DYEABLE LAYER
SPACER LAYER
POLYMERIC ACID LAYER
SUPPORT LAYER

FIG. 1

POLYVINYL ALCOHOL

FIG. 2

40/60 COPOLYMER OF DIACETONE ACRYLAMIDE-
ACRYLAMIDE

FIG. 3

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Jan. 14, 1969

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3,421,893

ACRYLIC POLYMER SPACER LAYERS FOR PHOTOGRAPHIC ELEMENTS

Filed May 26, 1967

Sheet 2 of 2

50/50 COPOLYMER OF
DIACETONE ACRYLAMIDE—
DIMETHYL AMINOETHYL
ACRYLATE

FIG. 4

0.4 MILS
0.325 MILS
0.150 MILS

0
0
50 60 70 80 90 100
TEMPERATURE °F

180
150
120
90
60
30
0

TIME IN SECONDS
(ALKALI PERMEABILITY)

100
90
80
70
60
50

TEMPERATURE °F

90/10 COPOLYMER OF
N-ISOPROPYLACRYLAMIDE—
DIMETHYL AMINOETHYL
ACRYLAMIDE

FIG. 5

0.125 MILS

0
0
50 60 70 80 90 100
TEMPERATURE °F

180
150
120
90
60
30
0

TIME IN SECONDS
(ALKALI PERMEABILITY)

0.25 MLS

0.4 MLS

0.1 MILS

0.05 MILS

0.01 MILS

0.005 MILS

0.001 MILS

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ABSTRACT OF THE DISCLOSURE

Novel image receiving elements for diffusion transfer color processes which include polymeric layers which maintain the high pH concentration necessary during development by their temperature-related permeability to alkaline solutions.

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

In processes of the type set forth in U.S. Patent No. 2,983,606, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkaline as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this image-wise distribution of unoxidized dye developer is transferred, by imbition, 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 distributing the image-wise distribution thereof to provide the reversed or positive color image of the developed image. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable immersion 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 developing function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho-para-amino substituted hydroxyphenyl groups. In general, the developing function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes. One technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in U.S. 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 redsensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element such as is disclosed in co-pending U.S. application Ser. No. 565,135, filed on Feb. 13, 1956 and now U.S. Patent No. 3,345,135, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement for the type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

Co-pending U.S. application Ser. No. 234,864, filed Nov. 1, 1962, now U.S. Patent 3,362,819 discloses image-receiving elements particularly adapted for employment in the preceding diffusion transfer processes which elements comprise a support layer having a photosensitive coating on one surface thereof, in sequence, a polymeric acid layer; an inert timing or spacer layer; and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substances.

As set forth in the last-mentioned 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 tertiarmethyl 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, non-diffusible 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 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 hydro- genphthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polyethylene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrophthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfite substituted aldehydes, e.g., α-, β-, or γ-pyrazoline 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 controlled so 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 hydroquinonemethyl developing radicals diffuse from the negative to the positive as the quaternary ammonium group, sodium or other alkali salt. The diffusion rate of such dye image-forming components is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves 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 poly-
determined time interval, irrespective of the temperature-dependent diffusion rate of the alkaline processing composition utilized; and novel image-receiving elements particularly adapted for employment in photographic diffusion transfer color processes, which comprise composite structures which include a permeable polyvinyl amide material; and novel transfer processes employing same.

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

A still further object of the present invention is to provide image-receiving elements particularly adapted for employment in photographic diffusion transfer color processes, which elements include a plurality of layers comprising, in sequence, a support layer; a first polymeric alkali metal ion acceptor layer; a second alkali metal ion temperature-inversely permeable polymeric layer comprising a polyvinyl amide; and a third polymeric layer adapted to be dyed from an alkaline solution; and novel transfer processes particularly adapted to employ same.

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

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

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

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

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

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

FIG. 4 is a graphical representation of the temperature-alkali permeability characteristics of films of a 50:50 copolymer of diaacetone acrylamide and dimethylaminoethyl acrylamide at various thicknesses when contacted with the processing composition of Example 1, below.

