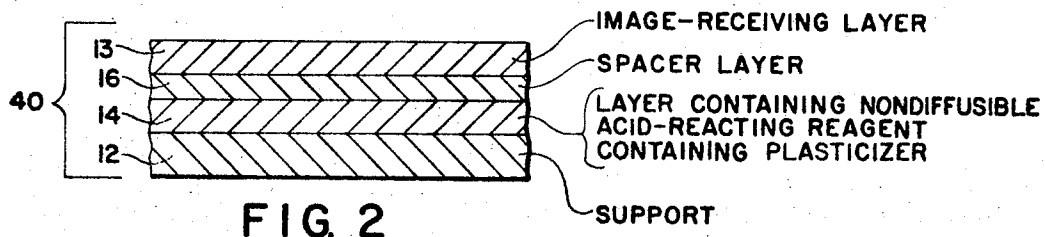
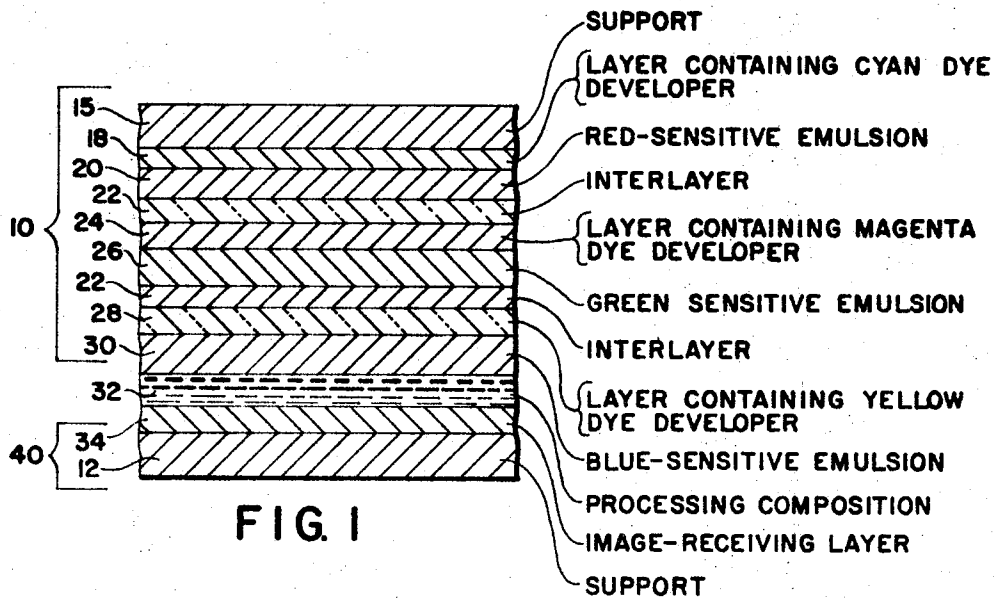


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DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCTS AND PROCESSES
COMPRISING ACID-REACTING REAGENTS AND POLYETHER BLOCK
COPOLYMERS AS PLASTICIZERS THEREFOR
Filed Sept. 23, 1968



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1

3,577,237

DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCTS AND PROCESSES COMPRISING ACID-REACTING REAGENTS AND POLYETHER BLOCK COPOLYMERS AS PLASTICIZERS THEREFOR

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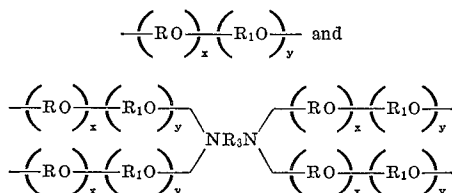
Int. Cl. G03c 7/00, 5/54

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27 Claims

ABSTRACT OF THE DISCLOSURE

Plasticization of the layer of a diffusion transfer image-receiving sheet containing an acid-reacting reagent may be accomplished by incorporating therein a compound selected from the group consisting of block polyether compounds of the formulae:



where R, R₁ and R₃ are alkylene groups and x and y are integers representing the molar ratio of respective blocks. Concomitant with the plasticization effect increased temperature latitude is imparted to the system.

This invention relates to photography and, more particularly, to photographic products and processes for forming photographic images in dyes by diffusion transfer processes.

U.S. Patent No. 2,983,606, issued May 9, 1961, to Howard G. Rogers, discloses processes employing dye developers to form color transfer images and products useful therein. U.S. Patent No. 3,345,163, issued Oct. 3, 1967, discloses the use of such dye developers in integral multilayer negatives to give multicolor transfer images. This invention is particularly concerned with an improvement in such diffusion transfer processes and, in particular, with the provision of novel diffusion transfer processes and products useful therein whereby images in dye developers are obtained which exhibit unobvious and unexpected properties.

An object of this invention is to provide novel image-receiving elements for use in diffusion transfer processes employing dye developers, and processes employing said novel image-receiving elements wherein the color transfer image is only slightly alkaline when it is separated from the exposed and developed photosensitive element.

Yet another object of this invention is to provide novel image-receiving elements adapted to effect a substantial reduction in the alkalinity of a color transfer image without interfering in the formation of the color transfer image.

A further object of this invention is to provide novel image-receiving elements containing a plasticized, nondiffusible acid-reacting reagent positioned in a layer adjacent the dye-receptive layer present in a diffusion transfer image-receiving element.

Still another object of this invention is to provide novel image-receiving elements which include a nondiffusible acid-reacting reagent containing a nonmigratable plasticizing composition.

A still further object of this invention is to provide a diffusion transfer image-receiving element containing a

2

nondiffusible acid-reacting reagent and a plasticizer which provides a temperature-inverse neutralization property to said acid-reacting agent with respect to alkaline compositions coming in contact therewith.

Another object of this invention is to provide novel diffusion transfer processes employing a photosensitive element and an image-receiving element which contains a layer of a polymeric acid plasticized with a material which imparts a temperature-inverse relationship to neutralization when said acid is contacted with an alkaline processing composition whereby the pH of the transfer image is reduced to very low levels prior to exposing any image dyes to air; and processing reagents which are harmful, or potentially harmful, to the image dyes are removed from effective proximity to such dyes by diffusion to said acid-containing layer.

