibit the cross-linking of said polymer by said lead ions at a pH greater than about 13.

16. A photographic film assembly as defined in claim 15, wherein said hydroxyalkyl ether substituted polymer comprises hydroxyethyl cellulose.

17. A photographic film assembly as defined in claim 15, wherein said processing composition includes zinc ions.

18. A photographic film assembly as defined in claim 17, wherein said hydroxyalkyl ether substituted polymer comprises hydroxyethyl cellulose.

References Cited

UNITED STATES PATENTS

3,183,090	5/1965	Jarrett	96—29
3,239,339	3/1966	Dershowitz	96—29
3,241,963	3/1966	Green, et al.	96—29
3,297,441	1/1967	Green, et al.	96—29

NORMAN G. TORCHIN, Primary Examiner

ALFONSO T. SUROPICO, Assistant Examiner

U.S. Cl. X.R.

96—29; 106—186, 194