FIG. 5 is a graphical representation of the temperature-alkali permeability characteristics of films of a 90:10 copolymer of N-hexypropyl acrylamide and dimethylaminoethyl acrylamide at various thicknesses when contacted with the processing composition of Example 1, below.

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, disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized, which techniques comprise, at least in part, reacting one or more developing agents and alkali 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, discloses the manufacture of photographic color screen elements; and U.S. Patents Nos. 2,968,554, issued Jan. 17, 1961, and 2,983,605, 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 and the previously cited U.S. Patent No. 2,982,606 disclose diffusion transfer processes wherein dyes are utilized to provide a positive color image into a superposed image-receiving layer.

The objects of the present invention, detailed hereinabove, are accomplished by employment in photographic diffusion transfer color processes of the preceding type of a novel image-receiving element which comprises a plurality of essential layers including, in sequence, a support layer; a polymeric acid layer; a permeable polymeric spacer layer which acts as a mechanism to compensate for temperature changes in the composition; and a permeable, solution dyeable polymeric layer.

Specifically, the image-receiving element preferably comprises a flexible composite structure including a plurality of polymeric layers which comprise, in sequence, a support layer; a polymeric alkali ion acceptor layer, for example, an alkali metal or quaternary ammonium ion acceptor layer; a polymeric layer having predetermined temperature-permeability characteristics; and a polymeric layer dyeable from contact with a dye-containing alkaline solution.

As disclosed in the aforementioned copending application Ser. No. 234,864, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when illumination is effected at temperatures above room temperature, for example, at 95 to 100°F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

It has been disclosed in copending U.S. application Ser. No. 447,100, filed on Apr. 9, 1965, now abandoned, that the diffusion rate of an alkali processing medium through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 90° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was disclosed to be especially true of alkali traversing an inert spacer layer possessing optimum alkali-permeability characteristics within the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 50° F., the last-mentioned inert spacer layer was found to provide an effective diffusion barrier timewise preventing effective interaction of the inert spacer layer by alkali having temperature depressed diffusion rates. This barrier resulted in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer image's color definition.

It was further disclosed in the last-mentioned application, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a
permeable polymeric layer exhibiting permeability inversely dependent upon temperature, and specifically a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defect result from the aforementioned over-extended pH maintenance and/or premature pH reduction were obviated.

As examples of polymers disclosed in the last-mentioned application which exhibit inverse temperature-dependent permeability to alkali, mention was made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methyl cellulose, partial acetal of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

Specifically, the spacer layer of the last-described print-receiving element comprises a permeable polymeric layer exhibiting, in a photographic diffusion transfer environment, a photographic processing-composition permeability inversely dependent on processing temperature, when compared with, or measured against, polymers disclosed in the art for the identified photographic use. In general, such polymers as are particularly adapted for formulation of the spacer layer exhibit the property of being relatively soluble in cold water, that is, at water at a temperature of less than about 40° C, the precise temperature being dependent upon the polymer specifically selected for employment; and relatively insoluble in hot water, that is, at a temperature above about 80° C, the precise temperature being dependent upon the polymer specifically selected.

A relatively large number of such polymers are substantially insoluble in caustic photographic processing media over the range of photographic diffusion transfer processing temperatures. Such polymers, however, are permeable to photographic alkaline processing composition as a function of their swelling, which, in turn, is believed to be a function of the free energy of solution decrease caused, at least in part, by the heat evolved as a result of the interaction between the polymer and the processing composition solvent and by an increase of the entropy of the system. This free energy decrease is believed to lessen with increased temperature of the environment and result in a decreased swelling, and thus decrease photographic processing composition permeability with such temperature increase.

It has now been unexpectedly discovered that if the spacer layer of the last-identified copending application generally comprises a polyvinyl amide and preferably a polycrylamide, vastly superior cold temperature processing performance, for example, processing at a temperature in the order of about 50° F is achieved.

Specifically, as a preferred embodiment, employment of polyvinyl amides which are temperature-inverting in the manner detailed above provides in a cold temperature processing environment higher transfer image maximum densities, increased photographic speed, increased flexibility of coating layer thickness parameters, and, in multicolor photographic diffusion transfer processes, improved color isolation.

