

April 9, 1968

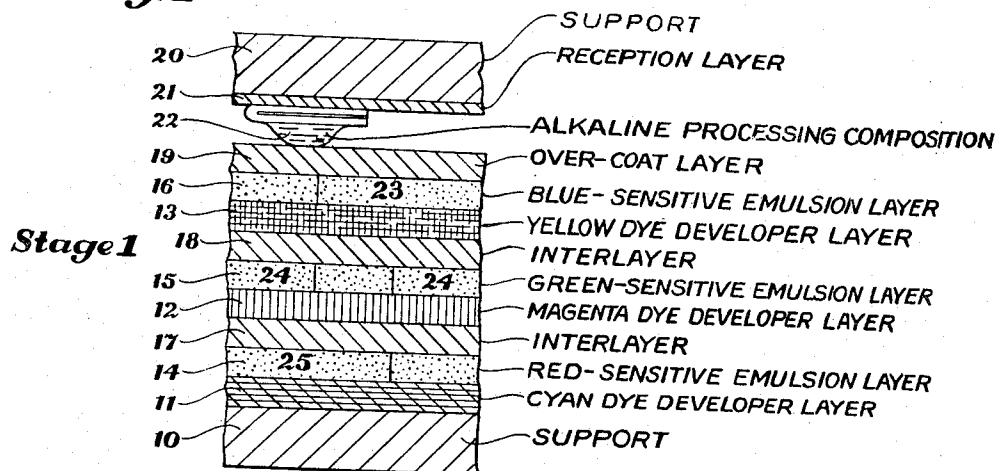
W. J. WEYERTS ET AL

3,377,166

PHOTOGRAPHIC IMAGE TRANSFER PROCESS UTILIZING IMIDAZOLE

Filed April 19, 1966

Fig. 1



Stage 2

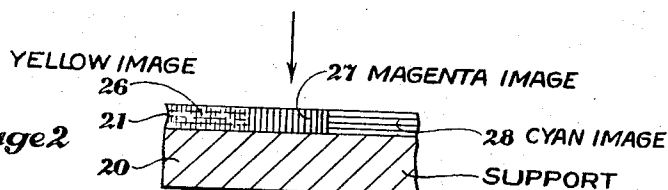


Fig. 2

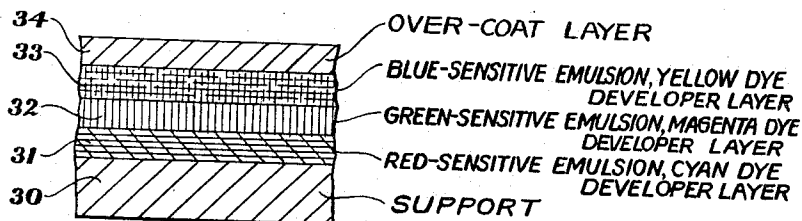
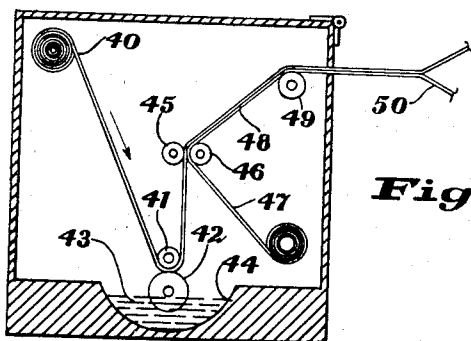


Fig. 3

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3,377,166

PHOTOGRAPHIC IMAGE TRANSFER PROCESS UTILIZING IMIDAZOLE

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Continuation-in-part of application Ser. No. 361,781, Apr. 22, 1964, which is a continuation-in-part of application Ser. No. 77,666, Dec. 22, 1960. This application Apr. 19, 1966, Ser. No. 543,633
5 Claims. (Cl. 96-29)

ABSTRACT OF THE DISCLOSURE

Exposed photographic elements comprising a support having coated thereon a light-sensitive silver halide emulsion layer and dye developer contiguous to the silver halide, are processed in the presence of imidazole. When treated with an alkaline liquid, latent image is developed in the emulsion layer, thereby immobilizing dye developer in regions of exposure. Dye developer from undeveloped regions diffuses imagewise to a dye developer reception layer.