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

The invention accordingly comprises 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:

FIG. 1 shows a photosensitive element in superposed relationship with an image-receiving element with a layer of processing liquid therebetween; and

FIG. 2 shows an image-receiving element containing a layer of a nondiffusible acid-reacting reagent with a plasticizer according to the instant invention admixed therewith, said image-receiving element being particularly useful in combination with the photosensitive element shown in FIG. 1.

As is now well known in diffusion transfer processes of the type contemplated herein, as set forth in detail, for example, in the aforementioned U.S. Patent No. 2,983,606, a processing composition is applied to an exposed photosensitive emulsion to effect development thereof and an imagewise distribution of diffusible, unoxidized dye developers is formed as a function of development. At least a portion of such diffusible dye developers is transferred imagewise to an image-receiving layer positioned in superposed relationship with said photosensitive emulsion. At the end of the appropriate imbibition period, the image-receiving layer is separated from its superposed relationship with the developed photosensitive emulsion to permit viewing of the transfer image.

In general, in the processes with which this invention is concerned, a photosensitive element containing a silver halide emulsion is exposed and wetted with a fluid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In one preferred embodiment, the photosensitive element contains a layer of dye developer, and a liquid processing composition is applied to the photosensitive element in a thin, substantially uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element.

The processing compositions employed in diffusion transfer processes of the type contemplated herein usually are highly alkaline, having a pH in excess of 12, and frequently have a pH of the order of 14 or even greater. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide

emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in the developed areas, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, 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. At least part of each such imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer, which layer receives a depthwise diffusion of the transferred unoxidized dye developer, without appreciably disturbing the imagewise distribution thereof, to provide a reversed or positive, colored image of the image developed in each silver halide emulsion. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer.

In an especially useful embodiment, the dye developers are dissolved in a water-immiscible solvent and the resulting solution is then dispersed in gelatin to provide the dye developer layers. Numerous examples of suitable dye developers are disclosed in the said U.S. Pat. No. 2,983,606 and copending applications noted therein. As set forth therein, a dye developer is a compound which is both a dye and a silver halide developing agent. Particularly useful and preferred dye developers are azo and anthraquinone dyes which contain one or more hydroquinonyl groups.

The above-mentioned U.S. Patent No. 2,983,606 discloses and claims a highly useful method of forming color images by diffusion transfer wherein the color-providing substances are dye developers. As set forth therein, a dye developer is a compound which is both a dye and a silver halide developing agent. Particularly useful and preferred dye developers are azo and anthraquinone dyes which contain one or more hydroquinonyl groups. It has been proposed that the silver halide developing group be linked to the chromophoric system of the dye developer through a suitable group of atoms which are effective to interrupt any system of conjugation and resonance between the silver halide developing group, e.g., a hydroquinonyl radical, and the chromophoric system or dye portion of the molecule. Such insulating linkages have been found to be quite effective in avoiding or essentially eliminating any significant change in the color characteristics of the dye developer by virtue of the hydroquinonyl group being oxidized to the quinone, e.g., by aerial oxidation of the dye developers in the separated image-receiving layer.

Although such oxidation may not change the characteristic color of the dye developer, such oxidation may have a material and substantial effect upon the stability to light of the resulting dye developer image, as set forth in U.S. Patent No. 3,362,819. It has been found that if, prior to exposing the surface of the image-receiving layer to air, the alkalinity or pH of the dye developer environment in the image-receiving layer is adjusted to a level at least substantially precluding alkaline oxidation of the developing radical, a tremendous and remarkable improvement in the stability to light of such dye developers is obtained. It has further been found that images of unusual brilliance and luminosity are obtained if the reduction in alkalinity is effected by diffusing the alkaline ions to an adjacent layer wherein they are captured and retained in place. It is with respect to these discoveries that this invention is concerned and particularly with the provision of products and processes for accomplishing these unobvious results.

The photographic transfer dye image frequently retains substantial amounts of photographic reagents, particularly alkali, with which it has been processed, even though the layer of processing composition is caused to adhere to and remain with the photosensitive layer. The presence

of these residual reagents may adversely affect the quality and stability of the image, particularly in the presence of significant quantities of alkali. For example, if the receiving layer is highly alkaline, oxidation by atmospheric oxygen of unreacted developing agent or other components of the processing composition is quite likely to occur, and such reactions or subsequent reactions may impart as stain or otherwise discolor the transfer image, and particularly the highlights thereof.

It has been proposed to treat the surface of the separated image-receiving layer with a solution which is effective to remove (as by a washing action), neutralize or otherwise render such residual processing reagents relatively innocuous. It has been found, however, where the transfer image is formed by the dye developer transfer process of the aforementioned U.S. Pat. No. 2,983,606, and particularly where development is effected in the presence of a quaternary ammonium compound which is capable of forming an active methylene base in alkali, that the color of some dye developer images nevertheless may change or otherwise become degraded. Although the exact mechanism of this color change is not known, it is believed to be due, at least in part, to a coupling reaction between the active methylene quaternary ammonium compound and an oxidation product of the dye developer or of an auxiliary or accelerating developing agent. This type of color change appears to be due to the formation of a new chromophore which, when superposed on the original chromophore, frequently results in dulling or "greying" of the image, and is particularly noticeable in reproduction of sky and clouds. Such a color-forming reaction has been observed particularly where the dye developer or the auxiliary developing agent contains a hydroquinonyl group, in which event the oxidation product involved may be the quinone or semiquinone. In addition to such undesirable color changes, it also has been found that the oxidation of the transferred dye developers may be an initial step in fading when the images are exposed to light.

Application of an acidic print-coating composition, e.g., a solution containing boric acid, as disclosed and claimed in U.S. Pat. No. 3,239,338, to the positive image is, of course, effective to reduce the pH of residual processing composition. In some instances, and particularly where such a print-coating composition is applied very shortly after separating the positive from the negative, at least part of the color degradation may even be reversed, i.e., it appears that at least some reactions responsible for such color degradation may go through an intermediate stage (or product) which is reversible by the print-coating operation. While such prompt print-coating frequently is effective to prevent a significant amount of permanent color degradation, it is not feasible in practice to print-coat quickly enough to prevent an adverse effect on light stability due to oxidation.