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

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

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 spacer layer, therefore, should provide the system which it comprises with the proper dye permeation-temperature properties so that dye may diffuse from the photosensitive part of the system to the receiving sheet, as a function of development, in order to form a positive image in the receiving sheet within a predetermined time, irrespective of the processing temperature employed.

The temperature inverting characteristic of members of the class of polymers useful in the instant invention is probably attributable to the presence of a predetermined balance of hydrophilic groups and hydrophobic 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 inter-actions responsible for temperature inversion are forces such as hydrogen-bonding and hydrophobic-hydrophobic bonding forces.

It has unexpectedly been found that a class of polymers based on the polyvinyl amide groups of the formula:

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[CH₂-CR₂]ₙ
```

where R is a carboxamido or a carbamyl group; provide far better results when considering the above-mentioned criteria, and those to be discussed below, than other groups of polymers heretofore employed for the instant purpose.
Preferred polymers within the scope of the present invention comprise polyvinyl amides of the formulae:

- \( \text{CH-CH} \) \( R_1 = \text{R}_2 \)
- \( \text{N} \text{HCH}_2 \text{OH} \)

and most preferably polyacrylamides of the last-identified formula, wherein \( R_1 \) and \( R_2 \) may be hydrogen, alkyl, and aryl groups. It should be understood that within the scope of the instant invention as claimed, both \( R_1 \) and \( R_2 \) are intended to encompass equivalents thereof and accordingly may comprise substituted or unsubstituted alkyl and aryl groups, etc. to conform to the desires of the operator. In general, then, \( R_1 \) and \( R_2 \) may be any group which functionally contributes the desired hydrophilicity or hydrophobicity to the polymer. Polymers useful for the instant invention are prepared by incorporating into each polymer molecule predetermined amounts of hydrophilic and hydrophobic groups so that a proper balance is achieved which results in the desired permeation characteristics at desired temperatures and thicknesses. Such polymers include graft, as well as random copolymers, in the former category would 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.

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-propyl)acrylamide; N-isopropyl acrylamide; N-\( \beta \)-hydroxy ethyl) acrylamide; N-[\( \beta \)-dimethylamino]ethyl acrylamide; N-4-t-butyl acrylamide; N-(acrylamido)ethyl trimethyl ammonium p-toluene sulfonate; N-\{\( \beta \)-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 butylamide; acrylamido acetamide; methacrylamido acetamide; 2-[2'-methacrylamido-3' - methyl butylamido]acetamide; N-vinyl pyrrolidone; diacetone acrylamide; dimethyaminomethyl acrylamide; dimethylaminomethyl acrylate; vinyl acetate, etc.

Polymers which are found to be useful in the instant process are:

1. Poly N-methacrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \)

2. Poly N-methylmethacrylamide:
   \( \text{CH}_3 \text{CHCH}_2 \text{N} \text{HCH}_2 \)

3. Poly N-ethylacrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \)

4. 31:1:1 Terpolymer of N-ethylacrylamide: N-methylolacrylamide: acrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

5. Poly N-ethylmethacrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

6. 9:1 copolymer of N - ethylacrylamide: 2 - vinyl pyridine
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

7. Poly N,N-dimethylacrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

8. Poly N,N-dimethylmethacrylamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

9. Poly N-\( \alpha \)-(propyl) acrylicamide:
   \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

10. Poly N-isopropylacrylamide:
    \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

11. 9:1 copolymer of N-isopropylacrylamide: acrylamide:
    \( \text{CHCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{HCH}_2 \text{OH} \text{N} \text{HCH}_2 \text{N} \text{H}_2 \)

12. 3:1 copolymer of N-isopropylacrylamide: methacrylamide:
(13) 9:1 copolymer of N-isopropylacrylamide: methyl acrylate

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_3
\end{align*}
\]