This application is a continuation-in-part application of our copending application Ser. No. 361,781, filed Apr. 22, 1964, now U.S. Patent 3,266,894, which in turn is a continuation-in-part application of Ser. No. 77,666 filed Dec. 22, 1960, now abandoned.

The present invention relates to the art of photography, and more particularly, to image transfer processes including processes utilizing dye developers.

Compounds which contain in the same molecule both the chromophoric system of a dye and a photographic silver halide developing moiety have been described in the photographic art as useful compounds in photographic elements for preparing color images by diffusion transfer processes. Such compounds are commonly called "dye developers." Photographic elements containing such dye developers generally comprise a plurality of photosensitive silver halide emulsions wherein each of the emulsions is selectively sensitized to a different region of the spectrum. A dye developer is positioned contiguous to the silver halide in each of such emulsions. Such a photoelement is processed with an alkaline composition and the latent image is developed in the negative image areas with the dye developers, this development immobilizing the dye developers in such negative image areas, and the dye developers in the unexposed areas diffuse to the surface imagewise and are transferred to a reception layer or receiving sheet to form a positive multicolor image. Similarly, dye diffusion transfer systems can be used to prepare single color transfer prints. Such color diffusion transfer processes are disclosed in U.S. Patents 2,983,606, and 3,146,102, as well as elsewhere in the literature.

In the above described dye developer diffusion transfer process, an alkaline processing composition is utilized partly to initiate the development of the emulsion layers and also to act as a medium through which the unoxidized dye developer images and other substances diffuse to and from the receiving layer. The processing composition is usually spread in limited quantity between the surface of the light-sensitive or negative element and a mordanted receiving sheet. It is therefore desirable to include in the processing composition a thickening agent which increases the viscosity thereof, particularly for in-camera processing wherein the processing composition is utilized in a rupturable pod or like container. Various other addenda can be added to such alkaline processing compositions to improve the quality of the transfer prints.

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It is an object of this invention to provide a novel dye developer diffusion transfer process.

It is another object of this invention to effect a dye developer diffusion transfer process in the presence of a novel processing composition addendum.

It is still another object of this invention to provide a new dye developer diffusion transfer process characterized as producing dye developer images having high contrast and brightness.

These and other objects of the invention are accomplished by processing photographic elements containing at last one photographic silver halide emulsion layer and a dye developer contiguous to the silver halide of the silver halide emulsion layer in the presence of imidazole, an alkaline processing solution being utilized to initiate development and a dye developer image being transferred to a dye developer reception layer. On applying an alkaline processing composition to such an exposed photographic element, the silver halide in the regions of exposure is developed and contiguous dye developers are immobilized, and thereafter dye developers from the unexposed and undeveloped areas of the photographic element diffuse and are transferred in register to a reception layer to form positive dye developer images.

The imidazole addendum is present in the present photographic system so that it is present during processing as an active addendum. The imidazole is preferably utilized in the alkaline processing composition, although it can be utilized in the light-sensitive element or in an image receiving sheet. Generally, about .005 to 1 gram, and preferably about .05 to .25 gram, of imidazole per 100 grams of alkaline processing composition is utilized.

Dye developers are well known in the photographic art. Such compounds function both as a silver halide developing agent and as a dye in photographic diffusion transfer systems. Dye developers are characterized as being relatively nondiffusible in colloid layers such as the hydrophilic organic colloids used in photographic emulsions at neutral pH, but diffusible in the photographic elements in the presence of alkaline processing solutions. Generally, such dye developers are substantially insoluble in water, which property usually necessitates the use of organic solvents to incorporate the dye developers into the organic colloid layers of the photoelements. The dye developers are particularly characterized as containing both a chromophoric or dye moiety and at least one moiety having a silver halide developing agent function. Particularly useful dye developers are those wherein the chromophoric moiety is an azo or anthraquinone dye moiety and the silver halide developing moiety is a benzenoid moiety such as a hydroquinonyl moiety.