It has been discovered, as set forth in aforementioned U.S. Pat. No. 3,362,819, that if, prior to exposure to atmospheric oxygen, the pH of the image layer is reduced to a level at which aerial oxidation of the developer radical of the dye developers or of auxiliary developing agents, e.g., hydroquinonyl radicals, does not occur, the undesired color degradation does not occur. In addition, the light stability of the dye images is substantially increased.

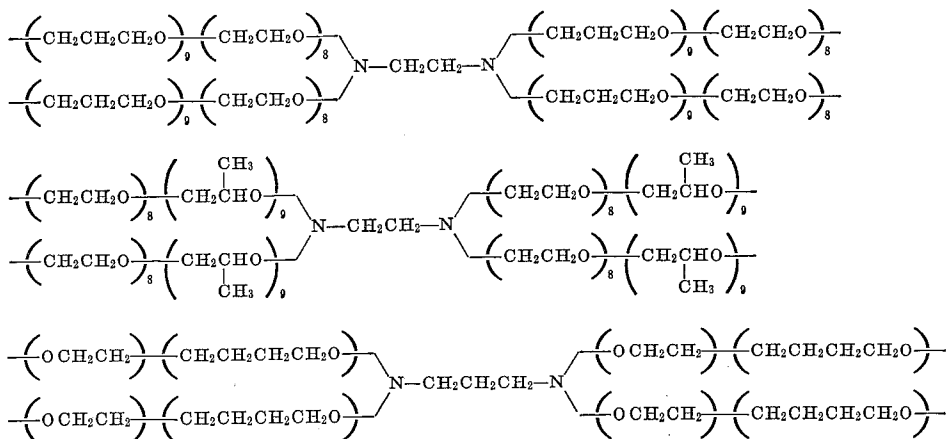
The aforesaid U.S. Pat. No. 3,362,819 discloses and claims the use in such diffusion transfer processes of an image-receiving element containing a nondiffusible acid-reacting reagent, or alkali-ion receptor, in a layer adjacent the image-receiving layer. This nondiffusible acid-reacting reagent, which preferably is a polymeric acid, acts to capture alkali ions thereby appreciably reducing the pH or alkalinity of the surface of the image-receiving layer. This reduction in pH is effected after the image dyes have been transferred to the image-receiving element and prior to exposure of the image layer to air. As a result, the alkalinity or pH of the dye developer environment in the image-

5

receiving layer is adjusted to a level at least substantially precluding aerial oxidation of the developing radical of the transferred dye developers. Transfer images obtained employing such image-receiving elements are characterized by unusual brilliance and luminosity, and the image dyes exhibit a remarkable increase in stability to light.

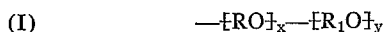
The acid-reacting reagent-containing layer includes non-diffusible acid groups, for example, acid groups attached to a polymer so as to be nondiffusible. This method of pH reduction, in effect, washes the image layer by internally diffusing the alkali ions and salt-forming reagents out of the image layer and into said acid-reacting layer where they are precipitated. The acid-reacting layer thus may be considered to be a mordant for alkali. In practice, a layer containing an acid-reacting polymer and, particularly, a polymer containing free carboxyl groups is provided in the image-receiving element and is positioned adjacent the support.

It has generally been found that the layer containing the alkali-neutralizing acid-reacting reagent is inherently brittle and very swift to react with alkali in contact therewith and cause premature neutralization. Bending an image-receiving sheet beyond a moderately tight curve might easily cause cracks in the layer containing the acid-reacting reagent thereby rendering any image on said image-receiving sheet to be unattractive. Accordingly, it is considered beneficial to plasticize the acid-reacting reagent-containing layer included in a diffusion transfer receiving sheet with a material which will not migrate and will present no deleterious functionality to the photographic process in which it is utilized.



It has been unexpectedly found that a certain class of compositions will not only provide plasticizer functionality to the acid-reacting reagent-containing layer to provide the requisite flexibility to the image-receiving sheet, but will, in addition, alter the temperature-neutralization characteristics of the acid-reacting reagent and will present markedly improved performance for the process of the present invention. More particularly, this class of compound has been found to impart an inverse temperature-neutralization property to the receiving sheet; that is, when compared to an unplasticized receiving sheet, the alkali-neutralization time at a low temperature is shorter; i.e., the rate of neutralization of alkali by the acid-reacting reagent in the plasticized sheet is greater than that of the unplasticized sheet; and in the hot, the neutralization time of the plasticized sheet is longer than that required for an unplasticized sheet.

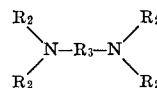
Generically, the plasticizers of the present invention are block polyethers and may be visualized with respect to the following formulae:



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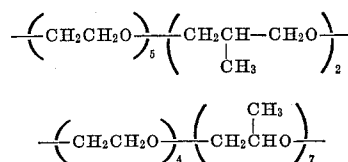
where: R and R₁ are alkylene groups, preferably containing less than five carbon atoms, and x and y are integers representing the molar ratio of respective blocks; and

(II)



where: R₂ is represented by the polymeric Formula I, above and R₃ is an alkylene group containing less than five carbon atoms; and mixtures thereof. x and y are integers wherein x/y represents the molar ratio of RO blocks to R₁O blocks reduced to lowest terms, and are not absolute molecular values. For example, in a compound containing 300 moles RO and 200 moles R₁O, x would be 3, and y would be 2. It is to be understood that within the scope of the instant invention, at the operator's option, R₂, as represented in the structural formula next above, may or may not comprise the same polymeric moiety since it may be determined that for various purposes, having different substituents in the R₂ positions might be beneficial to the intended process.

Exemplary compounds which are included in the present invention are:



where, as above, the ratio of the respective block subscripts are considered to be molar ratios and do not reflect absolute molecular values.