(14) 1:1 copolymer of N-isopropylacrylamide: N-ethylacrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(15) 3:1 copolymer of N-isopropylacrylamide: N-methylolacrylamide:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(16) 3:2 copolymer of N-isopropylacrylamide: N,N-dimethylacrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(17) 19:1 copolymer of N-isopropylacrylamide: acrylic acid

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{COOH} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(18) 3:1 copolymer of N-isopropylacrylamide: N-(β-hydroxyethyl)acrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(19) 9:1 copolymer of N-isopropylacrylamide: N-[β-(dimethylamino)ethyl]acrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(21) 9:1 copolymer of N-isopropylacrylamide: dimethylamino ethyl methacrylate

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(22) Poly N-isopropylmethacrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} & \quad \text{(CH)}
\end{align*}
\]

(23) Poly N,N-diethylacrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} & \quad \text{(CH)}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} & \quad \text{(CH)}
\end{align*}
\]

(25) Poly N-t-butylacrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} & \quad \text{(CH)}
\end{align*}
\]

(26) 1:2 copolymer of N-t-butylacrylamide: N-[β-(dimethylamino)ethyl]acrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

(28) 3:1 copolymer of methyl acrylate: N-[β-(dimethylamino)ethyl]acrylamide

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CO} \\
\text{NHCH} \quad \text{(CH)} & \quad \text{OCH}_2 \text{OH}
\end{align*}
\]
The present invention will be illustrated in greater detail in conjunction with the following specific example which sets out a representative photographic product and process which, however, is intended to be illustrative and not of limiting effect.

Example 1

An image-receiving element was prepared by coating a cellulose nitrate abscoted baryta paper with the partial butyl ester of polyethylene/maile acid anhydride copolymer which may be prepared by refluxing, for 14 hours, 300 gms. of a DX-840-31 resin (trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity polyethylene/maile anhydride), 140 gms. of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.7 mil thick. The external surface of said acid layer was coated with a solution of a 40:60 copolymer of diacetone acrylamide and acrylamide to provide a polymeric spacer layer approximately 0.53 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 mg./ft.², to provide a polymeric image-receiving layer approximately 0.30 mil thick. The thus prepared image-receiving element was then baked at 180°F. for 30 minutes and then allowed to cool.

The 40:60 copolymer of diacetone acrylamide and acrylamide was prepared as follows: 155 g. of diacetone acrylamide and 86 g. of acrylamide were dissolved in 201.0 l of distilled water. 20 ml. of isopropanol was added. The solution was aerated with nitrogen for one hour and 3.2 g. of (NH₄)₂S₂O₇ and 1.6 g. of Na₂S₂O₇ were added simultaneously. The solution was stirred under nitrogen overnight and coated.

A multicolor, multilayer photosensitive element was prepared in a manner similar to that disclosed in the aforementioned co pending U.S. application Ser. No. 565,133 and detailed hereinbefore. In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum. In turn, the emulsions had dispersed behind them in water-immiscible organic solvents and contained in separate gelatin polymer layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A gelatin interlayer was between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements may comprise, for example, 1,4-bis (a-methyl-β-hydroquinonyl-ethylami no) - 3.8 - dihydroxyanthraquinone (a cyan dye developer); 2- (p-(2′,5′-dihydroxyphenethyl)-phenylazo)-4-isoproxy-1-naphthol (a magenta dye developer); and 1-phenyl - 3- n-hexylcarbamyl - 4-p (hydroquinonyl ether phenylazo)-5-pyrrozole (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Patent No. 3,134,764.
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3,421,893

18

250 g. of N-isopropylacrylamide and 34.9 g. of N\(\beta\)-(dimethylamino)ethylacrylamide were dissolved in 2.56 l. of distilled water. 5 ml. of isopropanol was added and the solution was aerated with nitrogen for one hour. The solution was adjusted to pH 6.4 by addition of concentrated nitric acid and then 0.30 g. of sodium bisulphite and 0.30 g. of potassium persulphate were added simultaneously. The solution was stirred under nitrogen overnight and then dialysed against running water for 24 hours.

A comparison was made with a control formulated according to Example I. Examination of the resultant images showed the following differential maximum densities:

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{\max}) polyvinyl alcohol</th>