Representative dye developers of use in the dispersions of the invention have the general formula $M-N=N-D$ in which M is an aromatic or heterocyclic ring or ring system such as a benzene, naphthalene, tetralin, anthracene, anthraquinone, pyrazole, quinoline, etc., ring which can be substituted with such groups as hydroxyl, amino, keto, nitro, alkoxy, aryloxy, acyl, alkylamido, alkylaryl, carboxamido, sulfonamido, carboxyl or sulfo groups. D represents a silver halide developing agent moiety imparting the developing agent function to the dye developer such as a hydroquinonyl group which can be substituted with amino, alkylamino, alkyl, hydroxyl, alkoxy or halogen groups.

Typical useful dye developers are described in columns 9-13 of U.S. Patent 3,146,102, as well as elsewhere in the patent literature, including: Australian 220,279; German 1,036,640; British 804,971 and 804,973-5; Belgian 554,935; French 1,168,292; and Canadian 577,021 and 579,038.

In the photographic elements useful in the invention,

the dye developers are preferably incorporated in hydrophilic organic colloidal vehicles or carriers comprising the layers of the photographic element dissolved in high-boiling or crystalloidal solvents and dispersed in finely-divided droplets. Typical high-boiling, water-insoluble solvents that can be used to dissolve dye developers in preparing the dispersions of the invention are described on page 2, col. 2 and page 3, col. 1 of U.S. Patent 2,322,027.

The dye developers utilized in the photographic elements useful in the invention can also be incorporated into vehicles soluble in organic solvents which are also solvents for the dye developers. Likewise, other incorporating techniques for the dye developers such as ball-milling can be utilized.

The dye developers are utilized contiguous to the silver halide of the photographic silver halide emulsion layers of the present photographic elements. Such dye developers can be incorporated directly in the silver halide emulsions or preferably positioned in a sublayer contiguous to each silver halide emulsion layer. The contiguity of the dye developer with respect to the silver halide can take the form of a mixed packet system wherein the dye developer can be present in a matrix surrounding a particle or globule containing silver halide grains. The dye developers are preferably substantially complementary in color to the color of the light recorded or spectral sensitivity of the silver halide emulsions contiguous thereto.

A wide variety of colorless hydroquinone derivatives can be utilized in the dye developer diffusion transfer systems of the invention. Such colorless hydroquinone derivatives are substantially insoluble in water and diffusible in the hydrophilic organic colloids comprising the present photographic elements in the presence of alkaline processing compositions. Typical suitable colorless hydroquinone derivatives are listed in columns 7 and 8 of U.S. Patent 3,146,102 and are preferably employed in one or more layers of the light-sensitive element used in the present process.

A wide variety of diffusible onium compounds can also be utilized in the present invention. Such onium compounds, that is, compounds that contain an organic cation, are diffusible in the hydrophilic organic colloids comprising the present photographic elements in the presence of alkaline processing compositions. Such onium compounds are typically quaternary ammonium compounds, quaternary phosphonium compounds or tertiary sulfonium compounds. A particularly useful class of onium compounds are heterocyclic quaternary ammonium compounds that are capable of forming diffusible methylene bases in alkaline processing compositions such as those described in U.S. Patent 3,146,102. In dye developer diffusion transfer systems, the onium compounds are preferably utilized in the alkaline processing composition, although the onium compounds can also be utilized in the reception sheet, or less desirably, in one or more layers of the light-sensitive element, or in at least two of such positions.