While generic Formulae I and II, above, denote the plasticizers utilized in the present invention as repeating structures, it should be appreciated that the compounds of I and each of the R₂ chains of II may comprise a single X block and a single Y block capped off by a hydrogen atom. In the most preferred embodiment R is ethylene and R₁ is 2-propylene. In the same context it has been found that in order to provide acceptable results, the preferred compounds should contain between ten and eighty weight percent of polyethylene oxide, which results in a polyethylene oxide to polypropylene oxide molar ratio range of from 0.15 to 5.25. The preferred compounds contain twenty-five to fifty-five weight percent of polyethylene oxide resulting in a preferred polyethylene oxide to polypropylene oxide molar ratio range of 0.47 to 1.6. Within the preferred range, the best results have been obtained with the Formula I type compound when the polyethylene oxide is present in about thirty to forty weight percent; and with the branched compound when the polyethylene oxide is about forty to fifty weight percent.

The molecular weights of the compounds denoted above for utilization in the process of the present invention range from about 1,000 to 50,000. Preferred molecular weights for the Formula I compounds are between 3,000 and 9,000; and, for the branched compounds are between 9,000 and 16,000.

As has been alluded to above, it has been found that in a diffusion transfer photographic process, deleterious results due to aerial oxidation, etc. generally fail to occur after the pH of residual processing composition in the image-receiving sheet has reached approximately 8. It is accordingly evident that the most desirable neutralization period, that is, the time it takes the alkaline processing composition to go from its initial pH down to 8, should be substantially as long as is required for development and dye migration. If the pH is reduced too quickly, development will be incomplete and the resulting image will be imperfect. If neutralization occurs too long after the completion of development, aerial oxidation renders the image less attractive. In a typical diffusion transfer system, for example, Type 108 film sold by Polaroid Corporation, Cambridge, Massachusetts, it has been found that in order to so neutralize processing composition with a pH above 13, it requires approximately 120 seconds at 75° F. and 10 seconds at 100° F. At 50° F., after 600 seconds, the neutralization still has not progressed to pH 8. From the above figures, it will be seen that in the hot, neutralization occurs so rapidly that development has not had an opportunity to go to completion. At room temperature, or 75° F., a 120 second neutralization period will produce perfectly acceptable images. It will additionally be noted that at 50° F. deleterious results due to aerial oxidation are inevitable since pH reduction is so slow. It has been found that by utilizing the compounds of the present invention, not only will the acid-reacting reagent layer of the image-receiving sheet be plasticized to an extent that it can withstand sufficient deformation without cracking, but it provides an added bonus in that it imparts inverse temperature performance to the system; that is, it will speed up neutralization in the cold, it will slow down neutralization in the hot, and it will allow neutralization at room temperature to remain at approximately any predetermined level. Accordingly, it will be seen that with the addition of one compound to the polymeric acid layer, two problems have been solved, that is, the temperature neutralization characteristics of the sheet have been improved and it has been rendered more flexible without causing deforming cracks or sets.

Concomitant with the advantages discussed above, it will be evident that the maximum dye densities obtained in a given image, particularly red highlights in the hot, will be increased since, as is shown by the drawings, the cyan dye is last to migrate to the receiving sheet and is generally insufficient to provide the desired saturation due to too rapid a pH dropoff. This produces what is termed a "gappy" picture which may be defined as a picture deficient only in cyan dye. It will be appreciated that the magenta and yellow dyes will have come across before the cyan, principally due to the logistics of their placement within the photosensitive element. In the event that neutralization is not completely accomplished as, for example, when the temperature is too low, "salting" results, that is, aerial oxidation of the cyan chromophores takes place and the print assumes a hazy cast.

In order to provide the aforementioned inverse temperature-neutralization effect to the acid-reacting reagent layer, the plasticizers of the present invention render the alkali permeation vs. time curve of that layer less positive. This may be visualized as a counterclockwise rotation of the curve substantially about its room temperature point thereby reducing the neutralization time in the cold and raising it in the hot while allowing room temperature neutralization to remain essentially unchanged. While it is not intended that the slope of the alkali permeation vs. temperature curve of the acid-reacting reagent-containing

layer ever become negative, this "less positive" relativity to the curve defining alkali permeation of the unplasticized polymeric acid coat has been found to produce surprising results completely unanticipated prior to the present invention.

The temperature inversion-neutralization characteristics provided by the acid-reacting reagent-containing layer may be determined by altering the respective proportions of the polymeric blocks which comprise the plasticizers of the present invention. In the preferred embodiment, as further discussed above, the plasticized composition consists of a 4:7 block copolymer of polyethylene oxide and polypropylene oxide. This ratio has been found to present the most acceptable inversion characteristics thus far attained in the environment of the present invention.

Many of the temperature-inverting plasticizers of the present invention are commercially available and may be procured from Wyandotte Chemical Co. under the trade names "Plurionics" and "Tetronics."

The temperature inverting characteristics of the class of polymeric plasticizers useful in the instant invention is probably attributable to the presence of a predetermined balance of hydrophobic groups to hydrophilic groups in the polymer molecule. The probable mechanism through which temperature inverse neutralization of the present invention occurs is due to the formation of hydrogen bonds between the hydrophilic portion of the polymer and the hydrogen of the processing composition. As the temperature is increased, hydrogen bonding is discouraged due to thermal destruction. This system thereupon, with increasing temperature, takes the form of a less hydrated, less swollen, therefore, less permeable polymer as a function of the increase in temperature. Accordingly, it will be seen that at high temperatures there is more of a barrier to diffusing alkali while at low temperatures the barrier effect is less. It may be concluded 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 processing composition and hydrophobic groups which modulate the polymeric swelling so at some definite ratio of hydrophilic to hydrophobic groups, the resultant compound possesses temperature inverse permeation properties. Basically the forces responsible for such properties are probably bond interactions, such as hydrogen bonding and hydrophobic-hydrophobic bonding.

Accordingly, the precise molar percentage ratio of polymer blocks used in the instant invention will be determined on an ad hoc basis, prime consideration being given to the respective hydrophilicity and hydrophobicity of the individual blocks.

The pH of the alkaline processing composition preferably is of the order of at least 12 to 14. The acid polymer layer contains at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period. The pH of the positive image layer preferably is further reduced to a pH of about 5 to 8 within a short time after imbibition.