<th>(\Delta D_{\max}) control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.79</td>
<td>1.63</td>
</tr>
<tr>
<td>75</td>
<td>1.43</td>
<td>1.24</td>
</tr>
<tr>
<td>100</td>
<td>1.77</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Optimum thickness for the spacer layer with the instant compound was found to be 0.175 mil and excellent temperature-permeability properties were detected. Thicker coats, such as 0.3 mil, gave muddy reproduction at high temperatures. Adhesion was not as good as some of the other compounds tested.

Example III

The procedure of Example I was carried out using a receiving sheet which comprised a spacer layer comprising a 3:1 copolymer of N-isopropyl acrylamide and N-methyl acrylamide instead of the 40:60 copolymer of diacetone acrylamide and acrylamide and it was coated to a thickness of 0.1 mil. The 3:1 copolymer of N-isopropyl acrylamide and N-methyl acrylamide was prepared as follows:

23.06 g. of N-isopropyl acrylamide and 7.8 g. of N-methylacrylamide were dissolved in 300 ml. of distilled water and cooled to 5°C with an ice bath. The solution was aerated with nitrogen for one hour and 0.026 g. of \(Na_{2}SO_{4}\) and 0.034 g. of \(NaBrO_{3}\) were added simultaneously. The solution was stirred under \(Na_{2}\) for three hours and then an additional 0.026 g. of \(Na_{2}SO_{4}\) and 0.034 g. of \(NaBrO_{3}\) were added. The solution was stirred under \(Na_{2}\) overnight and then dialysed against running water for 48 hours.

A comparison was made with a control formulated according to Example I. Examination of the resultant images showed the following differential maximum densities:

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{\max}) polyvinyl alcohol</th>
<th>(\Delta D_{\max}) control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.71</td>
<td>1.66</td>
</tr>
<tr>
<td>75</td>
<td>1.45</td>
<td>1.68</td>
</tr>
<tr>
<td>100</td>
<td>1.74</td>
<td>1.65</td>
</tr>
</tbody>
</table>

The optimum thickness of the instant compound for the intended purpose was found to be 0.1 mil. Fine reproduction at room temperature and at 50° were produced. However, at 100° some "saltiness" occurred when the thickness of the layer was increased to 0.2 and 0.3 mil.

Example IV

The procedure of Example I was carried out using a receiving sheet which comprised a spacer layer comprising a 6:3:1 terpolymer of diacetone acrylamide and acrylamide and \(N(\beta\)-(dimethylamino)ethyl)methacrylate instead of the 40:60 copolymer of diacetone acrylamide and it was coated to a thickness of 0.325 mil. The 6:3:1 terpolymer of diacetone acrylamide and acrylamide was prepared as follows:

In addition to producing far better differential maximum transfer densities, particularly in the cold, it has been found that a somewhat more glossy image is achieved using the spacer layer of the instant invention than the standard polyvinyl alcohol spacer layer.

The optimum thickness with the instant compound was found to be 0.55 mil. Thinner coats of 0.45, 0.3 and 0.2 mils caused either a gappy appearance at high temperatures or reagent sticking to the surface at low temperatures. Good pH drop with the processing composition was detected. Likewise the compound was found to be quite immobile and adhered very well within the composite structure.

Example II

The procedure of Example I was carried out using a receiving sheet which comprised a spacer layer comprising a 9:1 N-isopropyl acrylamide and N\(\beta\)-(dimethylamino)ethylacrylamide instead of the 40:60 copolymer of diacetone acrylamide and acrylamide, which was coated to a thickness of 0.175 mil. The 9:1 N-isopropyl acrylamide and N\(\beta\)-(dimethylamino)ethylacrylamide was prepared as follows:

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

between said image-receiving element and said exposed multicolor element as they were brought into superposed relationship in a Polaroid Land Pack Camera. After an incubation of 60 seconds or 135 seconds, for tests carried out at 75° and 100° F. or 40° and 50° F., respectively, the pH of the processing composition having been reduced below about 8, the image-receiving element was separated from the remainder of the film assembly.

For purposes of comparison, an image-receiving element was fabricated in accordance with the above-described procedure with the exception that the spacer layer comprised a layer of polyvinyl alcohol approximately 0.30 mil thick, and was coated from a solution comprising 1% polyvinyl alcohol in water. The last-prepared image-receiving element was then processed, as detailed above, at various temperatures.