Water-soluble silver halide solvent can be employed in the alkaline processing compositions used in the dye developer transfer process of the invention, particularly in conjunction with onium compounds and colorless hydroquinone derivatives as described above, such addenda lending further improvement in color quality results. Preferred silver halide solvents are thiosulfates such as sodium, potassium and ammonium thiosulfate.

The silver halide emulsions utilized in preparing photographic or light-sensitive elements used in the present diffusion transfer systems can be any of the conventional negative-type, developing-out emulsions. Typical suitable silver halides include silver chloride, silver bromide, silver bromiodide, silver chloriodide, silver chlorobromiodide and the like. Mixtures of more than one of such silver halides can also be utilized. In accordance with usual practice, such silver halide emulsions can contain

spectral sensitizers, speed-increasing addenda, hardeners, coating aids, plasticizers, antifoggants and the like conventional emulsion addenda.

In preparing such silver halide emulsions, as well as in preparing the various layers of photographic elements used in the present diffusion transfer process, including the layers containing the dye developers and colorless hydroquinone derivatives, mordant-containing reception layers, interlayers, topcoat layers and the like, a wide variety of hydrophilic organic colloids can be utilized as the vehicle or carrier. Gelatin is preferably used as the hydrophilic colloid or carrier material although such material as polyvinyl alcohol and its water-soluble derivatives and copolymers, water-soluble copolymers such as polyacrylamide, imidized polyacrylamide, etc., and other water-soluble film-forming materials that form water-permeable coats such as colloidal albumin, water-soluble cellulose derivatives, etc., can be utilized in preparing the photographic elements. Compatible mixtures of two or more of such colloids can also be utilized.

The various layers utilized in preparing the diffusion transfer photographic elements used in the process of the invention can be coated on a wide variety of photographic supports. Typical supports include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polyethylene film, polypropylene film, paper, polyethylene-coated paper, polypropylene-coated paper, glass and the like.

Similarly, a wide variety of receiving sheets can be utilized to receive the transfer images from the photographic elements. Typical reception layers for receiving sheets include such materials as linear polyamides, proteins such as gelatin, polyvinyl pyrrolidones, poly-4-vinyl pyridine, polyvinyl alcohol, polyvinyl salicylal, partially hydrolyzed polyvinyl acetate, methyl cellulose, regenerated cellulose, or mixtures of such. These reception layers can be coated on a suitable support of the type described above for the light-sensitive elements of the invention and including transparent as well as opaque supports. Also, receiving sheets that release acidic material such as that derived from an acidic polymer or other acidic compound at a controlled rate as are described in U.S. Patent 2,584,030 are particularly useful. Such acidic materials are typically positioned in layers on the receiving sheet below the dye developer reception layer, there suitably being a spacer layer between the acid layer and the mordanting layer to control the release of acidic material. Such acidic materials serve to neutralize residual portions of the alkaline activator on the receiving sheet. A wide variety of nondiffusible cationic or basic dye-mordanting compounds can be used in liquid permeable reception layers including amines such as polymeric amines, quaternary ammonium compounds, quaternary phosphonium compounds and tertiary sulfonium compounds. Such mordants are nondiffusible in the alkaline processing composition and contain at least one hydrophobic ballast group. As described above, either or both of the onium compounds and colorless hydroquinones can be incorporated on the receiving sheets. The receiving sheets can also contain development arrestors such as mercaptoazoles and iodides.

Light-sensitive elements containing integral reception layers for dye developer images can also be utilized. Such integral reception layers can be coated beneath the emulsion and dye developer layers near the support. A stripping layer coated over the integral reception layer can be used to facilitate the removal of the over-coated layers after the diffusion of the dye developer images to the reception layer.