It is, of course, necessary that the action of the acid-reacting reagent 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 should be kept at a level of about pH 12 to 14 until the positive dye image has been formed after which the pH should be reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive image is 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 developers 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 nec-

essary quantity of dye developer has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. This processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor processes using multilayer negatives.

As used herein, the term acid-reacting reagent is intended to include 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, the acid polymer contains free carboxyl groups and the processing composition contains a large concentration of sodium and/or potassium ions. The acid polymers found 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 salts. One may 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 contemplated as being used in this invention, 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.

It has further been discovered that the provision of an inert interlayer between the image layer and the polymeric acid layer substantially improves the control of the pH reduction by the polymeric acid layer. While this spacer layer preferably is composed of a polymer such as polyvinyl alcohol, other polymers, such as gelatin, which are inert to alkali but through which the alkali may diffuse to the polymeric acid layer may be used. The presence of such an interlayer has been found quite effective in evening out the various reaction rates over a wide range of temperatures, e.g., by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, e.g., at 95–100° F. By providing an inert interlayer, the rate at which alkali is available for capture in the polymeric acid layer becomes a function of alkali diffusion rates. The pH reduction thus is made relatively independent of chemical reaction rates which would show a greater variation over similar wide changes in imbibition temperature.

In a particularly useful embodiment, the spacer layer referred to above comprises a polymer which exhibits a permeability to alkali ions which is inversely temperature dependent, i.e., it exhibits decreasing permeability to solubilized alkali ions, such as alkali metal and quaternary ammonium ions, under conditions of increasing temperature. The use as spacer layers of polymers which exhibit

such inverse temperature dependent permeability to alkali is disclosed and claimed in U.S. applications of Leonard C. Farney et al., Ser. No. 664,503, filed Aug. 30, 1967, now U.S. Patent No. 3,455,686, and Lloyd D. Taylor, Ser. No. 641,670, filed May 26, 1967, now U.S. Patent No. 3,421,893. The use of this type of polymeric spacer layer has resulted in improved processing results, particularly with respect to pH control and dye densities, over a wider temperature range, and especially at lower temperatures.

Referring to the drawing, there is shown in FIG. 1 an integral multilayer, multicolor photosensitive element 10 being positioned in superposed relationship with an image-receiving element 40 with a layer 32 of processing composition therebetween. The multicolor photosensitive element 10 comprises a support, 15, bearing, in turn, a layer 18 containing a cyan dye developer, a layer 20 of a red-sensitive silver halide emulsion, an interlayer 22, a layer 24 containing a magenta dye developer, a layer 26 of a green-sensitive silver halide emulsion, an interlayer 22, a layer 28 of a yellow dye developer, and a layer 30 of a blue-sensitive silver halide emulsion. The image-receiving element 40 comprises a support 12 carrying an image-receiving layer 34.

A preferred image-receiving element is depicted in FIG. 2, and comprises a support 12 carrying, in turn, a layer 14 containing a nondiffusible acid-reacting reagent and a temperature-inverting plasticizer therefor; a spacer layer 16 and an image-receiving layer 13.

The following example is given for the purpose of illustration only and is not intended to be taken in a limiting sense.

EXAMPLE 1

An image-receiving element was 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 gms. of DX-840-31 Resin [trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity poly-(ethylene/maleic anhydride)], 140 gms. of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.3 mil. thick. The external surface of the acid layer was coated with a 1% solution of polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.30 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-vinylpyridine, at a coverage of approximately 600 mgs. per square foot, to provide a polymeric image-receiving layer approximately 0.40 mil. thick. The thus-prepared image-receiving element was then baked at 180° F. for 30 minutes and then allowed to cool.

A multicolor, multilayer photosensitive element was prepared in a manner similar to that disclosed in the aforementioned U.S. Pat. No. 3,345,163 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 polymeric layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A polymeric interlayer was positioned between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements were 1,4-bis-(α -methyl- β -hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone (a cyan dye developer); 2-(p-[2',5'-dihydroxyphenethyl] - phenylazo)-4-isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl-carbamyl - 4-(p-[hydroquinonyl-ethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are

disclosed in U.S. Pat. No. 3,134,764 and the cyan dye developer is disclosed in U.S. Pat. No. 3,135,606.

In order to demonstrate the unique advantages of the present invention, image-receiving elements identical to the element described above were formulated with the exception that the layer containing the polymeric acid included 25 parts per 100 parts of polymeric acid of a block copolymer of polyethylene oxide and poly-2-propylene oxide containing approximately 30 weight percent polyethylene oxide.

Negative elements as described above were exposed to a step wedge to selectively filtered radiation and processed by spreading aqueous alkaline liquid processing compositions between said multicolor negative elements and respective image-receiving elements as described above, that is, image-receiving elements containing a polymeric acid layer which contained no plasticizer, and those which contained a block copolymer plasticizer exemplary of the compounds of the present invention. In order to appreciate the temperature latitude characteristics of the system of the present invention, comparative test measurements of maximum red dye density, $D_{\max}$, were carried out at 50°, 75°, and 100° F. After an imbibition period of 1 minute in the case where the development was carried out at 75° and 100° F., and 2 minutes, 15 seconds, in the case where development was carried out at 50° F., the image-receiving element was separated from the remainder of the film assembly. The processing solution utilized for all tests comprised:

Water—95 cc.
Hydroxyethyl cellulose—3.8 gms.
Potassium hydroxide—10 gms.
Benzyl- α -picolinium bromide—2.5 gms.

The following tabulation collectively and succinctly presents the results achieved during the instant comparative testing:

	Polymeric acid without plasticizer	Polymeric acid ¹
$D_{\max}$, Red 50° F. --	1.45	1.55
$D_{\max}$, Red 75° F. --	1.36	1.67
$D_{\max}$, Red 100° F. --	0.99	1.47

¹ With block copolymer of polyethylene oxide-polypropylene oxide.