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 Quamog Lac Macbeth Densimeter.

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{\max}) 40:60 copolymer of diacetone acrylamide and acrylamide spacer layer</th>
<th>(\Delta D_{\max}) polyvinyl alcohol control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.73</td>
<td>1.70</td>
</tr>
<tr>
<td>70</td>
<td>1.73</td>
<td>1.70</td>
</tr>
<tr>
<td>100</td>
<td>1.73</td>
<td>1.70</td>
</tr>
</tbody>
</table>

The optimum thickness with the instant compound was found to be 0.55 mil. Thinner coats of 0.45, 0.3 and 0.2 mils caused either a gappy appearance at high temperatures or reagent sticking to the surface at low temperatures. Good pH drop with the processing composition was detected. Likewise the compound was found to be quite immobile and adhered very well within the composite structure.
N\((\text{dimethylamino})\text{ethyl}\)methacrylate was prepared as follows: 30.5 g. of diaceteone acrylamide, 4.71 g. of N\((\beta\text{(dimethylamino)})\text{ethyl}\)acrylamide, and 6.4 g. of acrylamide were dissolved in 300 ml. of distilled water. 1 ml. of isopropanol was added and the solution was adjusted to a pH of 6.4 by addition of concentrated nitric acid. The solution was deaerated with \(N_2\) for one hour and 0.05 g. of \(K_2\text{SO}_4\) and 0.05 g. of NaHSO\(_4\) were added simultaneously. The solution was stirred under \(N_2\) overnight and then dialyzed against running water for 24 hours.

A comparison was made with a control formulated according to Example I. Examination of the resultant images showed the following differential maximum densities:

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{max}), polivinyl alcohol control spacer layer</th>
<th>(\Delta D_{max}), polyvinyl alcohol control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.66</td>
<td>1.78</td>
</tr>
<tr>
<td>70</td>
<td>1.80</td>
<td>1.90</td>
</tr>
<tr>
<td>80</td>
<td>2.00</td>
<td>2.10</td>
</tr>
</tbody>
</table>

Optimum thickness was found to be 0.325 mil. The instant compound displayed excellent temperature-permeability latitude. Thinner thicknesses, such as 0.2 mil, caused "gappiness" at high temperatures.

**Example V**

The procedure of Example I was carried out using a receiving sheet which comprised a spacer layer comprising a 50:50 copolymer of diaceteone acrylamide and N\((\beta\text{(dimethylamino)})\text{ethyl}\)acrylamide instead of the 40:60 copolymer of diaceteone acrylamide and acrylamide, and it was coated to a thickness of 0.5 mil. The 50:50 copolymer of diaceteone acrylamide and dimethylamino ethyl acrylate was prepared as follows: 30.74 g. of diaceteone acrylamide and 42.9 g. of N\((\beta\text{(dimethylamino)})\text{ethyl}\)acrylate were dissolved in 1.0 l. of distilled water. 2 ml. of isopropanol was added and the solution was adjusted to a pH of 6.4 by addition of concentrated nitric acid. The solution was deaerated with nitrogen for one hour and 0.10 g. of NaHSO\(_4\) and 0.10 g. of \(K_2\text{SO}_4\) were added simultaneously. The solution was stirred under nitrogen overnight and then dialyzed against running water for 18 hours.

A comparison was made with a control formulated according to Example I. Examination of the resultant images showed the following differential maximum densities:

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{max}), 50:50 terpolymer of diaceteone acrylamide, acrylamide and N((\beta\text{(dimethylamino)})\text{ethyl})acrylamide control spacer layer</th>
<th>(\Delta D_{max}), polyvinyl alcohol control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.61</td>
<td>1.60</td>
</tr>
<tr>
<td>60</td>
<td>1.75</td>
<td>1.70</td>
</tr>
<tr>
<td>70</td>
<td>1.85</td>
<td>1.80</td>
</tr>
<tr>
<td>80</td>
<td>2.05</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Optimum thickness was found to be 0.5 mil. Good inversion latitude was detected except for some dullness at very high or very low temperature. Thinner coats of, for example, 0.3 mil. caused severe "salting" at 50°.

**Example VI**

The procedure of Example I was carried out using a receiving sheet which comprises a spacer layer comprising a 3:2 copolymer of diaceteone acrylamide and N\((\beta\text{(dimethylamino)})\text{ethyl}\)acrylamide instead of the 40:60 copolymer of diaceteone acrylamide and acrylamide and it was coated to a thickness of 0.35 mil. The 3:2 copolymer of diaceteone acrylamide and N\((\beta\text{(dimethylamino)})\text{ethyl}\)acrylamide was prepared as follows:

<table>
<thead>
<tr>
<th>Temperature, °F</th>
<th>(\Delta D_{max}), 3:2 copolymer of diaceteone acrylamide and N((\beta\text{(dimethylamino)})\text{ethyl})acrylamide control spacer layer</th>