The processing compositions or activators used to initiate development of the exposed light-sensitive elements in accordance with the invention are strongly alkaline. Such processing compositions generally have a pH of at least 12 or contain at least .01 N hydroxyl ion. Alkali metal hydroxides, such as sodium hydroxide, and sodium

carbonate, are advantageously used in the composition for imparting such high alkalinity. However, volatile amines such as diethyl amine can also be used, such amines having the advantage of being volatilized from the prints to leave no residue of alkali. As mentioned previously, due to the unstable character of the hydroquinone derivatives in strong alkali, the colorless hydroquinone derivatives are preferably not used in the processing composition although when the pyridinium salts are present improved results are obtained. Such processing compositions are generally aqueous liquids or solutions, and when utilized in rupturable pods for in-camera processing such as described in U.S. Patent 2,435,717, generally contain thickening agents such as hydroxyethyl cellulose or carboxymethyl cellulose. Thickened processing compositions typically have viscosities of at least 5,000 cps. to 100,000 or even 200,000 cps.

In the accompanying drawing are shown in enlarged cross-sectional view representative elements that can be processed in accordance with the invention and processing means that can be suitably employed in the invention.

In FIG. 1 of the drawing is shown in flow-sheet form a typical process embodying our invention according to which in Stage 1 the light-sensitive element comprises support 10, layers 11, 12 and 13 containing subtractively colored cyan, magenta and yellow dye developers, respectively, light-sensitive silver halide emulsion layers 14, 15 and 16 sensitive to red, green and blue light respectively, interlayers 17 and 18 separating the green-sensitive emulsion and its contiguous subtractively colored magenta dye developer layer from the other layers and over-coat layer 19 which typically contains colorless hydroquinone derivatives described above. A receiving sheet comprising support 20 having coated thereon reception layer 21 is superposed to receive dye images transferring by diffusion from the light-sensitive element. Positioned between the light-sensitive element and the receiving sheet is a rupturable container or pod containing alkaline processing composition 22 preferably containing imidazole and typically a thickening agent and an onium compound as described above. Upon rupture of the container holding alkaline processing composition 22, such as by passing the assembly between rollers in a camera, the contents of the container are substantially uniformly spread across a predetermined area of the sensitive element. The alkaline processing composition penetrates through layers 19 to 11, latent images develop in light-sensitive layers 14, 15 and 16 and dye developers in contiguous layers 11, 12 and 13 respectively rendered nondiffusing in areas corresponding to latent image or negative areas such as 23, 24 and 25 respectively, and the dye developers in the remaining or positive image areas diffuse imagewise in register to mordant or reception layer 21 of the receiving sheet. Stage 2 of FIG. 1 illustrates receiving sheet support 20 with reception layer 21 containing transferred dye developers to form subtractively colored positive images, namely, yellow image 26, magenta image 27 and cyan image 28.

FIG. 2 of the drawing illustrates a typical light-sensitive element useful in the invention wherein the dye developers are incorporated directly in the light-sensitive silver halide emulsions. On support 30 is coated red-sensitive silver halide emulsion layer 31 containing a cyan dye developer. Over layer 31 is coated green-sensitive silver halide emulsion layer 32 containing a magenta dye developer. Over layer 32 is coated blue-sensitive silver halide emulsion layer 33 containing a yellow dye developer. Over-coat layer 34 is coated over layer 33, such over-coat layer typically containing a colorless hydroquinone derivative.

In accordance with usual practice, the positioning of the red, green and blue light-sensitive silver halide emulsion layers of the light-sensitive element illustrated in FIG. 1 as well as in FIG. 2 can be varied.

Single color photographic elements can also be proc-

essed in accordance with the invention. Such photographic elements comprise a support having coated thereover a dye developer layer and coated over the dye developer a light-sensitive silver halide emulsion layer. An over-coat layer can also be utilized. Likewise, such monochrome elements can be prepared wherein the dye developer and the silver halide emulsion are incorporated in a single layer.