The most prominent feature of the above-tabulated data is the fact that the $D_{\max}$ differential from 75–100° F. in the sheet containing the unplasticized polymeric acid is substantially greater than the $D_{\max}$ red differential of the sheet containing the polymeric acid plasticized with the block copolymer exemplary of the present invention. Note also the consistently high saturation obtained when the plasticizers of the present invention are utilized in a diffusion transfer photographic environment at varying temperatures. Of further moment is the well-defined increase in $D_{\max}$ of the sheet plasticized with the block copolymer over the unplasticized sheet, both at 75° F. and 100° F. In addition, it will be seen that a substantial improvement is noted at 50° F., though, in order to obtain viable test information, the imbibition period is two minutes, 15 seconds.

EXAMPLE 2

A polymeric acid layer, identical to that described in Example 1, was laid on a cellulose nitrate sub-coated baryta sheet in a thickness of 1.2 mils. Identical structures were then formulated by incorporating, in one case, 25 parts per hundred parts by weight of polymeric acid of a block copolymer of polyethylene oxide and polypropylene oxide containing about 30 weight percent polyethylene oxide; and in a second case, 25 parts per hundred parts by weight of polymeric acid of dioctyl phthalate plasticizer. A processing composition containing a pH indicator

was then formulated and comprised the following ingredients:

Water—100 cc.
Hydroxyethyl cellulose—5.5 gms.
Potassium hydroxide—5.2 gms.
Thymol blue—0.02 gms.

The processing composition was spread on each sheet and drawn through rollers with a gap of .0016 inch between the sheet and an inert spread sheet. The time was then observed for the pH of the processing composition to reach about 8, utilizing a color change in the pH indicator. The following results were noted at 50°, 75° and 100° F., as tabulated below.

TIME TO REACH pH OF APPROXIMATELY 8

	50° F., seconds	75° F., seconds	100° F., seconds
Unplasticized polymeric acid layer	30	15	6
Polymeric acid layer plasticized with block copolymer of polyethylene oxide-polypropylene oxide	20	20-25	10
Polymeric acid layer plasticized with dioctyl phthalate	45	30	11

When compared to the unplasticized polymeric acid layer, the layer plasticized with the block copolymer of the present invention at 50° F. demonstrates a faster pH dropoff, and at 100° demonstrates a slower pH dropoff. The faster pH dropoff at 50° is probably due to the dilution effect the processing composition has on the plasticizer thereby leaving gaping holes in the polymeric acid layer to present more surface area for neutralization of the processing composition. By way of comparison it will be seen that dioctyl phthalate plasticized polymeric acid causes an even greater barrier to neutralization in the cold, and when the figures are normalized at the 75° level it is evident that the pH dropoff in the hot will be greater than that achieved with the plasticizer of the present invention.

The specific amount of plasticizer required for utilization in the photographic environment within the present invention must, of course, be determined on an ad hoc basis. It may generally be assumed, however, that from four to thirty-five percent by weight, based upon the solids in the layer containing the acid-reacting reagent, will produce acceptable results. Empirically, it has been found that to provide similar results, less of the branched block copolymer, on a percent by weight basis, is required than the unbranched polymer. A preferred plasticizer level within the above-denoted range, based upon the solids in the acid-reacting reagent layer, is from six to fourteen weight percent. It is to be understood that within the context of the present invention, mixtures of the branched and unbranched copolymers described above may be used to provide properties desired by the operator, as, for example, certain viscosities, molecular weights, etc.

In the above examples, the polymeric acid layer has been exemplified by the partial butyl ester of polyethylene/maleic anhydride copolymer. As previously noted, many other acid polymers may be used. Thus, one may use cellulose acetate hydrogen phthalate mixed with cellulose acetate; the partial esters of poly-(ethylene/maleic anhydride) with 2-ethyl-hexyl alcohol, hexyl alcohol, propyl alcohol, amyl alcohol, etc., and the degree of substitution of the maleic anhydride groups may vary over a wide range but preferably is within the range of about 25 to 75%, etc. As an example of a cellulose half-ester which may be used without mixture with cellulose acetate, mention may be made of cellulose acetate hydrogen phthalate having a phthalyl content of approximately 16%.

The inert spacer layer, e.g., the polyvinyl alcohol helps to "time" control the pH reduction by the polymeric acid layer. This timing is a function of the rate at which

13

the alkali diffuses through this inert spacer layer. It has been found that the pH does not drop until the alkali has passed through this spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion of alkali into the polyvinyl alcohol interlayer, but the pH drops quite rapidly once the alkali diffuses through the polyvinyl alcohol layer.

It is an important feature of the preferred embodiments of this invention that the reaction of the polymeric acid with the diffusing alkali releases water. This water of reaction appears to have an accelerating effect upon the rate at which the pH is reduced. Prior to permeation of the alkali through the inert spacer layer, the equilibria favor the alkali remaining close to the negative and close to the image layer. Once alkali has permeated through to the polymeric acid layer, the equilibria are shifted by the trapping of that alkali. In addition, the water formed by reaction of the acid polymer with the alkali helps to remove alkali ions from the image layer and helps swell the inert polymer, thereby increasing the rate at which the alkali diffuses through the inert layer to the polymeric acid layer. These factors help to keep the pH high until the image is formed, and then to cause the pH to drop rapidly after the image has been formed. Thus, the pH may be kept high during development and transfer, and rapidly dropped after the transfer image has been formed. This also helps to effect the pH reduction within the same imbibition periods which otherwise would be employed. In addition, the released water of reaction permits the positive and negative to remain in superposed relationship for much longer imbibition times without sticking which is caused by drying out. In turn, this released water permits one to continue imbibition for periods long enough to assure more than the minimum desired pH reduction. The fact that the pH reduction also acts to create a self-limiting transfer density permits such continued imbibition to proceed without undesired color balance changes.

Examination of cross-sections of processed image-receiving elements containing inert spacer layers, e.g., a polyvinyl alcohol interlayer, showed that essentially all of the image dyes were contained in the image-receiving layer, the polyvinyl alcohol spacer layer being clear and essentially free of dye developer. Removal of the ions from the image layer permits the molecules around the dyes to come closer together for a tougher bond which imbeds the image dyes in a clear, brilliant, neutral or near neutral layer that permits unusually luminous colors.

In the preferred embodiments of this invention, the initial pH of about 14 is reduced to about 9 to 11 after about an imbibition period of about 45 to 90 seconds at 75° F., at which time the positive is separated.