<th>(\Delta D_{max}), polyvinyl alcohol control spacer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.67</td>
<td>1.70</td>
</tr>
<tr>
<td>60</td>
<td>1.81</td>
<td>1.75</td>
</tr>
<tr>
<td>70</td>
<td>1.95</td>
<td>1.80</td>
</tr>
<tr>
<td>80</td>
<td>2.12</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Optimum thickness of the instant compound was found to be 0.35 mil. Excellent temperature-permeability and flexibility characteristics were noted. Adhesion between the spacer layer and the polymer top layer was fair.

Although the preferred image-receiving layer is a mixture of polyvinyl alcohol and poly-4-vinylpyridine, the invention is not limited thereto. Other image-receiving layers are known in the art and may be employed. Similarly, while the preferred embodiment effects development in the presence of a quaternary ammonium compound (as disclosed and claimed in Patent No. 3,173,786, issued on Mar. 3, 1965) and particularly a quaternary ammonium compound capable of forming an active methylene base in alkalii, the invention is not so limited, even though the advantages are most dramatic when such an active methylene quaternary ammonium salt is used.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; alumnum; polymethacrylic acid, methyl and ethyl esters, vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as adipic acid; and cellulose derivatives such as cellulose acetate, acetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

Where desired, the support for the image-receiving layer may be transparent or opaque. Suitable opacifying agents may be incorporated in the negative and/or positive to permit immobilization to be completed outside of a camera, i.e., in an area exposed to light actinic to the silver halide emulsions.

Use of the novel image-receiving elements of this invention makes feasible the use, over an extended range of ambient temperature, of image dyes which are pH sensitive, and particularly the use of dye developers having less pH insulation since the final pH of the image layer can be more accurately and reproducibly controlled.

Processing preferably is effected in the presence of an auxiliary or accelerating silver halide developing agent which is substantially colorless, at least in the unoxidized form. Particularly useful are substituted hydroquinones, such as phenylhydroquinone, 4'-methylphenylhydroquinone, tolulhydroquinone, tertiary-butylyhydroquinone, and 2,5-tritycine diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative. Particularly useful results are obtained when 4'-methylphenylhydroquinone is dispersed in one or more of the gelatin interlayers and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

As noted above, this invention contemplates reduction of the positive image pH to a level substantially preclud-
ing aerial oxidation of developer moieties. The provisions of antioxidants, such as arbutin, prior to exposure of the image to air to provide additional protection against oxidation also is within the scope of this invention. Since the reduction in pH continues for at least a short time after the positive image is separated from the negative, provision of such an antioxidant permits the positive to be separated at a slightly higher pH than would be otherwise desirable. It is also contemplated to provide other adjuvants, e.g., ultraviolet absorbers, effective to improve the light stability or other properties of the positive image. Thus, an ultraviolet absorber may be included in the processing composition and deposited on the image-receiving layer during immersion, or it may be present in a thin overcoat on the image-receiving layer prior to immersion.

In all preferred embodiments of this invention the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg. per foot

The invention of claim 2 wherein said polyacrylamide is a copolymer of N-isopropyl acrylamide and N-methylol acrylamide.

10. The invention of claim 2 wherein said polyacrylamide is a terpolymer of dialcetone acrylamide, acrylamide, and N-dimethylaminomethyl acrylate.

11. The invention of claim 2 wherein said polyacrylamide is a copolymer of dialcetone acrylamide and dimethylaminoethyl acrylate.

12. The invention of claim 2 wherein said polyacrylamide is a copolymer of dialcetone acrylamide and dimethylaminoethyl acrylate.

13. The invention of claim 1 wherein said polyvinyl amide is present in the form of an acid salt.

14. The invention of claim 2 wherein said polyacrylamide is present in the form of an acid salt.