FIG. 3 of the drawing illustrates a typical light-imperious enclosure useful for processing exposed rolls of film containing silver halide emulsion layers and dye developers of the type described above. In utilizing the processing means of FIG. 3, film 40, wound emulsion side inwards, is passed between rollers 41 and 42. Roller 42 is immersed in alkaline processing composition 43 which preferably contains imidazole. Roller 42 transfers portions of alkaline processing composition 43 to the emulsion layers on film 40. Thereafter film 40 is conveyed between rollers 45 and 46 where the emulsion layer side of film 40 is brought into contact with mordanted receiving sheet 47 to form sandwich 48. In sandwich 48, the exposed silver halide in each emulsion layer develops, contiguous dye developers become immobilized and unreacted dye developers transfer to mordanted receiving sheet 47. Thereafter sandwich 48 is conveyed over roller 49 and stripped apart to provide positive dye developer images on mordanted receiving sheet 47 at 50.

The following example will serve to further illustrate the present invention.

Example

A photographic element having the structure substantially as shown in FIG. 1 of the drawing (layers 10 to 19) was prepared by coating successively the following layers on a subbed cellulose acetate film support:

(1) Cyan Dye Developer Layer (e.g., Layer No. 11 of FIG. 1).—A coating of the cyan dye developer, 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl- α 1methyl)ethylamino]-anthraquinone, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 120 mg. per square foot of the cyan dye developer, 150 mg. per square foot of gelatin and 180 mg. per square foot of N-n-butylacetanilide. The dye developer dispersion was prepared by adding to an aqueous gelatin solution 1 part by weight of the cyan dye developer dissolved in 1.5 parts by weight of N-n-butylacetanilide and 2 parts by weight of 4-methylcyclohexanone in the presence of a sodium diisopropyl-naphthalene sulfonate dispersing agent. The mixture was passed through a colloid mill several times, chill set, shredded, dried to volatilize the 4-methylcyclohexanone, melted and coated.

(2) Red-sensitive Emulsion Layer (e.g., Layer No. 14 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromide (6% iodide) emulsion sensitized to red light was coated at a coverage of 180 mg. per square foot of silver and 250 mg. per square foot of gelatin.

(3) Interlayer (e.g., Layer No. 17 of FIG. 1).—A coating of gelatin at a coverage of 300 mg. per square foot.

(4) Magenta Dye Developer Layer (e.g., Layer No. 12 of FIG. 1).—A coating of the magenta dye developer, 2 - [p - (2',5'-di-hydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol, dissolved in N-n-butylacetanilide-dispersed in gelatin and coated at a coverage of 60 mg. per square foot of the dye developer, 100 mg. per square foot of gelatin and 60 mg. per square foot of N-n-butylacetanilide. The dispersion of the dye developer was prepared by dispersing in an aqueous gelatin solution 1 part by weight of the dye developer in 2 parts by weight of cyclohexanone and 1 part by weight of N-n-butylacetanilide in the presence of the dispersing agent, sodium diisopropyl-naphthalene sulfonate. The resulting mixture was passed through a colloid mill several times, chill set, washed to remove the cyclohexanone, melted and thereafter coated.

(5) Green-Sensitive Emulsion Layer (e.g., Layer No. 15 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion sensitized to green light was coated at a coverage of 75 mg. per square foot of silver and 150 mg. per square foot of gelatin.

(6) Interlayer (e.g., Layer No. 18 of FIG. 1).—A coating of gelatin at a coverage of 300 mg. per square foot.

(7) Yellow Dye Developer Layer (e.g., Layer No. 13 of FIG. 1).—A coating of the yellow dye developer, 1-phenyl-3-N-n-hexylcarboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone, dissolved in ditetrahydrofurfuryl adipate and dispersed in gelatin was coated at a coverage of 60 mg. per square foot of the dye developer, 100 mg. per square foot of gelatin and 30 mg. per square foot of ditetrahydrofurfuryl adipate. The dispersion was prepared by dispersing in an aqueous gelatin composition, 1 part by weight of the dye developer dissolved in .5 part by weight of ditetrahydrofurfuryl adipate and 2 parts by weight of ethylene glycol monobenzyl ether in the presence of a sodium diisopropyl naphthalene sulfonate dispersing agent. The mixture was passed through a colloid mill several times, the resulting dispersion chill set, washed to remove the ethylene glycol monobenzyl ether, melted and coated.