Particularly good results have been obtained using image-receiving layers comprising polyvinyl alcohol and poly-4-vinylpyridine in ratios, by weight, for example, of from 1:3 to 3:1.

Although a preferred image-receiving layer is such a mixture of polyvinyl alcohol and poly-4-vinylpyridine (such receiving layers are disclosed and claimed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964), the invention is not limited thereto. Other image-receiving layers, such as the partial acetals of polyvinyl alcohol with trialkylammonium benzaldehyde quaternary salts, e.g., the p-trimethylammonium benzaldehyde p-toluene sulfonate partial acetal of polyvinyl alcohol (as disclosed and claimed in U.S. Pat. No. 3,239,337, issued Mar. 8, 1966), 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 U.S. Pat. No. 3,173,786, issued Mar. 16, 1965), and particularly a quaternary ammonium compound capable of forming an active methylene base in alkali, the invention is not so limited, even though the advantages are most dramatic when such an active methylene quaternary ammonium salt is used.

14

It is also contemplated to provide other adjuvants, e.g., ultraviolet absorbers, effective to improve the light stability or other properties of the positive image. Thus, an ultraviolet absorber may be included in the processing composition and deposited on the image-receiving layer during imbibition, or it may be present in a thin overcoat on the image-receiving layer prior to imbibition.

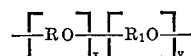
Where the dye mordant in the image-receiving layer is acid soluble, e.g., poly-4-vinylpyridine, and the image dye is alkali-soluble, e.g., a dye developer, the greatest increases in stability to light are found where the dye layer is rendered substantially neutral, and a stratum of an inert, substantially neutral polymeric material separates the image layer from the polymeric acid layer.

While this invention has been illustrated in connection with multilayer multicolor negatives, it will be understood that the inventive concepts also are applicable to monochrome negatives, e.g., for forming black dyes transfer images, and to screen-type negatives, such as those prepared by the procedures disclosed in the U.S. Pat. No. 3,032,008, issued to Edwin H. Land et al. on May 1, 1962.

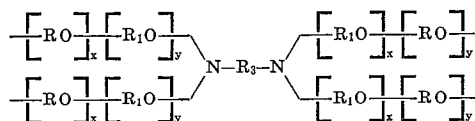
Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A receiving sheet for use in a photographic diffusion transfer process comprising a composite structure including a plurality of essential layers comprising, in sequence, a support; a layer comprising an acid-reacting reagent admixed with a plasticizer therefor, said plasticizer being selected from the group of polyether block copolymers represented by the formulae:



40 and



wherein: R, R₁ and R₃ are alkylene groups and x and y are positive integers representing the molar ratio of respective blocks; and mixtures thereof; and an alkali permeable and dyeable polymeric layer.

2. The receiving sheet of claim 1 wherein said plasticizer for said acid-reacting reagent contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide to said acid-reacting reagent predetermined temperature-alkali neutralization characteristics.

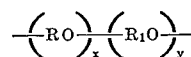
3. The receiving sheet of claim 2 wherein R is ethylene and R₁ is 2-propylene.

4. The receiving sheet of claim 3 wherein the molar ratio range of the ethylene-containing blocks to the 2-propylene-containing blocks is 0.47 to 1.6.

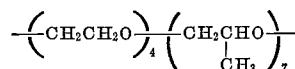
5. The receiving sheet of claim 4 wherein R₃ is ethylene.

6. The receiving sheet of claim 5 wherein the molecular weight range of said plasticizer is 3,000 to 16,000.

7. The receiving sheet of claim 6 wherein said compound represented by



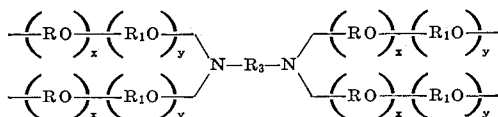
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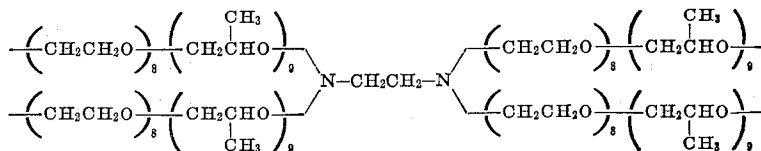
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8. The receiving sheet of claim 6 wherein said



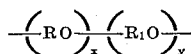
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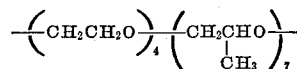
9. The receiving sheet of claim 6 wherein said plasticizer imparts to said acid-reacting reagent decreasing alkali neutralization characteristics with increasing temperature as compared with an unplasticized acid-reacting reagent.

10. 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 as a result of development, forming thereby an image-

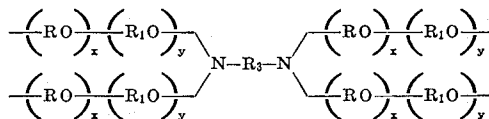
16. The process of claim 15 where in said compound represented by



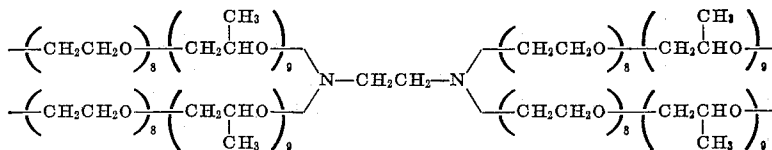
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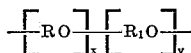
17. The process of claim 15 wherein said compound represented by the formula



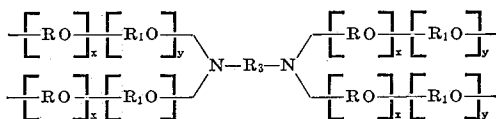
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wise distribution of mobile dye as a function of the point-to-point degree of exposure of said element, transferring by imbibition at least a portion of said imagewise distribution of mobile dye to a superposed image-receptive element which comprises a plurality of layers including, in sequence, a support; an acid-reacting reagent admixed with a plasticizer therefor, said plasticizer being selected from the group of materials represented by the formulae:



and



wherein: R, R₁ and R₃ are alkylene groups and x and y are positive integers representing the molar ratio or respective blocks; and mixtures thereof; and an alkali permeable and dyeable polymeric layer, transferring by imbibition subsequent to substantial transfer image formation at least a portion of the ions of said alkaline solution to said acid-reacting reagent-containing layer to thereby reduce the alkalinity of the processing solution.