15. A process for forming a diffusion transfer color image which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent, by contacting said element with an aqueous alkaline processing solution, immobilizing said dye in the exposed areas of said element as a result of development, 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 immersion at least a portion of said images distribution of mobile dye to a superposed image-receptive element which comprises a plurality of layers including, in sequence, a support layer; a polymeric acid layer; a permeable polymeric layer comprising a polyvinyl amide; and a solution dyeable and permeable polymeric layer to provide said dyeable polymeric layer a dye image, transferring by immersion subsequent to substantial positive image formation at least a portion of the ions of said alkaline solution through each of said permeable polymeric layers to said polymeric acid layer to thereby reduce the alkalfinity of the processing solution.

16. The invention of claim 15 wherein said polyvinyl amide is a polyacrylamide.

17. In 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 being contiguous to yellow, magenta and cyan dyes, respectively, each of said dyes being silver halide developing agents, by permeating said photosensitive element with an aqueous alkaline processing composition having an initial pH of not less than about 12; immobilizing said yellow, magenta and cyan dyes as a result of development; forming thereby an image-wise distribution of mobile yellow, magenta and cyan dye, as a function of the point-to-point degree of exposure of said element; transferring, by immersion, at least a portion of each of said image-wise distributions of mobile dye to a superposed image-receiving element comprising a plurality of essential layers including, in sequence, a support layer; a polymeric acrylamide acceptor layer; a permeable polymeric layer comprising a polyvinyl amide; and an alkaline solution dyeable and permeable polymeric layer, to provide said dyeable polymeric layer a multicolor dye image; transferring, by immersion, subsequent to substantial transfer image formation, at least a sufficient portion of the alkaline solution composition through each of said permeable polymeric layers to say polymeric acrylamide acceptor layer to thereby reduce a reduction of the pH of said composition to a pH of not greater than about 8, and then separating said image-receiving element from said superposed relationship.

18. The invention of claim 17 wherein said polyvinyl amide comprises a polyacrylamide.

19. The invention of claim 2 wherein said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-alkali permeability characteristics.

20. The invention of claim 3 wherein said polyvinyl amide is characterized by decreasing alkali solution permeability with increasing temperature.

21. The invention of claim 2 wherein said polyacrylamide contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide the polymer with predetermined temperature-alkali permeability characteristics.

22. The invention of claim 4 wherein said polyacrylamide is characterized by decreasing alkali solution permeability with increasing temperature.
19. The invention of claim 17 wherein said polyvinyl amide is characterized by decreasing alkali solution permeability with increasing temperature.

20. The invention of claim 18 wherein said polyacrylamide is characterized by decreasing alkali solution permeability with increasing temperature.

21. The invention of claim 18 wherein said polyacrylamide is a copolymer of diacetone acrylamide and acrylamide.

22. The invention of claim 18 wherein said polyacrylamide is a copolymer of N-isopropyl acrylamide and N\((\beta\text{-dimethylamino})\text{ethyl}\)acrylamide.

23. The invention of claim 18 wherein said polyacrylamide is a copolymer of N-isopropyl acrylamide and N-methylol acrylamide.

24. The invention of claim 18 wherein said polyacrylamide is a terpolymer of diacetone acrylamide, acrylamide and N-dimethylamino ethyl acrylate.

25. The invention of claim 18 wherein said polyacrylamide is a copolymer of diacetone acrylamide and di-methylamino ethyl acrylate.

26. The invention of claim 18 wherein said polyacrylamide is a copolymer of diacetone acrylamide and di-methylamino ethyl acrylate.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor</th>
<th>Classification</th>
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<tr>
<td>3,212,893</td>
<td>10/1965</td>
<td>Salminen</td>
<td>96—29</td>
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<td>3,225,283</td>
<td>6/1967</td>
<td>Barstow</td>
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<td>3,345,165</td>
<td>10/1967</td>
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ALFONSO T. SURO PICO, Assistant Examiner.

U.S. Cl. X.R.

96—3