(8) Blue-Sensitive Emulsion Layer (e.g., Layer No. 16 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion that is inherently sensitive to blue light was coated at a coverage of 65 mg. per square foot of silver and 150 mg. per square foot of gelatin.

(9) Overcoat Layer (e.g., Layer No. 19 of FIG. 1).—A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenylhydroquinone (referred to hereafter as "MPHQ"), dissolved in di-n-butylphthalate at a coverage of 120 mg. of gelatin per square foot and 40 mg. of MPHQ per square foot. Samples of the resultant element were exposed in an intensity scale sensitometer and wetted with aqueous alkaline activators as described below in contact with a receiver described below composed of a support and a mordant-containing reception layer. The silver halide in the exposed silver halide areas (e.g., areas 23, 24 and 25 of FIG. 1) of each sample developed and the dye developers in the contiguous areas of the dye developer layers (e.g., 11, 12 and 13 of FIG. 1) thereunder became immobilized as a function of the development and the unreacted dye developers diffused imagewise and in register to the receiving sheet to yield a three color positive image composed of dye images (e.g., images 26, 27 and 28 as shown in FIG. 1, Stage 2 of the drawing). The processing and transfer time was about 2 minutes at 70° F. Particularly noteworthy was the improved blue contrast resulting from the imidazole in the alkaline processing solution as summarized by the data set out in the table below.

TABLE

Alkaline Activator:	Blue Contrast (Blue D_{max} -Blue D_{min})
I -----	1.14
II -----	1.32

Activator I.—An aqueous solution containing on a weight basis: 3.5% HEC,¹ 4.5% NaOH and 2.0% 1-phenethyl-2-picolinium bromide.

Activator II.—Activator I+0.2% imidazole.

Receiver.—A paper support carrying a gelatin (300 mg. per square foot) layer containing a mixture of poly-4-vinyl pyridine mordant (300 mg. per square foot) and 1-phenyl-5-mercapto tetrazole (15 mg. per square foot).

The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. In the processing of an exposed photographic element comprising a support, a light-sensitive silver halide emulsion layer and a dye developer which is both a silver halide developing agent and a dye contiguous to the silver halide of said silver halide emulsion layer, said processing being effected by treating said photographic element with an alkaline liquid, developing a latent image in the regions of exposure of said silver halide emulsion layer and thereby immobilizing said dye developer in said regions of exposure, dye developer in undeveloped regions diffusing imagewise in register to a dye developer reception layer, the improvement which comprises effecting said processing in the presence of imidazole.

2. In the processing of an exposed photographic element comprising a support, superposed red, green and blue light-sensitive silver halide emulsion layers, and a dye developer which is both a silver halide developing agent and a dye contiguous to the silver halide of each of said silver halide emulsion layers, said processing being effected by treating said photographic element with an alkaline liquid, developing latent images in the regions of exposure of said silver halide emulsion layers and thereby immobilizing dye developers in said regions of exposure, dye developers in undeveloped regions diffusing imagewise to the surface of said photographic element, and transferring the resulting diffused images from said undeveloped regions in register to a dye developer receiving sheet superposed on said photographic element, the improvement which comprises using imidazole in said alkaline liquid.

3. The process as described in claim 2 wherein the imidazole is utilized at a concentration of about .005 to 1 gram per 100 grams of alkaline liquid.

4. The process as described in claim 2 wherein the alkaline liquid contains hydroxyethyl cellulose as a thickening agent.

5. The process as described in claim 2 wherein the silver halide emulsion layers are gelatino silver bromiodide emulsion layers.

¹ High viscosity hydroxyethyl cellulose sold by Hercules Powder Co. as Natrosol 250 Type H having a viscosity of about 10,000-15,000 cps. at 25° C. as 2% aqueous solution.

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