11. The process of claim 10 wherein said plasticizer for said acid-reacting reagent contains hydrophilic and hydrophobic moieties which have been quantitatively adjusted to provide to said acid-reacting reagent predetermined temperature-alkali neutralization characteristics.

12. The process of claim 11 wherein R is ethylene and R₁ is 2-propylene.

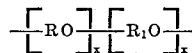
13. The process of claim 12 wherein the molar ratio range of the ethylene-containing blocks to the 2-propylene-containing blocks is 0.47 to 1.6.

14. The process of claim 13 wherein R₃ is ethylene.

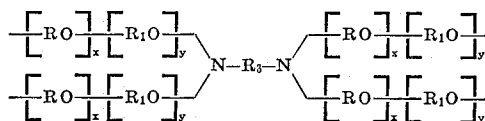
15. The process of claim 14 wherein the molecular weight range of said plasticizer is 3,000 to 16,000.

18. The process of claim 15 wherein said plasticizer imparts to said acid-reacting reagent decreasing alkali neutralization characteristics with increasing temperature as compared with an unplasticized acid-reacting reagent.

19. 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 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 imagewise distribution of mobile yellow, magenta and cyan dye, 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; an acid-reacting reagent admixed with a plasticizer therefor, said plasticizer being selected from the group of materials represented by the formulae:



and



wherein: R, R₁, and R₃ are alkylene groups and x and y are positive integers representing the molar ratio of respective blocks; and mixtures thereof; and an alkali permeable

and dyeable polymeric layer; transferring, by imbibition, subsequent to substantial transfer image formation, at least a sufficient portion of the alkali of said processing composition through said dyeable polymeric layer to said acid reacting reagent-containing layer to provide thereby a reduction of the pH of said image-receiving element to a pH of not greater than about 8.

20. The process of claim 19 wherein said plasticizer for said acid-reacting reagent contains hydrophilic and hydro-

phobic moieties which have been quantitatively adjusted to provide to said acid-reacting reagent predetermined temperature-alkali neutralization characteristics.

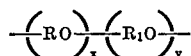
21. The process of claim 20 wherein R is ethylene and R₁ is 2-propylene.

22. The process of claim 21 wherein the molar ratio range of the ethylene-containing blocks to the 2-propylene-containing blocks is 0.47 to 1.6.

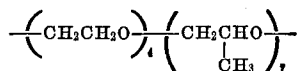
23. The process of claim 22 wherein R₃ is ethylene.

24. The process of claim 23 wherein the molecular weight range of said plasticizer is 3,000 to 16,000.

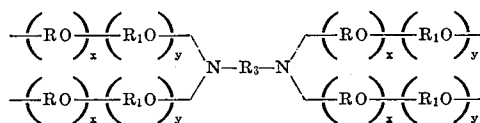
25. The process of claim 24 wherein said compound represented by



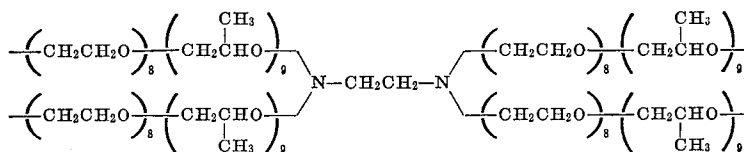
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26. The process of claim 24 wherein said compound represented by the formula:



is



27. The process of claim 24 wherein said plasticizer imparts to said acid-reacting reagent decreasing alkali neutralization characteristics with increasing temperature as compared with an unplasticized acid-reacting reagent.

References Cited

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3,455,686	7/1969	Farney et al.	96—3

MURRAY KATZ, Primary Examiner

R. HUSACK, Assistant Examiner

U.S. Cl. X.R.

96—29, 76

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

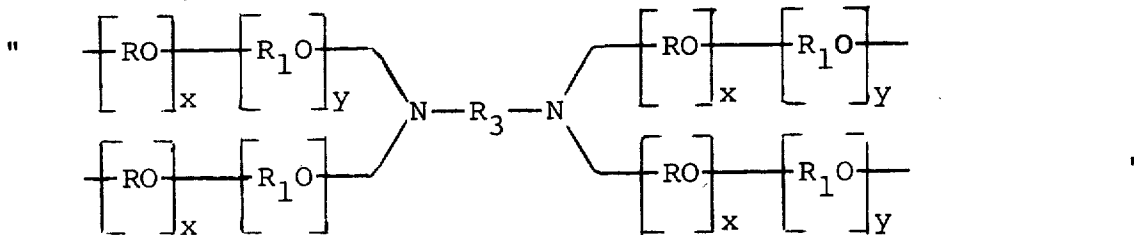
Patent No. 3,577.238 Dated May 4, 1971

Inventor(s) Lloyd D. Taylor

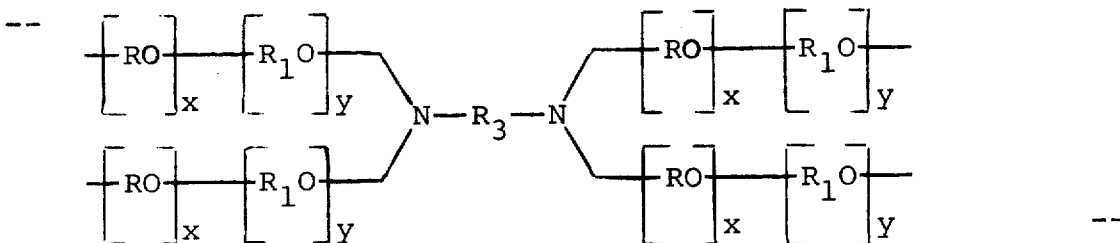
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, claim 8, between the formula should be --is--.

Column 15, claim 10, line 50



should be



Signed and sealed this 6th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents